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**CAN ELECTROCHEMISTRY ENHANCE THE REMOVAL OF ORGANIC
POLLUTANTS BY PHYTOREMEDIATION?**

**Virtudes Sánchez¹, Francisco Javier López-Bellido², Pablo Cañizares³ and Luis
Rodríguez^{1*}**

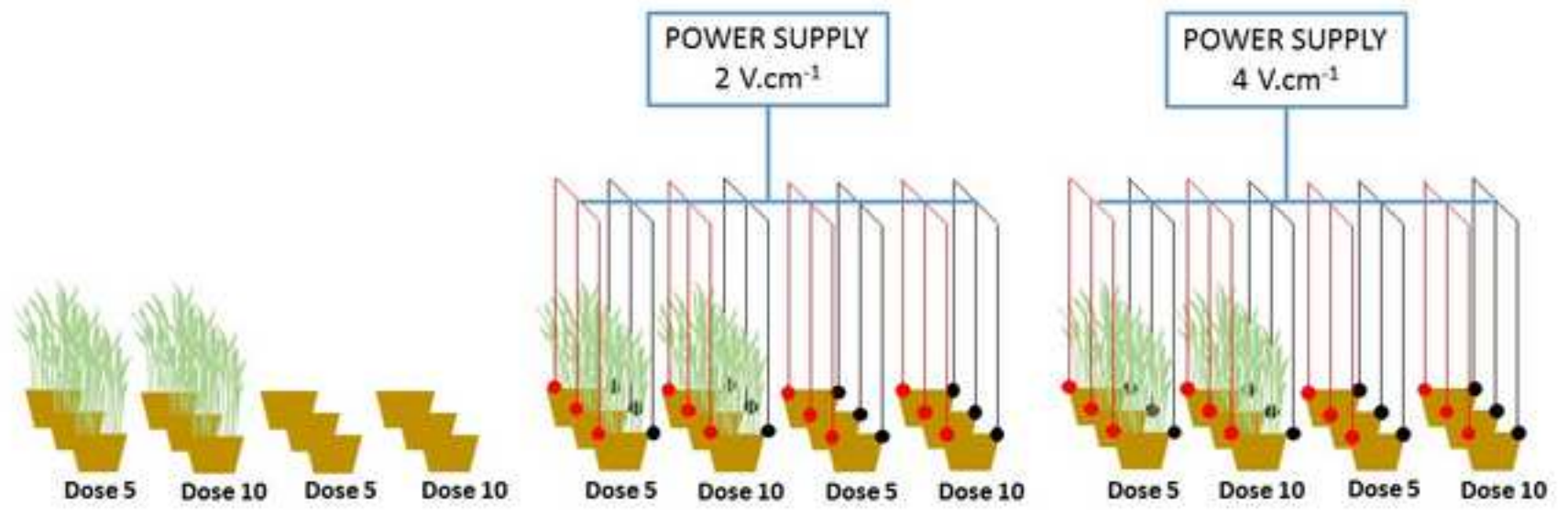
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Graphical abstract



HIGHLIGHTS

Electric field application enhanced plant uptake and soil degradation of atrazine

Soil pH did not changed using electricity 4 h a day and switching polarity each 2 h

The application of an electric voltage of 2 V.cm^{-1} increased the mobility of atrazine

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1 **ABSTRACT**

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5 3 An electrokinetic-assisted phytoremediation test using maize (*Zea mays* L.) was
6
7 4 conducted in order to assess the role of the electric field on the enhancement of plant
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9 5 uptake and degradation of the moderate polar pesticide atrazine in spiked soils. Twelve
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11 6 different treatments, including two different initial atrazine soil doses (5 and 10 mg kg⁻
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13 7 ¹) and two different values of the electric field applied (2 and 4 V cm⁻¹), together with
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15 8 the corresponding control treatments without plants and/or without electric current,
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17 9 were tested. The application of an electric field during a period of 4 h a day and with
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19 10 periodical polarity inversion (each 2 h) did not caused significant changes in soil pH;
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21 11 moreover, maize plants increased the buffering capacity of the soil. The application of
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23 12 an electric field of 2 V cm⁻¹ led to a slight decrease on maize biomass while the
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25 13 accumulation of atrazine and its main metabolites in plant tissues was significantly
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27 14 enhanced. On the overall, the yield of atrazine removal by electrokinetic-assisted
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29 15 phytoremediation with maize was increased up to 36.5% with respect to the
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31 16 phytoremediation process without electricity. On our knowledge, this work is the first
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33 17 one specifically focused on the removal of organic pollutants from soils by using the
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35 18 combination of phytoremediation and electrokinetic remediation.
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58 **Keywords:** atrazine, maize, electrokinetic-assisted phytoremediation, polluted soils
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1. INTRODUCTION

Hazardous organic pollutants, as pesticides, represent a threat to human, animal and environmental health (Rodrigo et al. 2014). Changes in agricultural practices have led to the widespread use of pesticides and the succeeding increase in their concentrations in the environment (Kang, 2014). Consequently, soil remediation is becoming a key area of study for the development of novel and efficient treatment systems (such as the electrokinetic-assisted technologies) in order to reduce the hazards of pesticides and other pollutants in the environment (Vieira dos Santos et al., 2016).

