Scaling up the electrokinetic-assisted phytoremediation of atrazine-polluted soils using reversal of electrode polarity: a mesocosm study

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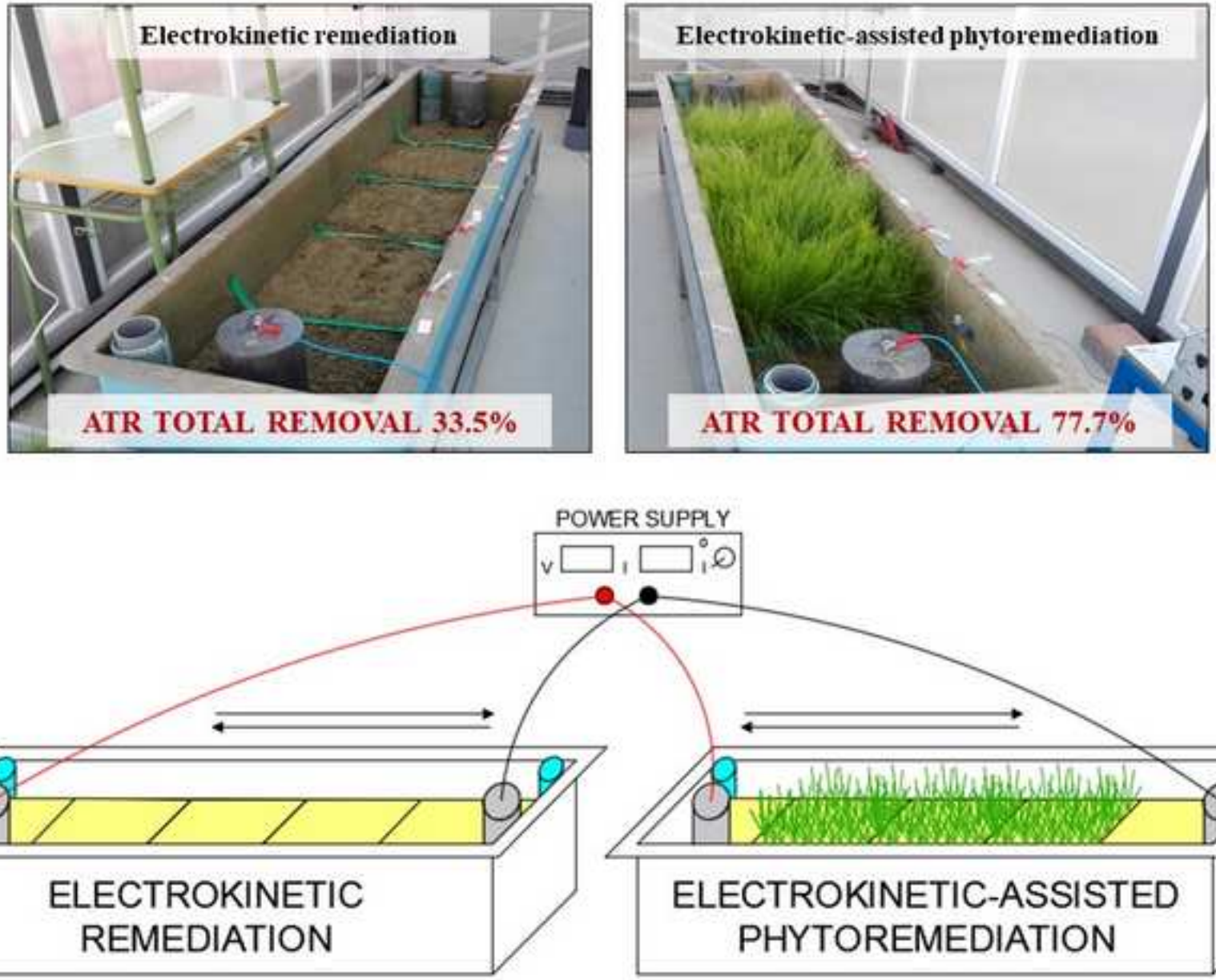
Graphical Abstracts



HIGHLIGHTS

The successfully EKPR of atrazine-polluted soils in a mesocosm scale has been demonstrated

Electro-osmosis was the most relevant transport mechanism for atrazine in soils

Atrazine overall removal efficiency was improved by ryegrass plants in approximately 44%

The extent of biochemical and electrokinetic processes greatly varied with the setup scale

ABSTRACT

Electrokinetic-assisted phytoremediation (EKPR) has been recently proposed for the removal of pesticides from polluted soils. In this work, we report the results from an EKPR experiment that was carried out in a mesocosm mock-up of 0.386 m^3 using ryegrass (*Lolium perenne* L.) and a low permeability soil spiked with atrazine. Plants were initially grown for 35 days; then, the soil was spiked with atrazine at a dose of 2 mg kg^{-1} soil. A DC electrical field of 0.6 V cm^{-1} was applied 24 hours every day, switching polarity daily. Another identical mock-up with the same experimental conditions but without plants was used for comparison purposes. The duration of the EKPR test was 19 days during which some operational parameters were registered (electric current intensity, soil pH and temperature) and soil porewater samples were taken and analyzed. Plant tissues and soil samples from the different sections in which the mock-ups were divided, were also collected and analyzed at the end of the experiment. 3-D profiles of soil pH, water content and atrazine residues concentration in plants and soil were obtained and discussed. The results of this experiment were compared with others previously reported by us from a similar EKPR pot test. In spite of the difficulties to get an adequate geometric and operational similarity between setups of different scale, the main output parameters of the EKPR process (electric current, specific current charge, overall atrazine removal, specific atrazine removal efficiency, root biomass:soil weight ratio) were discussed. It was shown that, although the processes carried out are essentially the same in both scales, their extent may be quite different; it highlights the limitations of small-scale experiments to predict the results at field conditions.

Keywords: atrazine; ryegrass; electrokinetic-assisted phytoremediation; scaling-up; soil

1. INTRODUCTION

Crop production is economically important in the European Community. The use of pesticides is one of the most significant actions in order to protect plants and crops against harmful organisms and it can also improve agricultural production. However, pesticides involve risks and hazards for humans, animals and the environment, especially groundwater and soils (Baraud et al., 1997), due to their stability, persistence and toxicity (Masiá et al., 2015). Between pesticides, atrazine has been one of the most studied in the context of soil and water pollution (Fan and Song, 2014).

Technologies which can be used to remove pesticides from soils, groundwater or flushed water include bioremediation, adsorption, advanced oxidation, membrane processes and electrokinetic remediation (Anastopoulos et al., 2018; Rodrigo et al., 2014); all of them possess advantages and limitations but the scaling-up has been shown as one of the important challenges of most of these technologies (Rodrigo et al., 2014). Electrokinetic remediation (EKR) has been extensively examined over the last two decades and widely accepted as a promising technique to treat different types of contaminated soils (especially low-permeability soils) (Ren et al., 2014). In many cases, the application of EKR is not adequate to decontaminate soils to an acceptable level, being advisable to combine it with other technologies, e.g. phytoremediation, as part of a more complex remediation process. That synergy can lead to results that are better than those from the sum of individual technologies (Yeung and Gu, 2011). The coupling of electrokinetic remediation with phytoremediation (named as electrokinetic-assisted phytoremediation, EKPR) has been proposed in order to, on one hand, accelerate the

processes carried out by plants due to the increased pollutant bioavailability and their proximity to roots, and, on the other hand, improve the soil morphology and its characteristics in the application of soil remediation technologies (Cameselle and Gouveia, 2019). In EKPR electrodes are directly inserted in the soil on both sides of the planted area and a DC electric field is applied; it causes, by means of different transport mechanisms, the movement of ionic pollutants between the electrodes (Baraud et al., 1997) with the subsequent increase in the extent of absorption or degradation by plants (Cameselle et al., 2013; Rocha et al., 2019).

The combined EKPR technology, when applied at laboratory scale to spiked soils, has given promising results in the removal of metals (Bi et al., 2011; Cang et al., 2012, 2011; Lim et al., 2004; Putra et al., 2013; Zhou et al., 2007) and pesticides (Sánchez et al., 2019a, 2019b, 2018). Those papers also revealed the complexity of the overall phenomena that results from the coupling between hydraulic, electrical and chemical driving forces and fluxes. Moreover, previous studies on electrokinetic remediation of pesticide-polluted soils concluded that the size of the experimental set-up has a relevant role on the pollutant removal, the 3-D profiles of soil parameters (pH, moisture and electrical conductivity) and the balance between electrochemical fluxes (López-Vizcaíno et al., 2017a, 2017b; Risco et al., 2016b). In general, it has been shown that, although a same voltage gradient is used, electrochemical fluxes and, particularly, the electroosmotic flux, become less important in the larger scales (López-Vizcaíno et al., 2017a). So, it seems reasonable to carry out EKPR experiments at mesocosm scale in order to have a more exhaustive understanding of the process at scales closer to the real field conditions.