The coupling of phytoremediation and the electrokinetic (EK) remediation (electrokinetic-assisted phytoremediation, EK-phytoremediation) has been proposed to overcome the current disadvantages of the individual technologies, such as the difficulties for pollutant mobilization towards the plant roots observed in phytoremediation and the long-term accumulation of contaminants in distant electrodic wells, which occurs in some EK remediation practical cases (Hodko et al., 2000; Lobo et al., 2009). EK-phytoremediation has already shown very promising results for metals and semimetals (O'Connor et al., 2003; Lim et al., 2004; Zhou et al., 2007; Bi et al., 2011; Cang et al., 2011 and 2012; Kubiak et al., 2012; Putra et al., 2013). To date, the combination of phytoremediation and electrokinetic remediation has not been deeply assessed in soils polluted by organic compounds. To our knowledge, there are only two recent papers reporting the remediation of a soil contaminated by a mixture of metals and organic pollutants (PAHs), but without conclusive results (Chirakkara et al., 2015; Acosta-Santoyo et al., 2017). The cited works were mainly focused on soils polluted by metals while the aspects regarding the organic pollutants, such as the influence of

1 electric current on the its bioavailability, the effect on its degradation and/or
2 accumulation in plant tissues, and the changes in soil microbial activities, were not
3 deeply addressed.

4
5 Another important point that must be considered is the selection of the plant species,
6 which should be studied in combination with the specific operating conditions. Only a
7 reduced group of plants species have been tested in the EK-phytoremediation tests, i.e.
8 *Brassica juncea* (Indian mustard) and *Brassica napus* (rapeseed), *Nicotiana tabacum*
9 (tobacco), *Avena sativa* (oat), *Poa pratensis* (Kentucky bluegrass), *Lolium perenne*
10 (ryegrass) and *Helianthus annuus* (sunflower). As a clear pattern in the choice of plant
11 species has not yet been found, to date, it has been preferred to conduct EK-
12 phytoremediation using plant species with a successful performance on
13 phytoremediation tests.

14
15 This work constitutes the first attempt to check if the application of an electric field
16 really improves the phytodegradation of organic contaminants in soils. We report the
17 results obtained in a pot experiment using a combination of maize (*Zea mays*) and an
18 electric field to decontaminate a low permeability soil spiked with atrazine. Maize was
19 selected based on its good efficiency for atrazine degradation (Sánchez et al., 2017).
20 Atrazine was selected because it is a moderately polar herbicide, whose octanol
21 partition coefficient below 3 ($\log K_{ow} = 2.68$) and its water solubility of 33 mg.L^{-1}
22 (Amadori et al., 2016) should be enough for it to be transported by electromigration
23 and/or electroosmosis under the application of an electric current to the soil. The interest
24 of studying this herbicide is also motivated because, in spite it was banned in the
25 European Union since 2004, it remains being one of the most plentiful pesticide

1 contained in waterways in Europe (Weber et al., 2018). Moreover, the results obtained
2 here could be extrapolated to other moderately polar or polar organic pesticides. The
3 specific goals of this work were: (i) to study the changes caused by the electric current
4 in soil pH during the electrokinetic assisted phytoremediation (EK-phytoremediation);
5 (ii) to investigate how this innovative technology influence the uptake of atrazine by
6 maize and the soil-plant degradation processes; (iii) to assess if EK-phytoremediation is
7 capable to increase the effectiveness of atrazine removal from soil with respect to the
8 phytoremediation by maize.

10 **2. MATERIALS AND METHODS**

12 **2.1. Soil and plants**

14 A natural soil with no antecedents of pollution coming from an agrarian area located in
15 central Spain (Mora de Toledo, Toledo) was used in the experiment. After removing the
16 surface layer of the soil (0-10 cm) and the vegetal cap, an enough amount of sample was
17 collected from a depth of 10 to 100 cm. The soil was disaggregated, homogenised, air-
18 dried and, finally, sieved to 2 mm prior to its use in the pot experiment. The soil has a
19 pH (in water) of 9.42, a cation exchange capacity (CEC) of 23.42 $\text{cmol}_c.\text{kg}^{-1}$, a total
20 organic carbon content of 0.60% and an electrical conductivity of 0.15 $\text{mS}.\text{cm}^{-1}$. It was
21 classified as a low plasticity clay (CL) soil according to the Unified Soil Classification
22 System (USCS); the values for the liquid limit, the plastic limit and the plasticity index
23 were 42, 24 and 18, respectively. Likewise, this soil can be considered as a low
24 permeability soil for which electrokinetic technology is recommended.

1 A commercial variety of maize (*Zea mays* L., dent corn hybrid cultivar) was used in the
2 EK-phytoremediation experiment. Seeds were pre-germinated in a growing medium
3 (0.5 mM CaSO₄) and kept moist during three days at 28°C. After the germination
4 period, healthy seeds with uniform size were selected and carefully transplanted to the
5 soil.

7 **2.2. Experimental design**

8
9 The EK-phytoremediation experiment was carried out using plastic pots (16 cm
10 diameter and 18 cm depth) located in a growth chamber equipped with control of
11 lighting, temperature and humidity. The experimental conditions were a photoperiod of
12 16-h, a relative humidity in air of 60-70% and day/night temperatures of 27/16°C.
13 Additional technical details of the growth chamber can be found in a previous paper
14 (Sanchez et al., 2017).

15
16 The experiment was carried out using a completely randomized design with three
17 replicates (individual pots) per treatment. Thus, twelve treatments were applied in this
18 study; they resulted from the combination of planted and unplanted pots with initial soil
19 atrazine concentrations of 5 and 10 mg kg⁻¹ and the application (or not) of an electric
20 field with voltage values corresponding to 2 and 4 V cm⁻¹. These values have been
21 chosen taking into account the previous literature on EK-phytoremediation of metal-
22 polluted soils (Cang et al., 2011 and 2012; Cameselle et al., 2013) and our previous
23 research on atrazine phytoremediation (Sanchez et al., 2017).

1 One kilogram of dry soil was placed in each individual pot forming a layer about 6 cm
2 deep. The electric field was applied using a pair of graphite electrodes (15 cm in length
3 and 6 mm in diameter) connected to a DC (direct current) power supply which worked
4 in the range 0-120 V and 0-13 A (Delta Elektronica S.V., model SM120-13, The
5 Netherlands). Graphite rods were used since graphite can be considered as an inert
6 material which avoid the release of additional chemical species (different to H⁺ and OH⁻
7) to the soil (Virikutyte et al., 2002); they were vertically inserted into the soil at both
8 sides of the pots (at a distance of 14 cm between them and 1 cm from the wall of the
9 pot); metal clamps were used to connect the top part of the electrodes with the DC
10 power supply. The pots were kept 7 days in the growth chamber; the soil moisture
11 content was kept at 60-70% of its water holding capacity (by daily weighting) in order
12 to ensure an optimum contact between soil and the graphite rods. Next, 14 pre-
13 germinated maize seeds were planted in each pot. After 35 days of plant growth, the
14 soils were spiked with the adequate volume of an aqueous solution of atrazine (prepared
15 from a 250 mg.L⁻¹ solution of atrazine in methanol; solid atrazine was supplied by
16 Sigma-Aldrich, USA) in order to achieve initial concentrations of 5 and 10 mg of
17 atrazine per kg of soil (corresponding to 23.18 and 46.36 μmol per pot, respectively).
18 Atrazine was sprayed homogeneously on the soil surface, getting soil at water holding
19 capacity (WHC) state. Electrical DC current (2 or 4 V cm⁻¹) was started to be applied
20 the same day of atrazine addition with the following conditions: 4h/day and switching
21 the polarity every 2 h (in order to avoid extreme soil pH values). During the 14-day
22 duration of the EK-phytoremediation experiment, the electrical intensity of each pot was
23 recorded daily.

1 At the end of the experiment, soil and maize samples were collected from pots. The soil
2 samples were air-dried and disaggregated and, later, analysed to determine soil pH (pH
3 values were obtained of the homogenised soil) and the concentration of ATR and its
4 metabolites (see Section 2.3). The maize shoots were harvested by cutting the stem 1
5 cm above the soil surface. The roots were harvested by separating the biomass from the
6 soil and removing the external soil particles; next, they were thoroughly rinsed with
7 deionized water. The plant samples (shoots and roots) were air dried at room
8 temperature until constant weight and, finally, homogenized using a grinder (Retsch
9 Model MM200, Germany). The dry matter biomass was recorded and the concentration
10 of ATR and its metabolites was analysed (see Section 2.3).