In this paper, we assess the scaling-up of the EKPR technology applying it to a low-permeability soil spiked with atrazine placed in a mesocosm-scale mock-up that held 0.386 m^3 of soil planted with ryegrass (*Lolium perenne* L.). This process has been previously studied by us using pot experiments and several plant species (Sánchez et al., 2019b, 2019a, 2018). Atrazine was selected as a model of moderately polar pesticide while ryegrass was chosen based on its good performance in both our previous studies and those conducted by other authors (Acosta-Santoyo et al., 2017; O'Connor et al., 2003). The periodic polarity inversion of the DC electric field was used in order to avoid the characteristic extreme pH values reached in the EKR of soils due to the acidification and alkalinisation of anode and cathode regions, respectively (Virkutyte et al., 2002). The results from the EKPR mesocosm test were compared with those obtained in another unplanted mock-up with the same size containing an atrazine-spiked soil to which a DC electric field (with the same characteristics of that of the EKPR test) was applied. The soil of both mesocosms was divided in five cross sections and two layers in depth; the main process parameters (pH, water content, atrazine concentration) were separately registered in each of those sections, allowing us to obtain the corresponding three-dimensional profiles in the mock-ups.

2. MATERIALS AND METHODS

2.1. Materials

Certified seeds (Oregon Seed Certification Service, Corvallis, USA) of ryegrass (*Lolium perenne* L.) were used in this experiment. They were not subjected to a pre-germination treatment before planting in the mock-ups. During the sowing, care was taken to ensure

a homogeneous distribution over the entire surface of the soil. The soil used in this research was a low plasticity clay one (CL type, Unified Soil Classifications Systems, USCS) coming from a brick manufacturer company located in central Spain (Mora de Toledo). It proceeded from the soil layer between 15 and 50 cm and did not contain plant roots or stones. The soil was not sieved before its use although it was air-dried for 2 days at atmospheric conditions (mean day/night temperatures of about 26/7.5 ºC). The main physical-chemical properties of the soil were analysed by means of normalized methods; they are shown in Table SM-1 (Supplementary Materials). The initial pH of the soil was 9.42 and its high acid/base buffer capacity has been described elsewhere (Sánchez et al., 2019b). Solid atrazine with analytical standard quality (Fluka, purity 99.1%) was used to prepare the aqueous solutions that were added to the soil. High-purity deethylatrazine (Sigma-Aldrich, solution 100 ng μL^{-1} in methanol, purity HPLC 99.9%) and deisopropylatrazine (Sigma-Aldrich, solid, purity HPLC 97.5%), considered the main atrazine metabolites, were used to obtain their calibration curves in HPLC. Table SM-2-in Supplementary Materials shows the main properties of atrazine and its metabolites. Acetonitrile HPLC gradient grade (Merck, Germany) was used as solvent for extraction of solid samples. Ultrapure water (Millipore Milli-Q system, resistivity 18.2 MΩ cm at 25 ºC) was used to prepare all aqueous solutions.

2.2. Experimental setup

FIGURE 1

Two glass fibre reinforced PVC mock-ups with dimensions 2.25(L) x 0.49(W) x 0.50(H) m were used in the experiments (Figure 1). An electrokinetic-assisted phytoremediation (EKPR) and an electrokinetic remediation (EKR) tests were conducted in the two different mock-ups used. Each mock-up was loaded with 0.386 m^3 of the unpolluted natural soil, which was compacted manually. Two graphite electrodes (length 0.50 m, diameter 0.15 m) provided by Carbosystem (Madrid, Spain) were directly inserted in the soil at both ends of the mock-ups, with 2 m of separation. They were connected to the power supply (Delta Electronika S.V., model SM120-13, 0-120 V; 0-13 A) by means of metal clamps. Two cylindrical wells made of PVC (0.10 m in diameter and 0.5 m in depth) were located at both ends of the mock-ups and at approximately 10 cm from the electrodes; they were used to irrigate (by means of subirrigation) and control the water level in the mock-ups. For this purpose, a window of 0.25 cm deep and 0.10 m wide was perforated in the PVC cylinder and covered by a geotextile layer and a plastic mesh (1 x 1 cm) in order to avoid the siltation of the wells (Figure SM-3). Throughout the process of filling the mock-ups with the soil, ten Rhizon samplers were placed in order to take individual samples of soil pore water.

2.3. Experimental procedure

The experiments were carried out in a greenhouse with temperatures varying in the range 22-36/17-21 ºC day/night. Soil in the mock-ups was virtually divided into ten sections corresponding with five cross sections of 0.45 m width, each one divided in two layers in depth (Figure 1). The upper and bottom layers were 0.12 and 0.23 m deep, respectively. In the EKPR mock-up, the three central cross sections of the upper layer were sown with ryegrass (22 g of seed in each section). In the day 35 after planting, the

soil was superficially spiked with atrazine at a dose of 2 mg kg^{-1} soil (9.27 µmol kg^{-1}), corresponding to 1250 mg or 5.80 mmol of atrazine per mock-up. DC electric current was switched on twelve hours after spiking. EKPR and EKR experiments were performed in a potentiostatic mode, applying a continuous voltage gradient of 0.6 V cm^{-1} and changing the electrode polarity each 24 h. The total duration of the trial was 19 days (counted from the moment the electric current was switched on).

The electric current of each mock-up was recorded daily and the soil temperature was measured in the surface layer of the soil (2-5 cm) by means of a digital probe thermometer (TFA, Germany). Irrigation of the mock-ups was carried out daily by adding tap water in the well located near the electrodes; a variable water amount, ranging from 2 to 5 L per day, was added in order to balance the water level of both wells.

Soil pore water samples were taken by means of ten Rhizon samplers located in the centre of each soil section in days 0, 1, 2, 3, 5, 7, 9, 13 and 19 after connecting the electric field (the sample corresponding to the initial day 0 was taken 2 hours before connecting the power supply). Separated soil samples corresponding to the ten sections of the mock-ups (Figure 1) were collected at the end of the experiment. Water and soil samples were analysed for pH and ATR residues concentration (atrazine and its metabolites, i.e. deethylatrazine, DEA, and deisopropylatrazine, DIA). Water moisture was also determined in the soil samples by using a gravimetric method (24 h at 105ºC). Finally, plants grown in the three central cross sections of the mock-ups (sections 2, 3 and 4, Figure 1) were harvested at the end of the experiment and the dry plant biomass recorded. Ryegrass shoots were harvested by cutting the stem 1 cm above the soil

surface. Roots were harvested by carefully separating the biomass from the soil and rinsed them thoroughly with deionized water. Plant samples were air-dried for 2 days and homogenized using a grinder (Retsch Model ZM200, Germany) before analysing the concentration of ATR residues in shoots and roots.

2.4. Analysis of atrazine residues

Atrazine and its main metabolites (DEA and DIA) were quantified in soil and plant samples by analysing the extracts obtained by using a shaking-centrifuging extraction procedure described elsewhere (Amadori et al., 2013; Sánchez et al., 2018). In brief, homogeneous samples of approximately 2 g were extracted with 3 mL of pure acetonitrile (gradient grade, Sigma-Aldrich, USA) in three successive times obtaining an only extract which was analysed by HPLC. Times of shaking and centrifugation corresponding to each extraction step were 30 and 15 min, respectively. Soil and plant extracts and soil pore water samples were filtered with 0.45 µm nylon syringe filters before HPLC analysis.

Atrazine, DEA and DIA were analysed by reversed-phase liquid chromatography using a Shimadzu Prominence UFLC XR (Japan) HPLC system equipped with a diode array detector (SPD-M20A, Shimadzu, Japan) and an analytical C18 reversed-phase column (5 µm, 240 x 4 mm). A mobile phase consisting of pure acetonitrile (ACN) and a 0.01 M phosphate buffer solution (pH=7.1), with a flow rate of 0.5 mL min^{-1} for 25 min, was used. Temperature oven was kept constant at 30 ºC. The HPLC determination was conducted in a linear gradient mode with the following conditions: from 30:70 (v/v) ACN:buffer to 40:60 in 3 min, from 40:60 to 50:50 in 4 min, from 50:50 to 30:70 in 3 min and a final isocratic gradient of 30:70 ACN:buffer for 15 min. The detection

wavelength used for all ATR residues was 222 nm and the retention times were 16.1, 7.9 and 4.5 min for ATR, DEA and DIA, respectively. Atrazine recovery values in the range of 89-106% were obtained using the described extraction/analysis procedure.

3. RESULTS AND DISCUSSION

3.1. Influence of the electric field on water and soil properties

The electric current varied in the ranges of 0.40-0.47 A and 0.37-0.41 A for the planted (EKPR experimental series) and unplanted (EKR experimental series) mesocosms (see Figure SM-4 in Supplementary Materials). When a continuous electric field is applied to a soil, electric current depends on the soil resistance, which varies with parameters such as temperature, water content, ion concentration, porosity and the extent of the electrokinetic processes. Since the applied voltage gradient and the initial soil properties were the same for both experimental series, it would be expected that electric current would be as well. Therefore, the higher values of electric current found for the EKPR series can be attributed to the presence of ryegrass plants. It has been reported that plant roots increase the movement of water and ions by enhancing soil porosity (Sánchez et al., 2018); additionally, plants release root exudates with charged chemical groups which increase the soil ionic concentration (Lefevre et al., 2013; Vassilev et al., 2004). Electrical intensity was kept approximately constant or even slightly increasing for the EKPR series (Figure SM-4); it means that the reversal of electric polarity ensured the maintenance of an adequate flow of ions in the soil throughout the entire experiment.