12 **2.3. Atrazine analysis**

14 Atrazine and its main derivatives were quantified in soil and plant samples by HPLC
15 analysis of the extracts obtained by using a shaking-centrifuging extraction procedure
16 (Amadori et al., 2013). A sample of 2.0 g of soil or plant tissues (previously chopped,
17 crushed and blended) was weighted in a glass flask, suspended in 3 mL of acetonitrile
18 (Acetonitrile Chromasolv for HPLC, gradient grade, Sigma-Aldrich, USA) and shaken
19 for 30 min and, finally, centrifuged for 15 min. This procedure was carried out three
20 times and the respective supernatants phases were reserved and finally combined. The
21 resulting extracts were filtered using 0.45 µm nylon syringe filters before HPLC
22 determination.

24 The concentration of atrazine residues, i.e. atrazine (ATR) and its main metabolites
25 (deethylatrazine, DEA, and deisopropylatrazine, DIA), were analysed in soil and plant

1 extracts. Sample aliquots of 20 μL were injected into a HPLC system (Shimadzu
2 Prominence UFLC XR, Japan) and analysed using a C18 reversed-phase column (240
3 mm x 4 mm) kept at 30 $^{\circ}\text{C}$. Pure acetonitrile and 0.01 M phosphate buffer solution (pH
4 = 7.1) were used as mobile phase at a flow rate of 0.5 mL min^{-1} for 25 min. The mobile
5 phase used in the HPLC analysis was a mixture of acetonitrile and phosphate buffer
6 with the following conditions: (i) 0-3 min, linear gradient from 30:70 (v/v) mixture to
7 40:60; (ii) 3-7 min, linear gradient from 40:60 to 50:50; (iii) 7-10 min, linear gradient
8 from 50:50 to 30:70; (iv) 10-25 min, isocratic gradient of a 30:70 acetonitrile:phosphate
9 buffer. Atrazine and its metabolites were measured at 222 nm using a diode array
10 detector (SPD-M20A, Shimadzu, Japan). According to these conditions, the retention
11 times of ATR, DEA and DIA were determined: 16.1, 7.9 and 4.5 minutes, respectively.
12 All chemicals used in the analysis were analytical grade. Deionized water was used to
13 prepare all solutions.

14
15 Throughout the text, concentrations of atrazine, DEA and DIA in soils and plants have
16 been expressed as μmol (per kg o per pot) instead of μg , due to different molecular
17 weight of the atrazine and its metabolites (215.68, 187.63 and 173.60 g.mol^{-1} for ATR,
18 DEA and DIA, respectively).

20 **2.4. Statistical analysis**

21
22 One-way ANOVA analysis was used to compare the mean values of the analysed
23 experimental parameters from different treatments. It was done by using Duncan's
24 honestly significant difference test at $p < 0.05$. The data normality was previously

1 checked by using the Kolmogorov-Smirnov test. The SPSS 22 Statistical Software was
2 used for the analysis.

3. RESULTS AND DISCUSSION

3.1. Changes in soil properties caused by electric field application.

FIGURE 1

Figure 1 shows the daily variation of the electric current for all the experimental series. Electric current did not vary with the different initial atrazine doses in soil; thus, data series showed in the Figure 1 are mean values of the corresponding series for 5 and 10 mg ATR kg⁻¹. When 2 V cm⁻¹ were applied to the soil, the electric current varied in the ranges 21.7-30.0 and 20.0-28.3 mA, corresponding to maize pots and unplanted pots (control), respectively. As expected, for the electrical field of 4 V cm⁻¹, the electric current values registered were higher, with ranges of 50.0-76.7 for maize pots and 38.3-46.7 mA for control pots, respectively.

The current values in pots without plants were lower than those of maize pots for the same applied voltage. It means that maize increased the current density in soils which can contribute, in turn, to enhance the mechanisms of decontamination related with the electrochemical processes. The water content in all pots (with and without plants) was kept at the same level by daily irrigation (around 60-70% of the water holding capacity); so, since the low permeability of the soil used here, the higher values of current observed in the planted pots may be reasonably attributed to the increase in soil porosity

1 caused by plant roots. Moreover, the presence of a greater amount of mobile ions in the
2 pots with maize coming from the root exudates could also contribute to the increase of
3 electric current in some extent. This fact could be also related with the slight decrease in
4 current observed from approximately 120-150 hours of treatment time (Figure 1), when
5 the first visual symptoms of phytotoxicity were detected and, therefore, plant activity
6 began to decline.

8 **TABLE 1**

10 In Table 1 are shown the soil pH values at the end of the EK-phytoremediation
11 experiment. pH mean values for planted pots were in the range 8.83-9.53 with no
12 significant differences between different voltages and initial atrazine soil doses. The
13 only statistically significant difference between the treatments with electricity
14 application and those without it was found for the 4 V cm⁻¹ treatment, which pH was
15 significantly higher than that of the 0 V cm⁻¹ treatment. Cang et al. (2011) reported that
16 the soil pH increased with the applied voltage; our results showed this trend only for the
17 5 mg kg⁻¹ ATR soil dose but without statistical significance. Unplanted pots did not
18 show significant differences in soil pH values with respect to planted pots; however, the
19 range of pH values was higher than that of the planted pots, i.e. 9.50-9.84. It means that
20 maize activities enhanced the buffering capacity of the soil used in this study in some
21 extent. Some authors (O'Connor et al., 2003; Aboughalma et al., 2008) reported that the
22 DC electric field might cause acidification in the anode region and alkalisation in the
23 cathode region, which was ascribed to the generation of H⁺ and OH⁻ ions from water
24 electrolysis under DC treatment. However, in our work, the application of the electric
25 field did not involve important changes in soil pH and, moreover, it was kept, for all the

1 treatments, closed to the initial soil pH (9.42). The reason for this might be the short
2 time interval of the electric field application (4 hours a day) and the change of polarity
3 each 2 hours.

3.2. Influence of the electric field on plant growth

FIGURE 2

9 Figure 2 shows the mean values of root and shoot biomass reached by maize plants in
10 the EK-phytoremediation test. Regarding the ATR dose of 5 mg kg^{-1} , the application of
11 the electric field led to a significant decrease, as compared to the biomass values
12 reached by the pots without electric current, in root biomass for both applied voltages
13 while the shoot biomass only decreased significantly for the highest voltage. On the
14 overall, total plant biomass decreased in a significant extent, between 10 and 15%, with
15 the application of electric current. These results are in agreement with those previously
16 reported by Cang et al. (2011) for Indian mustard, who found that the application of
17 voltages in the range $2\text{-}4 \text{ V cm}^{-1}$ had a negative effect on plant growth, especially for
18 root biomass. These authors also found a slight increase on the biomass of Indian
19 mustard when a voltage of only 1 V cm^{-1} was applied (Cang et al., 2011). However, Bi
20 et al. (2011) reported a decrease of 13-33% for tobacco biomass in an electrokinetic-
21 assisted phytoremediation test using a DC field of 1 V cm^{-1} with changes of polarity
22 every 3 hours; the same conditions did not negatively influenced the biomass of
23 rapeseed plants. Aboughalma et al. (2008) reported adverse effects on the growth of
24 potato plants when a DC of 500 mA was continuously applied. All the works mentioned
25 above are relative to metal polluted soils, so that the affection of plant growth can be

1 attributed to the stress caused by the increased amounts of soluble toxic metals towards
2 plant roots (Cameselle et al., 2013). Moreover, the extremely low and high pH values
3 found in the anode and cathode regions when polarity change was not used, could also
4 contribute to decrease plant growth in some extent (Aboughalma et al., 2008). In our
5 experiment, changes in soil pH were not significant; so, the slight decrease observed in
6 maize biomass may be attributed to the increased mobility of atrazine, which could
7 affect root growth. Stenz and Weisenseel (1993) also reported damages in maize roots
8 for electric fields above 3 V cm^{-1} while roots of other plant species, e.g. *Lepidium*
9 *sativum*, were not affected. Therefore, the mentioned data and our own results seem to
10 demonstrate that the effect of the electric field application on plant growth would be
11 partially dependent on plant species.

12
13 Finally, the addition of an atrazine dose of 10 mg kg^{-1} to the soil led to a significant
14 decrease in maize root, shoot and total biomass with respect to those of 5 mg kg^{-1} dose
15 (39%, 19% and 26%, respectively) (Figure 2). This negative effect of atrazine in plant
16 growth was also reported in a previous work by us, being attributed to the toxic
17 response of plants to atrazine uptake and accumulation (Sánchez et al., 2017). In fact,
18 from approximately six days after applying atrazine and electricity, visual toxicity
19 symptoms such as chlorosis, stunting and leaf death were observed. Regarding the
20 effect of the electric field application, no significant differences in plant biomass were
21 detected between pots with and without electricity (with the exception of the roots in the
22 4 V cm^{-1} treatment, Figure 2). Mean values of root, shoot and total biomass were
23 slightly higher for 2 V cm^{-1} treatment as compared to those without electricity, but this
24 increase was not statistically significant. In general, the toxicity caused by the high dose
25 of atrazine covered up the possible effects of the electric field.