The heating of the soil is an expected effect of the electrokinetic remediation (Risco et al., 2016c). This phenomenon was observed in our experiments, where the longitudinal temperature profiles for both mock-ups showed maxima values for the electrode soil sections (sections 1 and 5, Table SM-5 in Supplementary Materials) and minima ones for the central soil section (section 3); nevertheless, the differences of temperature between the different soil sections seldom reached more than 1 ºC. This fact agrees with previous findings from the electrokinetic remediation of soils polluted by the pesticides 2,4-D and oxyfluorfen in mock-ups with a similar size than those used here (Risco et al., 2016a, 2016b). The mean values of surface soil temperature for the planted and unplanted mock-ups were 26.3ºC and 25.2ºC (Table SM-5 and Figure SM-6). This moderate difference may be attributed to the lower heat dissipation in the soil with a vegetal cover. Lastly, the observed daily variations of soil temperature (Figure SM-6) were similar to those measured in the greenhouse air (data not shown).

FIGURE 2

Figure 2 shows the pH values of the different soil sections at the end of the experiment together with the pH changes of the corresponding pore water throughout the experiment.

As it can be seen, soil pH ranged between 8.56 and 9.53 for the EKR series (Fig. 2A and 2C) and between 8.74 and 9.44 for the EKPR series (Fig. 2B and 2D). It means that there were not important changes in the soil pH from the initial value, i.e. 9.42, especially for the planted mock-up. This is very important from a practical point of view, because EKPR with polarity reversal is able to avoid the extreme pH values as

would be expected from the generation of H^+ and OH^- in anode and cathode, respectively, in the water electrolysis processes (Virkutyte et al., 2002):

Anode: $H_2O \rightarrow 2\ e^- + ½\ O_2 + 2\ H^+$ (1)

Cathode: $2\ H_2O + 2\ e^- \rightarrow H_2 + 2\ OH^-$ (2)

This fact is well illustrated from the pH values of some of the Rhizon water samples, which were not expected to be in equilibrium with the solid phase of bulk soil, especially in the first days of the experiment. Some samples corresponding to the top layer of the mock-ups showed pH values in the range 2.4-4.2 (Figures 2A and 2C); they are indicative that, in the top soil layer, where no water saturation was achieved, there were specific areas in which the neutralization of the acid and basic fronts did not take place, leading to very low pH values (Risco et al., 2016c). Since the soil from the lower part of the mesocosms was partially saturated of water, the mobility of ionic species was improved, avoiding extreme pH values. Together with the reversal of electric polarity, it has been reported that the buffer capacity of the soil helps keep moderate soil pH values (Cang et al., 2011; Sánchez et al., 2019b). Nevertheless, the soil pH profiles showed a slight decreasing trend to the left side which could be due to the left electrode was acting as anode in the last day of the tests.

FIGURE 3

Figure 3 shows the longitudinal profiles of soil water content in the different sections belonging to both top and bottom soil layers for the two experimental series. In general, soil moisture values of the top layer soil sections were lower than those of the bottom

layer, especially for the EKR mock-up (Figure 3A). On the other hand, longitudinal soil profiles corresponding to the EKPR mock-up showed a clear trend of predominant water accumulation in the middle sections of the mock-up (Sections 2, 3 and 4, Figure 3B); this trend was not observed for the EKR mock-up, in which the water content showed a flatter profile with small variations between different soil sections (Figure 3A). Three different water fluxes can be cited in order to explain those profiles (Risco et al., 2015): (i) the electroosmotic flux, which causes the longitudinal transport of the soil pore water from the anode to the cathode, (ii) the gravity flux, responsible of the vertical water movement and (iii) the water flux caused by the suction of plant roots (only for the EKPR series). Moreover, the periodical changes in the electrical polarity also involved the inversion of the electroosmotic flux; as a result, soil moisture profiles in the EKR did not showed a clear increasing or decreasing trend. The presence of ryegrass plants in the sections 2, 3 and 4 of the planted mock-up (EKPR series) led to longitudinal profiles reaching higher soil moisture values in these sections; additionally, soil moisture values of the samples from the top layer of the EKPR mesocosm were higher than those of the samples from the EKR one. The gravity water flux together to the irrigation method (section 2.3) were the responsible of the higher water content in the bottom soil layer. So, the irrigation method used in the mesocosms probably influenced the extent of the electroosmotic flux and therefore the mobility of the pollutants under the electric field; as alternative, a surface irrigation could be more appropriate in order to increase atrazine availability in the soil area in contact with the roots.

3.2. Biomass production and ATR residues accumulated in plant tissues

TABLE 1

The values of harvested biomass (root and shoot, g) at the end of the experiment are shown in Table 1 together with the concentration of atrazine and its metabolites (DEA+DIA) in the ryegrass tissues. Plant biomass production was similar for the soil sections 2 and 4 but lower than that of the middle section (section 3). It may be attributed to the higher water availability in the middle soil section, as it was discussed in the previous paragraph, as well as the proximity of the sections 2 and 4 to the electrode sections, for which worse plant growth conditions were expected (Sánchez et al., 2019b). In fact, it has been previously reported that the electric field application caused negative and crossed effects on ryegrass biomass (Fang et al., 2001; O'Connor et al., 2003; Sánchez et al., 2019a; Zhou et al., 2007).

Total plant ATR concentrations were in the range of 189.66-243.69 μmol kg^{-1}, following the trend: section 2 > section 4 > section 3. Concentrations of ATR metabolites (deethylatrazine, DEA, and deisopropylatrazine, DIA) were quite lower (34.93-49.50 μmol kg^{-1}) and followed the opposite trend, suggesting that atrazine biodegradation inside the ryegrass tissues influenced ATR plant concentrations. The highest concentrations of ATR metabolites were found in shoots, indicating that atrazine degradation takes mainly place in the aerial tissues of ryegrass and/or metabolites are more efficiently translocated to shoots because of their higher water solubility (Table SM-2). Total plant ATR concentration in the different soil sections decreased as the total biomass was increased; so, atrazine toxicity could also influence ryegrass growth as it was previously reported by us (Sánchez et al., 2019a). The order of magnitude of ATR residues (atrazine, DEA and DIA) plant concentrations was the

same than that previously found by us in a EKPR pot experiment using ryegrass (Sánchez et al., 2019a).

3.3. Atrazine soil removal

FIGURE 4

FIGURE 5

Concentration values of atrazine residues remaining in the different soil sections of both mock-ups at the end of the experiment are shown in Figure 4. Figure 5 shows the concentration of atrazine residues (μmol L^{-1}) in the water samples taken by the Rhizon samplers located in the centre of the ten soil sections in which the mock-ups were divided (Figure 1).

Firstly, it may be pointed out that ATR residues concentrations were much higher for the top layer soil sections than for the bottom layer ones (up to one order of magnitude, Figures 4 and 5); it shows that atrazine and its derivatives were mainly transported by the electrokinetic fluxes, with a much lower extent of the vertical (gravity) flux. That hypothesis is additionally supported by the lower concentrations of atrazine residues detected in soil pore water samples corresponding to the bottom soil layer (Figure 5C and 5D) as compared to those of the top layer (Figure 5A and 5B). Therefore, it seems that the experimental spiking procedure used here did not ensured a homogeneous distribution of atrazine throughout the entire depth of the mock-ups at the beginning of the tests, and, later, when the electric field was connected, atrazine soil distribution was

strongly determined by the electrokinetic processes. It is an important limitation for laboratory or greenhouse experiments as compared to the real conditions in the field and it should be considered before the practical application of EKPR to polluted soils.

Regarding the longitudinal profile of atrazine residues remaining in the soil of the mock-ups at the end of the experiment, the highest values of atrazine residues were found for the electrode soil sections (sections 1 and 5), reaching concentrations up to three times higher than the corresponding to the theoretical one initially added to the soil, i.e. 9.27 μmol kg^{-1} (for the section 5 of the top soil layer in the EKR series, Figure 4A). It means that atrazine and its metabolites were effectively transported between both electrodes due to the electrokinetic transport mechanisms, i.e. electroosmosis and electromigration; again, it agrees with that observed for the concentration of atrazine residues in the soil pore water belonging to the top layer, where high values were only detected in the electrode soil sections and, in a higher extent, in the section 5 (Figure 5A and 5B). The periodical change of the electrode polarity should have led to similar concentrations of ATR residues in both electrodes; however, since most of water samples and the soil ones were taken in odd days (see Section 2.3), that is, when the left (section 1) and right (section 5) electrodes acted as anode and cathode, respectively, it means that the main electrokinetic transport mechanism for atrazine residues was electroosmosis. It is the flow of soil pore water, together with the dissolved chemical species, from the anode to the cathode caused by the application of an electrical gradient (Reddy and Cameselle, 2009). Additionally, atrazine, DEA and DIA are polar enough to be partially ionized (forming negatively charged species) in moderate acidic to alkaline soils (Ahmed et al., 2011); therefore, they could move from the cathode to anode by electromigration under an electric potential (Sánchez et al., 2018; Yeung and Gu, 2011).