3.3. Accumulation of atrazine in plant tissues

TABLE 2

Table 2 shows the concentration of atrazine residues (atrazine and its metabolites, i.e. deethylatrazine and deisopropylatrazine), in roots, shoots and total plant for all the treatments at the end of the experiment. Plant uptake of atrazine and/or its metabolites was observed for all the tested voltages and initial soil doses of atrazine. The application of 2 V cm⁻¹ to the pots with an initial ATR dose of 5 mg kg⁻¹ enhanced significantly the accumulation of ATR residues in the plant tissues with respect to the pots with no electric field. However, when the voltage was increased to 4 V cm⁻¹, concentrations of ATR residues in maize were lower than those of the treatments with no electricity and 2 V cm⁻¹ (Table 2). In the case of the soils spiked with 10 mg kg⁻¹ of atrazine, the application of 2 V cm⁻¹ did not decrease significantly the ATR residues plant concentrations but they did it when the voltage was increased to 4 V cm⁻¹. These results demonstrate the hypothesis that motivates the present research: electric field application can enhance, in some conditions, plant uptake of organic pollutants from soils. It agrees with the conclusions of other researchers for electrokinetic-assisted phytoremediation of soils polluted by metals who reported that the application of low to moderate voltages (using AC electric current), i.e. up to 2 V cm⁻¹, led to an increase of plant metal uptake in Indian mustard (Cang et al. 2011), potato (Aboughalma et al. 2008), rapeseed and tobacco (Bi et al. 2011). However, the application of 4 V cm⁻¹ had a slightly adverse effect on the metal accumulation in Indian mustard (Cang et al. 2011); again, it is in agreement with the results showed here about atrazine uptake by maize. We can

1 conclude that the application of moderate electric voltage can increase the mobility of
2 polar organic pollutants such atrazine enhancing plant uptake; however, when the
3 applied voltage is too high, it negatively affects plant metabolism leading to detrimental
4 effect on plant growth and pollutant accumulation.

FIGURE 3

8 ATR residues concentrations in roots greatly exceeded those corresponding to shoots
9 for plants grown in pots with an initial ATR soil dose of 5 mg kg⁻¹ (Table 2). This
10 preferential accumulation of ATR in the roots of maize was found in previous
11 experiments without electric current (Sánchez et al., 2017) and followed the same
12 pattern for EK-phytoremediation. It was suggested that the reason of this behaviour was
13 to avoid atrazine toxicity in some extent (Li et al., 2012; Sánchez et al., 2017). On the
14 other hand, atrazine deethylation and deisopropylation (leading to DEA and DIA,
15 respectively) would be another way of plant detoxification because both metabolites are
16 less toxic than the parent atrazine (Fan and Song, 2014). In Figure 3, it can be seen that
17 maize plants had problems to metabolize ATR for the highest soil dose (dose of ATR 10
18 mg kg⁻¹ for 0, 2 and 4 V cm⁻¹ series), with values of the ratio (DEA+DIA)/ATR
19 significantly lower than those of the plants corresponding to pots with initial ATR soil
20 doses of 5 mg kg⁻¹ (dose of ATR 5 mg kg⁻¹ for 0, 2 and 4 V cm⁻¹ series). Moreover, the
21 higher proportion of atrazine metabolites in roots than in shoots (especially for the
22 treatments corresponding to soil doses of 5 mg kg⁻¹) seems to demonstrate that atrazine
23 uptake and translocation are phenomena faster than its degradation inside the plants. In
24 any case, results from Figure 3 show that the application of electric current did not lead
25 to important changes in the pattern of atrazine degradation inside the plants, mainly for

1 the highest dose of atrazine. It can be only noticed an increase in DEA and DIA
2 formation for the 5 mg ATR kg⁻¹/ 2 V cm⁻¹ treatment with respect to the series with no
3 electric field application; this effect was not found for the 5 mg ATR kg⁻¹/ 4 V cm⁻¹
4 treatment and for the treatments corresponding to initial ATR soil doses of 10 mg kg⁻¹
5 (Figure 3). Lastly, it must be pointed out that, as it was previously reported, DEA was
6 the main ATR metabolite in maize tissues for all the treatments (Sánchez et al. 2017).

8 **3.4. Atrazine residues in soil**

10 **TABLE 3**

12 The amount of atrazine residues (ATR, DEA and DIA) remaining in the soil after the
13 electrokinetic-assisted phytoremediation tests are shown in Table 3 expressed as % of
14 the initial atrazine concentration in the pots. When no electric current was used, the
15 amount of ATR residues remaining in the soil of the planted pots was significantly
16 lower than those of the unplanted (control) ones independently of the initial atrazine soil
17 dose. Thus, atrazine removal for the treatments with maize and without electric current
18 were 37.34 and 62.90%, respectively, while control treatments without electricity
19 showed atrazine removal yields of 18.86 and 38.46%, respectively. This is in agreement
20 with the previously reported effectiveness of maize in the phytoremediation of atrazine
21 from soils (Sánchez et al., 2017). The application of an electric field (2 or 4 V cm⁻¹) to
22 the pots with an initial ATR dose of 5 mg kg⁻¹ led to a significant increase in the
23 percentage of atrazine removed for both planted and unplanted soils as compared to pots
24 without electricity (between 30-37%, Table 3). For the experiments using an initial soil
25 ATR dose of 10 mg kg⁻¹ that enhancement was also found for the planted pots to which