Both transport mechanisms, with opposite direction, caused that atrazine residues were mostly accumulated in the sections 1 and 5 of the top soil layer (Figures 5A and 5C) from the first hours after the electric current was connected. Nevertheless, data shown in Figure 5 should be carefully considered since very low volumes of water, not enough to be analysed, were collected in some days; those ATR residues concentration values were assumed to be equal to zero. Lastly, it has to be pointed out that the described findings strongly agree with our previous results from the study of EKPR of atrazine by maize; in that case, electroosmosis was the main mechanism for the transport of atrazine residues when an electric field of 2 V cm^{-1} with polarity reversal was applied (Sánchez et al., 2019b).

The presence of ryegrass plants led to very different longitudinal profiles of atrazine concentration in both top and bottom soil layers. In the EKR mock-up, atrazine remained mainly in the left soil sections, reaching concentration values up to four times higher than those of the other sections (Figure 4A). However, for the EKR series mock-up, atrazine remaining in both electrode sections of the soil top layer (1 and 5) was similar, with values higher than those found in the planted soil ones (section 2, 3 and 4). It means that, while electroosmotic transport of atrazine was the main responsible of the final ATR concentration profile in the unplanted mock-up, ryegrass plants had a decisive role in the removal and fate of atrazine in the EKPR mesocosm.

The overall atrazine removal from soil after 19 days has been calculated for the EKPR and EKR mesocosms. Concentration of DEA and DIA remaining in the soil was not taken into account in this calculation because those metabolites are considered to be less toxic than the parent atrazine. In fact, while atrazine affects nervous, endocrine and

immune systems of vertebrates and inhibits photosynthesis in plants, DEA and DIA are not toxic to plants or aquatic photosynthetic microorganisms (Fan and Song, 2014; Lerch et al., 1996). The percentage of atrazine removed from the unplanted mock-up was 33.47% while it was improved up to 77.72% when ryegrass was used in combination with electrokinetic remediation. As it was previously shown (Sánchez et al., 2019a, 2018), atrazine may be removed by three main mechanisms in electrokinetic-assisted phytoremediation processes: (i) degraded inside the plant tissues (phytodegradation); (ii) accumulated in plant tissues (phytoextraction); and (iii) degraded by soil microorganisms, especially those growing in the rhizosphere (rhizodegradation). The relevant presence of DEA and DIA in plant tissues (Table 1) and in the soil of the EKPR mock-up after the treatment (Figure 4) is an evidence of microbial and plant degradation; moreover, those metabolites, which are only two of the first products from a complex metabolic pathway that leads to the final mineralization of atrazine (la Cecilia and Maggi, 2016), were also present in significant concentrations in the EKR mock-up, i.e. 7.26 and 16.82% of the initial ATR for the top and bottom soil layers, respectively (see Table SM-7 in Supplementary Materials), therefore showing that microbial degradation seems to be the main mechanism of atrazine removal in this case (note that the soil used here was not previously sterilized). Moreover, the values of the ratio (DEA+DIA)/ATR soil concentrations were much higher in the planted mock-up as compared to those of the unplanted one (25.67 vs 1.41, Table SM-7); it means that plant roots increased biological degradation because they affect the structure and the activity of microbial communities near the roots (Chaudhry et al., 2002; Piutti et al., 2002). Soil bottom layer also showed higher values of the (DEA+DIA)/ATR ratio than those of top layer due to the higher water solubility of DEA and DIA (Table SM-7) which reasonably favoured plant uptake in the top layer and the enrichment in ATR

metabolites of the water located in the bottom layer. Lastly, since ATR residues accumulated in ryegrass tissues only accounted for 1.26% of the initial atrazine (Table SM-7), it does not seem that plant accumulation was the main mechanism of ATR removal from soils. It does not mean that atrazine was not effectively taken up by roots because its mineralization inside the plant should be also considered. Lastly, some minor losses of atrazine by volatilization could have taken place due to the water evaporation from the top layer soil caused by the slight ohmic heating.

3.4. Considerations about the scaling-up of the EKPR technology

TABLE 2

Based on the shortage of medium to large-scale EKPR studies, one of the goals of this research was to study the main differences between the results obtained in the mesocosm test presented here and those belonging to a previously reported EKPR pot experiment with an atrazine spiked soil (Sánchez et al., 2019a). That pot test was also conducted using ryegrass as plant species and applying continuously an electric field of 1 V cm^{-1} with periodical polarity reversal each 2 h. In Table 2 are shown the main operational parameters (geometrical, pollution concentration, electrical, plant biomass and efficiency) of both experiments.

Soil, plant species, initial atrazine soil concentration, material of the electrodes and duration of the experiment were the same in both tests; however, others input parameters such as the maximum voltage of the power source (120 V) and the size of

containers and electrodes, were varied due to the limitations of the available equipment. Other operational parameter that was different in both tests was the frequency of the polarity reversal, i.e. each 2 and 24 h in pots and mesocosms, respectively; the reason was the larger distance between electrodes in the mock-ups, which advised to allow more time for the establishment of the electrokinetic flows. Thus, the values of the ratio between several of the parameters in mock-ups and pots were quite different, i.e. 320, 625, 55 and 18 for soil volume, soil weight, surface area and cross area, respectively. All this highlights the difficulties of obtaining geometrical and operational similarity between setups of different scale. Nevertheless, some interesting comments regarding output process parameters can be done.

Although the total voltage of 120 V applied in the mock-up was about 8.6 times higher than that of the pots, mean electric current registered was 26.4 times higher in the mock-ups due to the different ohmic resistance of the soil (it is a parameter that cannot be controlled). However, if the electric current values are expressed as specific current charge, that is, the total electric current applied during the test referred to the unit of soil weight, the value obtained for the mesocosm, i.e. 0.33 Ah kg^{-1}, was much lower than that of the pots, i.e. 7.82 Ah kg^{-1}. Moreover, the ratio root biomass:soil weight was 6 times lower for mock-ups as compared to pots (Table 2). Both facts should lead to a lower effectiveness of atrazine mobilisation and degradation, with the subsequent decrease of the ATR removal yield. In fact, overall atrazine removal was 94.4% and 77.72% for pot and mesocosm experiments, respectively. However, it can be easily seen that those values were not proportional to the differences observed for the output parameters analysed. Lastly, the mass of atrazine removed from the soil by the total applied current charge was 4.74 mg A^{-1} h^{-1} in the mesocosm vs 0.24 mg A^{-1} h^{-1} in the

pots; it means that the EKPR process was more efficient, from the point of view of energy use, at larger scale. It can be concluded that there are great difficulties in extrapolating small-scale results at larger scales, as it had previously shown in some studies of electrokinetic remediation of soils (López-Vizcaíno et al., 2017b, 2017a, 2016). It is also evident that a much more detailed study of the processes that occur on a large-scale is required, as well as greater care in achieving an adequate similarity between setups of different scale.

4. CONCLUSIONS

In this paper, the ability to successfully conduct the EKPR of atrazine-polluted soils in a mesocosm scale has been demonstrated. The periodical change of the electric field polarity together with the high buffer capacity of the used soil and the presence of ryegrass plants (in the planted mock-up) led to avoid significant soil pH changes, although very low pH values were punctually detected in soil pore water due the electrolysis reactions which takes place in the electrokinetic remediation processes. The presence of plant roots greatly influenced both the final soil water distribution and the longitudinal profiles of atrazine soil concentrations. Electroosmosis was the most relevant mechanism for the movement of atrazine and its metabolites through the soil. In the EKPR mesocosm, atrazine was removed from soils by a combined biological process consisting of rhizodegradation, phytodegradation and, in a minor extent, phytoaccumulation. Atrazine overall removal efficiency was greatly improved by ryegrass plants leading to an overall increase from 33.47% (unplanted mock-up) to 77.72% (planted mock-up). It clearly highlights the enhancement on the removal of

organic pollutants from soils when the electrokinetic remediation is used in combination with phytoremediation. A preliminary analysis of the scaling up of EKPR technology showed that while is difficult to keep the similarity, in terms of both geometric dimensions and electrical parameters, between setups of different scale, the extent of biochemical and electrokinetic processes that take place in the soil greatly varied with the size of the setup. So, it can be concluded that it is very difficult to adequately predict the efficiency of the EKPR technology in field conditions using data obtained from reduced-scale tests.

ACKNOWLEDGEMENTS

Authors acknowledge the Spanish Ministry of Economy, Industry and Competitiveness and European Union for the funding of the project CTM2016-76197-R (AEI/FEDEKR, EU). They also thank to the Regional Government of Castilla-La Mancha and the European Social Fund for the PhD grant number PRE2014/8027. Lastly, the assistance of Arcadio Nielfa in carrying out the experimental work is also gratefully recognized.

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Table 1. Total plant biomass and concentration of atrazine (ATR) and its metabolites (DEA: deethylatrazine; DIA: deisopropylatrazine) in the ryegrass tissues for the EKPR experimental series.

Soil section	Biomass*		ATR concentration (µmol kg^{-1})			(DEA+DIA) concentration (µmol kg^{-1})		
	Root (g)	Shoot (g)	Root	Shoot	Total plant	Root	Shoot	Total plant
2	47.96	39.21	172.25	331.08	243.69	4.39	72.28	34.93
3	58.56	47.88	57.59	351.20	189.66	1.82	107.82	49.50
4	50.70	41.45	32.61	421.52	207.54	1.63	99.30	45.56

(*) Soil sections 2, 3 and 4 had the same surface area (2,205 cm^2)

Table 2. Dimensions, operating conditions and output parameters of the two different-scale EKPR experiments used for the scaling up analysis. Results of mock-up refers to the research presented here while pot experiment refers to the results previously reported by Sánchez et al. (2019a).