1 an electric field of 2 V cm^{-1} had been applied. It clearly shows that the application of an
2 electric field improves the performance of phytoremediation on the removal of atrazine
3 from spiked soils. As it was pointed out in the Introduction section, EK-
4 phytoremediation had been previously showed to increase the effectiveness of metal
5 removal from soils (Cameselle et al., 2013) and, from our results, it can be said that this
6 beneficial effect may be also achieved in the remediation of soils polluted by organic
7 pollutants, as it has been previously suggested (Gomes et al., 2012).

8
9 The role of the electric field would be to increase the mobility of the contaminants by
10 desorption and transport in the soil and, therefore, leading to an enhancement of the
11 plant activities (Cameselle et al., 2013). Taking into account the pK_a values of atrazine,
12 DEA and DIA, i.e. between 1.50 and 1.70 (Amadori et al., 2016), these chemical
13 species can be partially ionized in a soil with an alkaline pH (Ahmed et al., 2011); so,
14 they can be transported by electromigration under the influence of an electric field.
15 Moreover, the contribution of the electro-osmotic transport is also expected since those
16 compounds show moderate to high water solubility values, i.e. 33, 3200 and 670 mg.L^{-1}
17 for ATR, DEA and DIA, respectively. In any case, the observed increase in the atrazine
18 residues uptake and accumulation in maize tissues (Section 3.3) is an indirect evidence
19 of the mobilization of atrazine caused by the application of an electric field to the soil.

20
21 Four different processes can be considered for the removal of atrazine from soils in this
22 EK-phytoremediation experiment: (i) uptake and
23 accumulation/degradation/mineralization in the plant tissues (phytodegradation); (ii)
24 degradation/mineralization by the soil rhizosphere microorganisms (rhizodegradation);
25 (iii) electrochemical oxidation; and, (iv) volatilization. In spite of the experimental

1 methodology used here do not let us to quantitatively account the contribution of the
2 different processes for the overall atrazine removal, some remarks can be made.

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7 4 First, electrochemical oxidation of atrazine can be discarded because the graphite
8 electrodes would be burned at a lower overpotential that required for atrazine oxidation
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10 5 electrodes would be burned at a lower overpotential that required for atrazine oxidation
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12 6 (Vieira dos Santos et al., 2016). Regarding volatilization, the temperature of the soil was
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14 7 increased when the electric field was applied; more specifically, soil temperatures
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16 8 (measured in the middle area of the pots) increased in approximately 1-2°C and 4-8°C
17
18 9 for the 2 V cm⁻¹ and 4 V cm⁻¹ treatments, respectively, after 4 h of electric current
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20 10 application with respect to the initial values. Therefore, volatilization of atrazine could
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22 11 take place in some extent because the relatively high vapour pressure of atrazine and the
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24 12 locally higher temperatures that can be reached in the vicinity of the electrodes (Vieira
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26 13 dos Santos et al., 2016 and 2017). Nevertheless, it must be taken into account that those
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28 14 increases in soil temperature only occurred during the period of time in which electric
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30 15 field was connected (4h a day). Moreover, the similar values of atrazine removal
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32 16 reached for the three treatments without plants corresponding to the initial ATR soil
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34 17 dose of 10 mg kg⁻¹ (Table 3) seem to suggest that the contribution of atrazine
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36 18 volatilization is not relevant in our experiment, at least for these treatments.

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46 20 The role of plants in atrazine removal has been analysed in the previous section;
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48 21 nevertheless, as shown in Table 3, it seems that the contribution of the accumulation of
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50 22 atrazine in the maize tissues to the overall removal yield is quite limited: only between
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52 23 1.10 and 3.75% of the initial parent atrazine remained in the plant tissues at the end of
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54 24 the EK-phytoremediation test (Table 3). Likewise, from the comparison of the ATR
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56 25 removal percentages between 5 mg ATR kg⁻¹ / 2 V cm⁻¹ and 5 mg ATR kg⁻¹ / 4 V cm⁻¹

1 treatments and their corresponding control treatments (without plants), it can be seen
2 that the contribution of maize to the ATR removal enhancement was not relevant when
3 a voltage of 4 V cm^{-1} was applied to soils. It is in agreement with the observed negative
4 effect of the highest voltage over plant growth and atrazine accumulation (Section 3.3).
5 However, it must be pointed out that other metabolites (hydroxyatrazine,
6 deethylhydroxyatrazine or deisopropylhydroxyatrazine) not analysed here together with
7 mineralization of atrazine inside the plant has been previously reported elsewhere (Lin
8 et al., 2008; Fan and Song, 2014) and could contribute to the overall atrazine plant
9 degradation in some extent.