Process parameters	Pot experiment	Mock-up experiment
Length/width (diameter)/depth (m)	- /0.16/0.06*	2.25/0.49/0.35
Soil volume (L)	1.21	386
Soil mass (kg)	1.0	625
Electrode distance (m)	0.14	2.0
Initial soil atrazine concentration (mg kg^{-1})	2.0	2.0
Electric field (V cm^{-1})	1.0	0.6
Total voltage applied (V)	14	120
Time between changes in polarity (h)	2	24
Duration of the experiment (h)	460	456
Mean electric current intensity (A)	0.017	0.449
Specific current charge (Ah kg^{-1})	7.82	0.33
Specific atrazine removal efficiency (mg A^{-1} h^{-1})	0.24	4.74
Root biomass: soil weight (g kg^{-1})	1.50	0.25

(*) Pots were cylindrical with a diameter of 16 cm.

FIGURE CAPTIONS

Figure 1. Diagram of the experimental mock-ups, including sampling points for Rhizon samplers (dimensions in meters).

Figure 2. pH of the pore water Rhizon samples over time and soil pH at the end of the experiment. Values from the different soil sections.

Figure 3. Soil water content profile of the mock-ups (% in mass) corresponding to EKR (electrokinetic remediation) and EKPR (electrokinetic-assisted phytoremediation) experimental series.

Figure 4. Atrazine (ATR) and its metabolites (DEA: deethylatrazine; DIA: deisopropylatrazine) concentration (µmol kg^{-1} soil) in the different soil sections at the end of the experiment. A: EKR series and B: EKPR series.

Figure 5. Spatial distribution and time course of atrazine residues (ATR+DEA+DIA) concentration in the soil pore water (µmol L^{-1}) (ATR: atrazine, DEA: deethylatrazine, DIA: deisopropylatrazine). Time axis: 0 days corresponds to 2 hours after applying the electric field.

Figure

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FIGURE 1

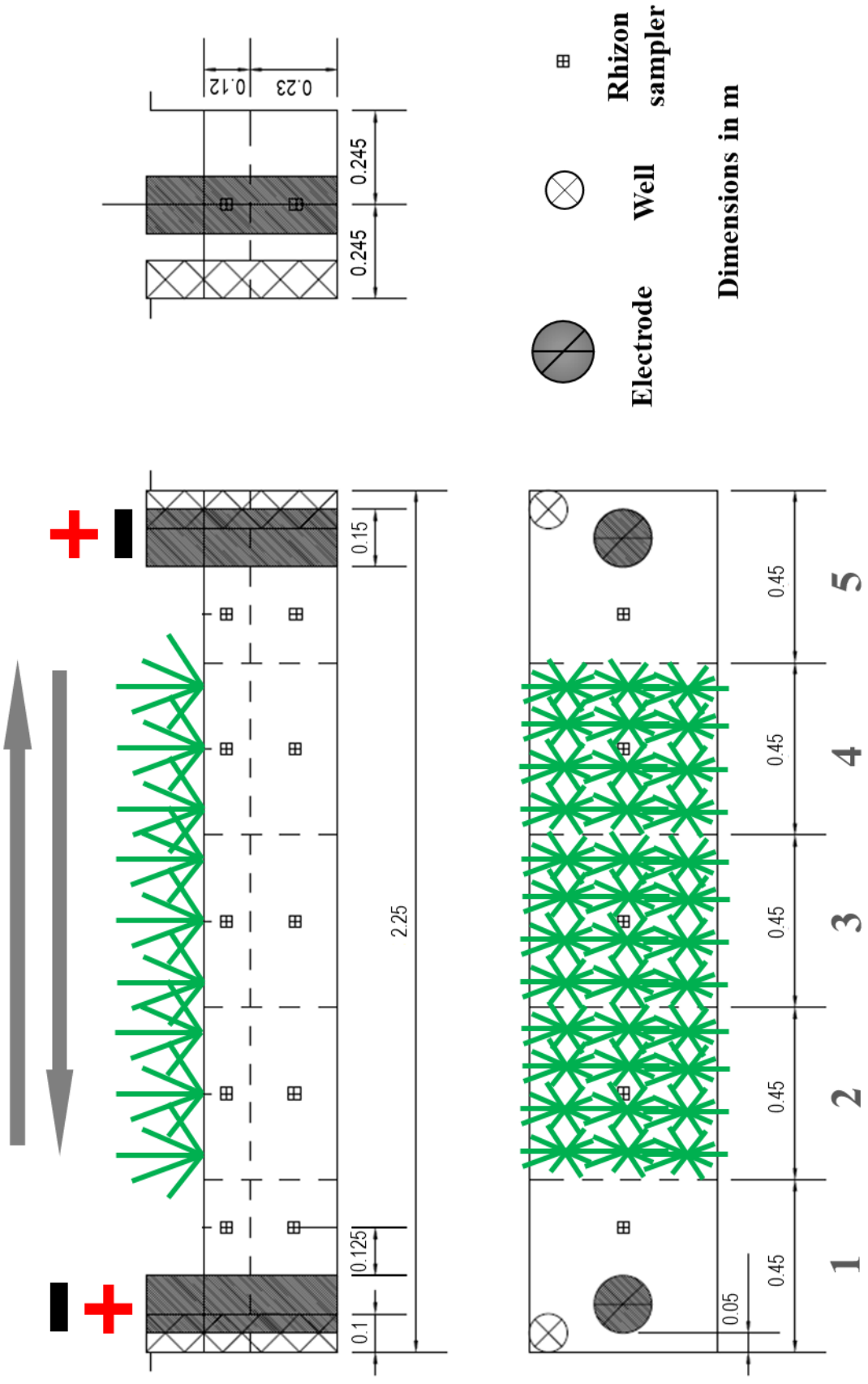


FIGURE 2

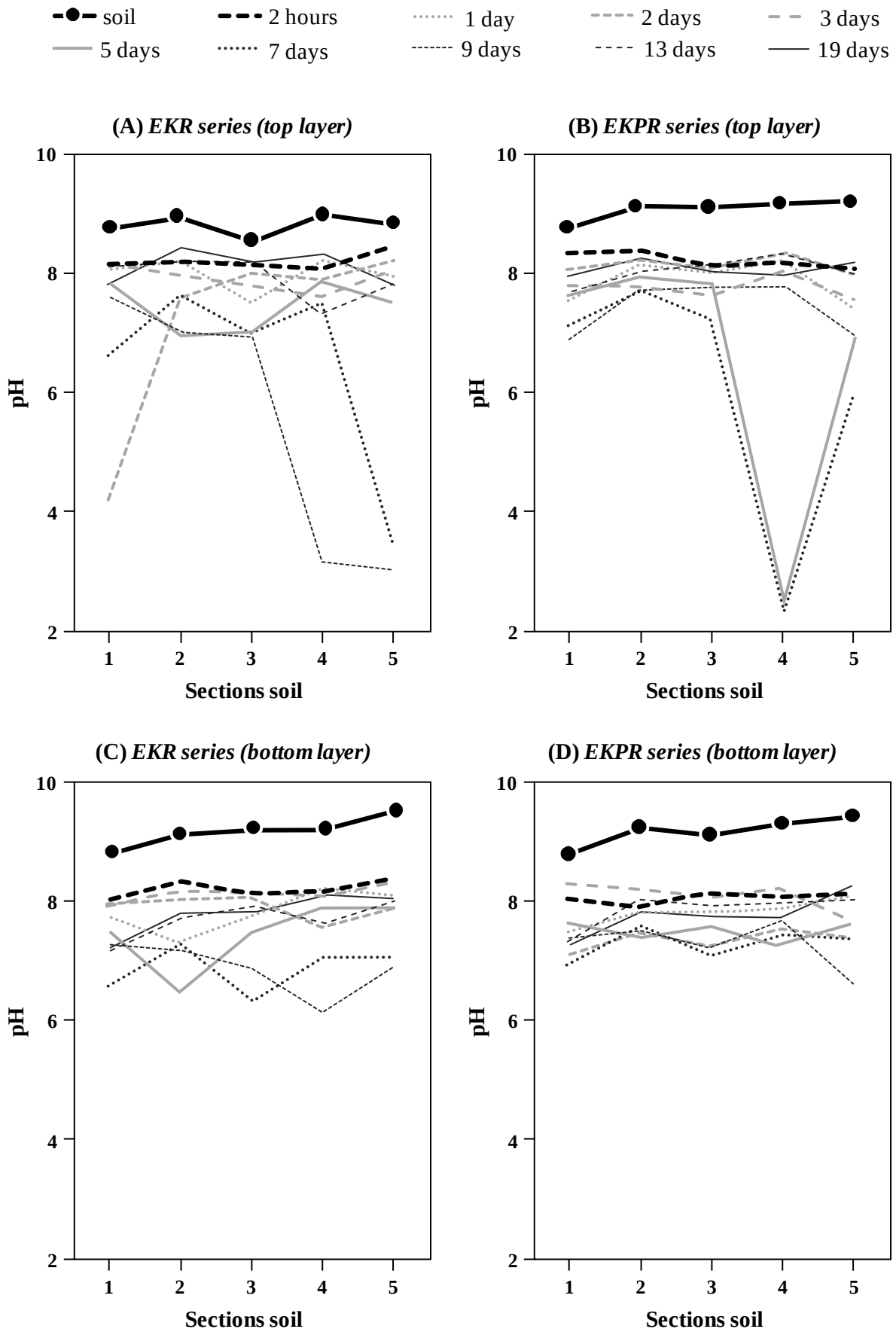

soil
2 hours
1 day
2 days
3 days
5 days
7 days
9 days
13 days
19 days
(A) EKR series (top layer)
(B) EKPR series (top layer)
(C) EKR series (bottom layer)
(D) EKPR series (bottom layer)
pH
Sections soil
10
8
6
4
2
1
2
3
4
5

FIGURE 3

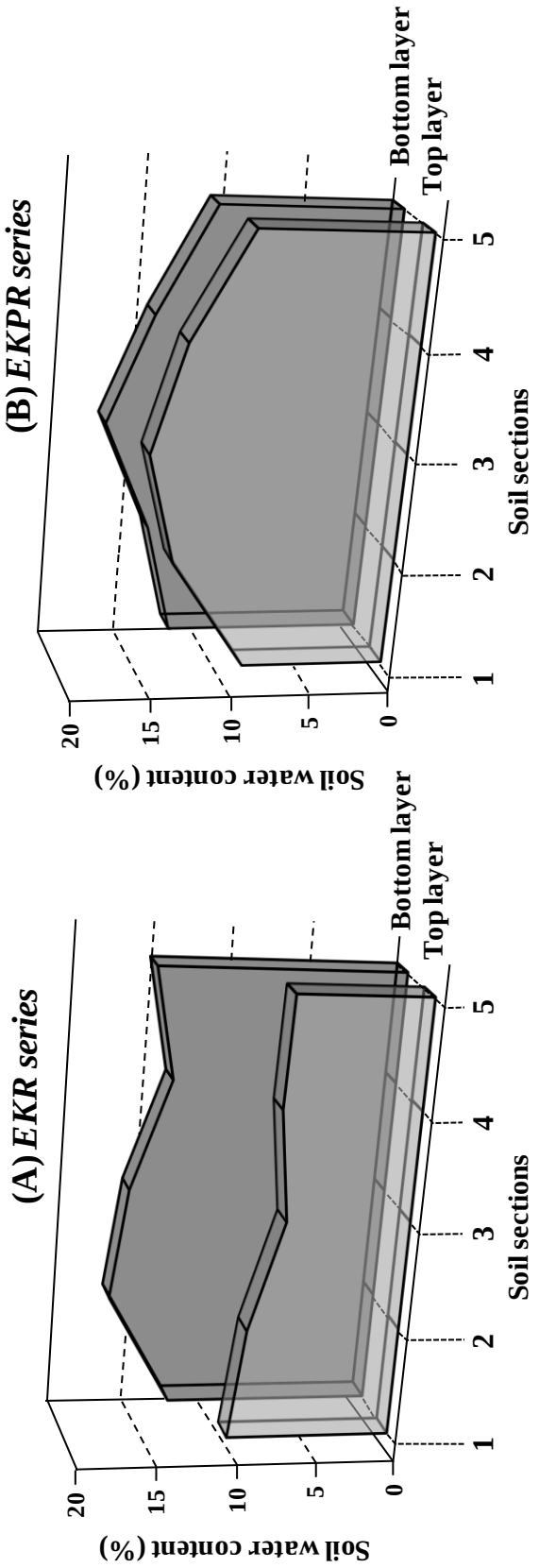
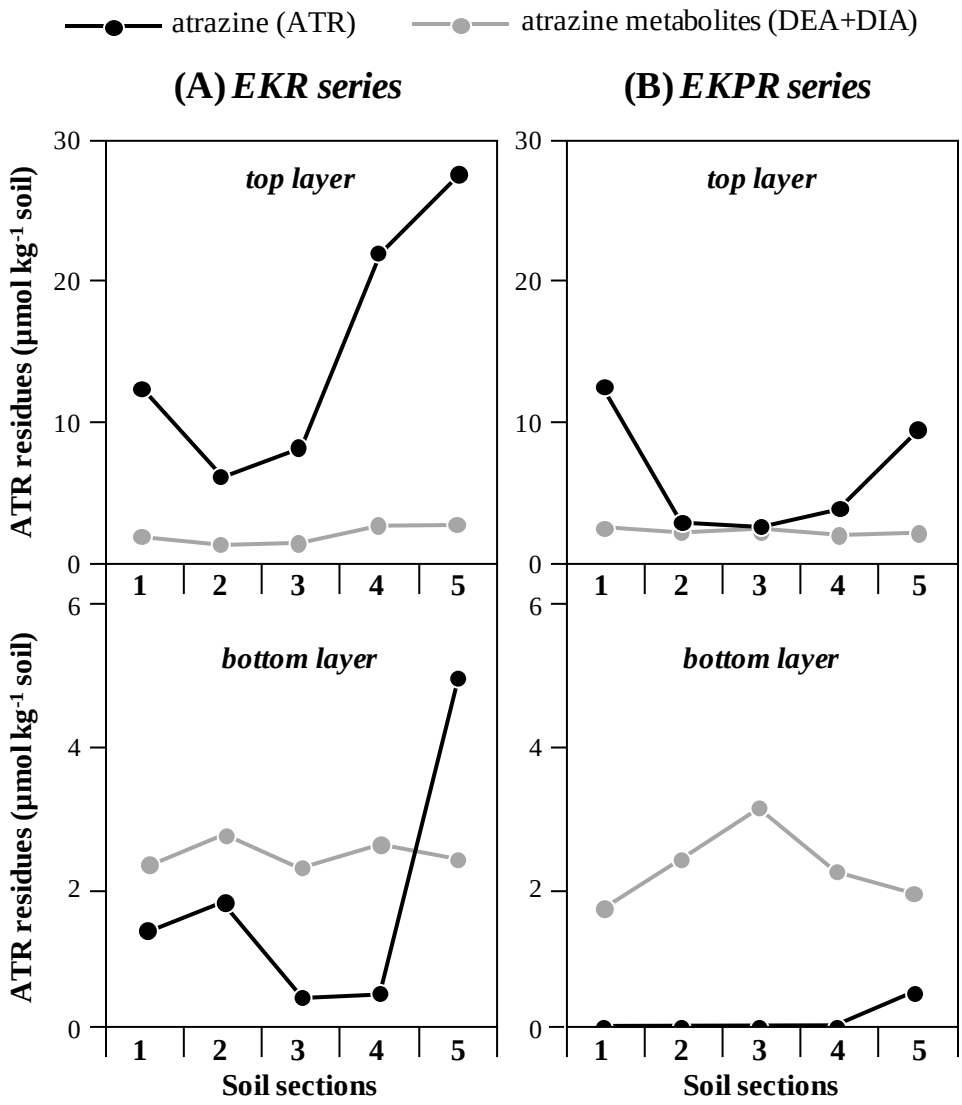

(A) EKR series
(B) EKPR series
Soil water content (%)
0
5
10
15
20
Soil sections
1
2
3
4
5
Top layer
Bottom layer

FIGURE 4


atrazine (ATR)
atrazine metabolites (DEA+DIA)
(A) EKR series
(B) EKPR series
top layer
bottom layer
ATR residues (µmol kg-1 soil)
Soil sections
30
20
10
0
6
4
2
1
2
3
4
5

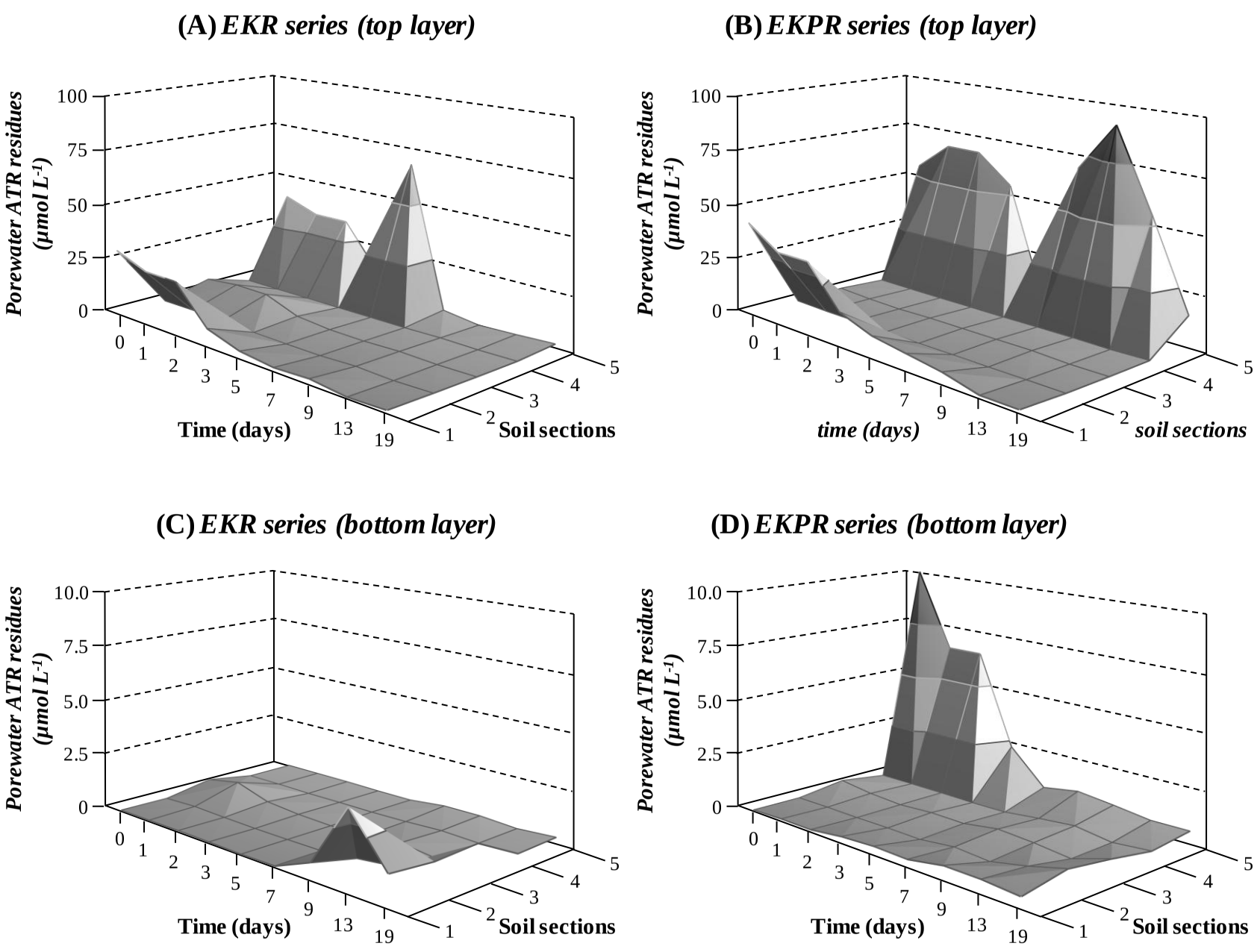

(A) EKR series (top layer)
(B) EKPR series (top layer)
(C) EKR series (bottom layer)
(D) EKPR series (bottom layer)
Porewater ATR residues (µmol L-1)
Time (days)
time (days)
Soil sections
soil sections
0
1
2
3
5
7
9
13
19
25
50
75
100
2.5
5.0
7.5
10.0
4

FIGURE 5

SUPPLEMENTARY MATERIAL

Scaling up the electrokinetic-assisted phytoremediation of atrazine-polluted soils using reversal of electrode polarity: a mesocosm study

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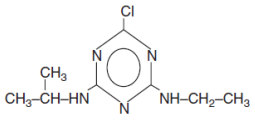
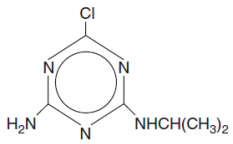
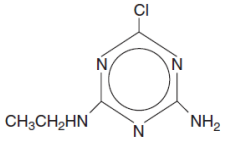
Table SM-1. Main physical and chemical properties of the soil used in this experiment.

Soil property	Method	Value
pH	1:5 soil/water mixture	9.42
Electrical conductivity ($\mu S\ cm^{-1}$)	1:5 soil/water mixture	150
CEC ($cmol\ kg^{-1}$)	Ammonium acetate saturation method	23.41
Soil organic carbon content (%)	Total organic carbon analyser	0.60
Bulk density ($kg\ m^{-3}$)	ASTM Standards D-854	1,540
Liquid limit (%)		42
Plastic limit (%)	ASTM Standards D-4318	24
Plasticity index (%)		18
Soil classification	USCS	CL (a low plasticity clay)
Hydraulic conductivity ($m\ s^{-1}$)	UNE 103405:1994	2.10^{-10}

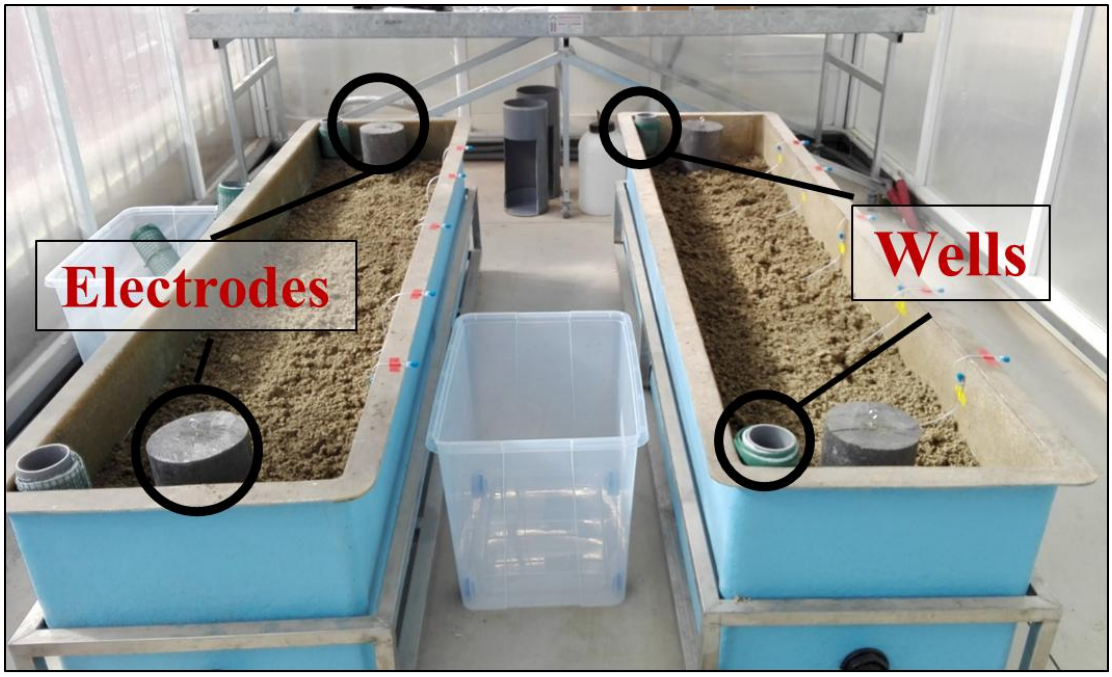
Table SM-2. Chemical structure and main properties of atrazine and the metabolites studied in this work (taken from Amadori et al. 2016*).

	Name	Key properties	Formula
	Atrazine (ATR)	215.68 g mol^{-1} 33 mg L^{-1} (water) pK_a 1.68-1.71	
ATR metabolites	**Deethyltrazine (DEA)**	187.63 g mol^{-1} 3200 mg L^{-1} (water) pK_a 1.30-1.65	
	Deisopropylatrazine (DIA)	173.60 g mol^{-1} 670 mg L^{-1} (water) pK_a 1.30-1.58	

(*) Amadori, M.F., Cordeiro, G.A., Rebouças, C.C., Peralta-Zamora, P.G., Grassi, M.T., Abate, G., 2013. Extraction method for the determination of atrazine, deethylatrazine, and deisopropylatrazine in agricultural soil using factorial design. J. Braz. Chem. Soc. 24, 483-491.

FIGURE SM-3

Pictures of mock-up preparation.



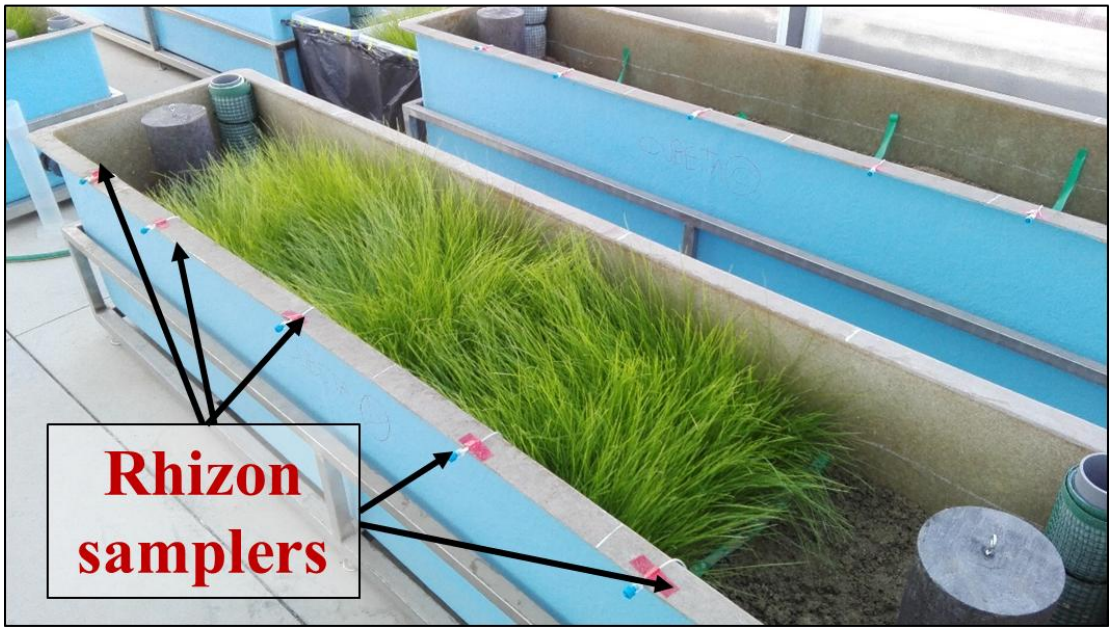


FIGURE SM-4

Time course of the electric current for the EKR (electrokinetic remediation) and EKPR (electrokinetic-assisted phytoremediation) experimental series.

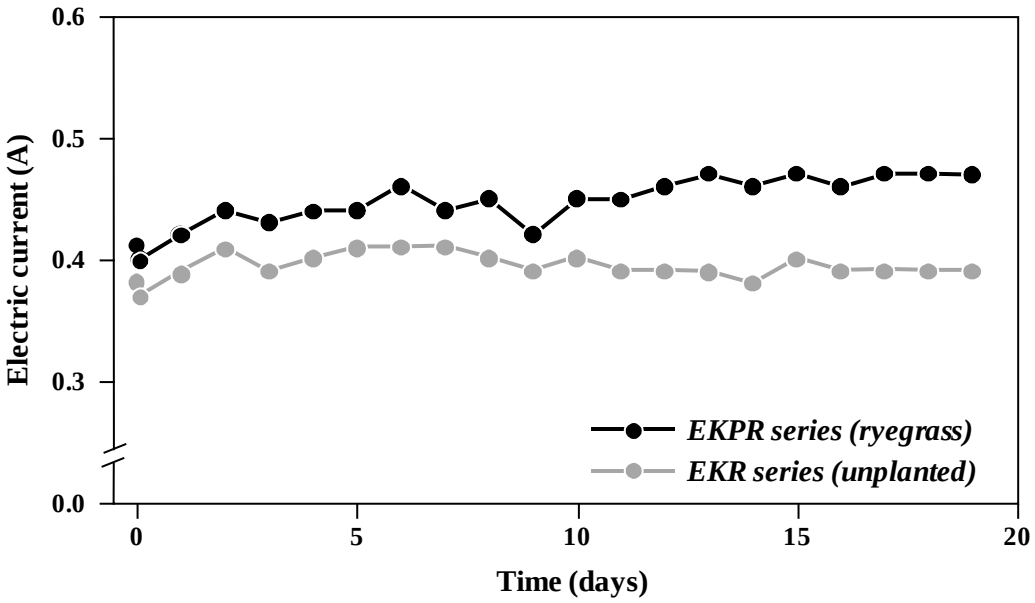


Table SM-5. Time course of the surface soil temperature during the entire experiment.

		Time (days)																			
		0	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
UNPLANTED mock-up (EKR series)																					
Soil sections	1	25.7	25.1	25.3	25.1	25.5	26	25.3	25.8	25.6	25	25.5	25.7	26.2	25.7	25.7	25.2	25.9	25.5	25.5	25.5
	2	25.7	24.2	24.5	24.3	24.3	25.4	24.8	25	25.2	24.8	25.1	25.1	25.1	25.3	25	25.1	25.1	25.3	25.1	25.1
	3	25.3	23.6	23.9	23.8	24.2	25.3	24.5	24.9	24.8	24	25.2	25.5	25.5	25.2	24.5	24.5	25.2	25.8	24.5	24.6
	4	25.7	24.2	24.0	23.5	25.3	25.8	25.2	25.7	24.8	24.7	24.8	25.5	26.4	26	24.6	24.8	25.5	25.3	24.3	25
	5	25.3	25.1	24.7	24.0	25.5	26.5	25.6	26.1	25.8	24.5	25.8	26.0	26.6	25.8	26.0	26.1	25.6	25.7	25.5	25.5
	Mean	25.5	24.4	24.5	24.1	25.0	25.8	25.1	25.5	25.2	24.6	25.3	25.6	26.0	25.6	25.2	25.1	25.5	25.5	25.0	25.1
	(STD)	(0.2)	(0.7)	(0.6)	(0.6)	(0.7)	(0.5)	(0.4)	(0.5)	(0.5)	(0.4)	(0.4)	(0.3)	(0.6)	(0.3)	(0.7)	(0.6)	(0.3)	(0.2)	(0.6)	(0.4)
RYEGRASS mock-up (EKPR series)																					
Soil sections	1	26.0	25.0	25.5	24.8	26.0	26.4	26.2	25.8	26.6	24.8	26.2	26.3	27.0	26.5	26.0	26.2	25.9	26.1	25.6	25.7
	2	25.5	25.3	25.5	24.9	25.9	27.2	26.6	27.1	26.2	25.8	26.2	26.6	27.4	28.4	26.6	26.4	26.4	26.6	26.7	26.1
	3	25.3	25.7	25.8	25.1	26.4	27.5	26.6	27.1	26.8	26.0	26.4	26.8	27.8	27.5	27.0	26.8	26.7	26.6	26.2	26.4
	4	25.0	25.8	26.2	25.2	26.4	27.7	27.2	27.6	27.0	26.2	26.7	27.2	28.3	28.3	27.2	27.2	27.2	27.2	27.0	26.8
	5	26.2	25.5	25.3	24.5	26.0	26.6	26.3	26.2	25.8	24.3	25.9	26.8	27.4	27.5	26.8	26.4	26.3	26.4	26.5	25.9
	Mean	25.6	25.5	25.7	24.9	26.1	27.1	26.6	26.8	26.5	25.4	26.3	26.7	27.6	27.6	26.7	26.6	26.5	26.6	26.4	26.2
	(STD)	(0.5)	(0.3)	(0.4)	(0.3)	(0.2)	(0.6)	(0.4)	(0.7)	(0.5)	(0.8)	(0.3)	(0.3)	(0.5)	(0.8)	(0.5)	(0.4)	(0.5)	(0.4)	(0.5)	(0.4)

Figure SM-6. Time course of the mean values of surface soil temperature. (Symbols represent mean values of the five soil sections in which mock-ups were divided; error bar represents STD)

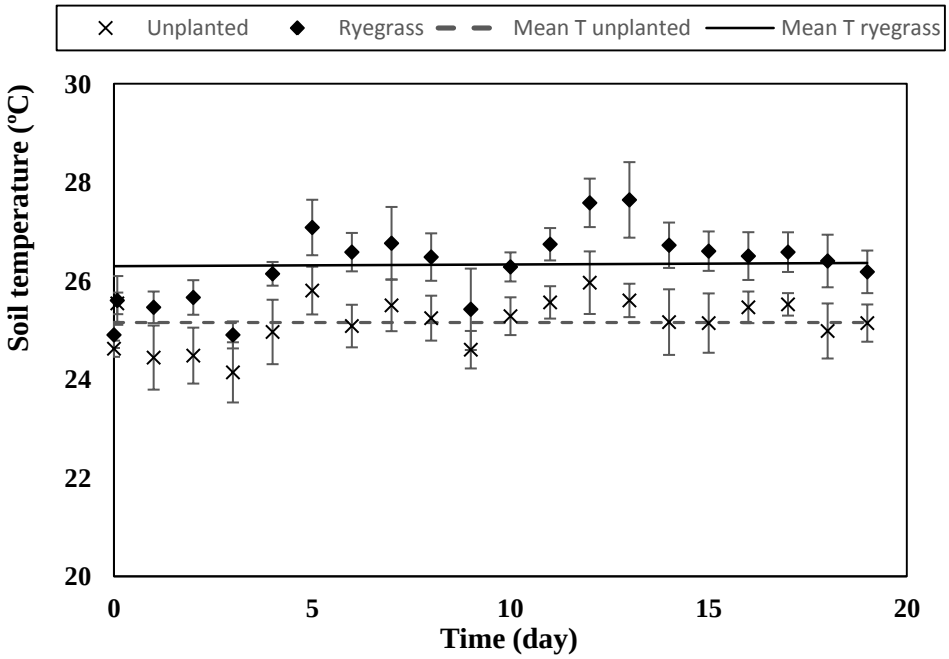


Table SM-7. Atrazine (ATR) and its metabolites (DEA: deethylatrazine; DIA: deisopropylatrazine) remaining in soils and plants at the end of the EKR (electrokinetic remediation) and EKPR (electrokinetic-assisted phytoremediation) tests, ATR removal from soils (both expressed as % of the initial ATR) and (DEA+DIA)/ATR ratio.

Experimental Series*	EKR series	EKPR series
ATR remaining in soil (%)		
Top layer	54.63	21.67
Bottom layer	11.90	0.61
Overall ATR removal (%)	**33.47**	**77.72**
(DEA+DIA) remaining in soil (%)		
Top layer	7.26	8.21
Bottom layer	16.82	15.66
(DEA+DIA)/ATR soil		
Top layer	0.13	0.38
Bottom layer	1.41	25.67
ATR in total plant (%)	-	1.04
(DEA+DIA) in total plant (%)	-	0.22

(*) EKR: electrokinetic remediation
EKPR: electrokinetic-assisted phytoremediation