10
11 It is well known that plant roots favour significantly the growth of the microbial
12 population in the rhizosphere by means of root exudates (nutrients, carbohydrates,
13 enzymes, etc.) and by enhancing the environmental soil conditions (Huesemann et al.,
14 2009; Cameselle et al., 2013). According to this, the presence of the atrazine N-
15 dealkylated metabolites, DEA and DIA, in the soil samples at the end of our
16 experiments is indicative of bacterial degradation in soils (Mudhoo and Garg, 2011). On
17 the other hand, the stimulation of the soil microorganism activities with the application
18 of an electric field has been previously reported for the bioremediation of
19 organochlorines (Gomes et al., 2012; Gill et al., 2014). The observed significant
20 increase in the proportion of ATR metabolites in the soil for $5 \text{ mg ATR kg}^{-1} / 2 \text{ V cm}^{-1}$
21 and $5 \text{ mg ATR kg}^{-1} / 4 \text{ V cm}^{-1}$ treatments (with respect to the $5 \text{ mg ATR kg}^{-1} / 0 \text{ V cm}^{-1}$
22 treatment and the corresponding treatments without plants, Table 3) gives evidence of
23 the enhanced bacterial activity caused by both the maize roots and the electric field. The
24 worse results found for atrazine removal corresponded to the initial ATR dose of 10 mg
25 kg^{-1} ; it can be attributed not only to the toxicity effects on maize plants, as it was

1 described in the previous sections, but also to the inhibitory effect of high
2 concentrations of atrazine to microorganism metabolism (Lima et al., 2009).

4. CONCLUSIONS

6 The following conclusions can be observed as a result of this study:

8 - The application of an electric field to the soil can provoke changes in soil
9 properties, like pH. However, our results showed that the application of electric
10 current during a short time, i.e. 4 hours a day, together to the switching of the
11 polarity (each 2 hours) did not lead to significant changes in soil pH. Moreover, the
12 presence of maize plants apparently increased the buffering capacity of the soil
13 avoiding pH changes caused by the electric field. Maize roots also increased current
14 density in the soil with respect to the unplanted pots.

16 - The effects of the electric field on plant growth were different regarding the initial
17 ATR dose applied to the soil. When an ATR soil dose of 5 mg kg^{-1} was used, shoot
18 biomass only decreased significantly for the highest voltage applied (4 V cm^{-1}).
19 However, for the treatments corresponding to an initial ATR soil dose of 10 mg kg^{-1}
20 ¹ some visual toxic symptoms were observed in plants independently of using or
21 not electric current and, therefore, covering up its possible effect.

23 - The application of a relative low electric voltage (2 V cm^{-1}) enhanced atrazine
24 uptake by maize plants due to the increase of its mobility. However, from our
25 results it seems that plant accumulation was not the most important process

1 involved in atrazine removal. Other important processes such as rhizodegradation,
2 phytodegradation and volatilization were also enhanced by the application of a
3 moderate electric field, increasing significantly the overall removal of atrazine from
4 soils.

5
6 On summary, our results show that combining phytoremediation and the application of
7 an electric field with periodical polarity reversion is an interesting option to improve the
8 effectiveness of the phytoremediation of atrazine-polluted soils. Nevertheless, additional
9 research at higher scale (mesocosmos and/or pilot plant) and a detailed economic study
10 are necessary in order to check if the improvement in the atrazine removal compensates
11 the additional cost of the electric current application.

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14
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Table 1. Soil pH at the end of the EK-phytoremediation experiment for the different treatments.

Values are given as the mean \pm standard deviation (n = 3). The different letters indicate significant differences (p < 0.05, Duncan's test) between soil treatments.

Plant	Atrazine dose (mg kg ⁻¹ soil)	Voltage (V cm ⁻¹)	pH
Maize	5	0	8.83 \pm 0.28a
		2	9.29 \pm 0.08abcd
		4	9.53 \pm 0.22bcde
	10	0	9.19 \pm 0.63abc
		2	9.05 \pm 0.08ab
		4	9.22 \pm 0.35abc
Control	5	0	9.52 \pm 0.01bcde
		2	9.69 \pm 0.10cde
		4	9.84 \pm 0.42e
	10	0	9.54 \pm 0.03bcde
		2	9.78 \pm 0.003de
		4	9.82 \pm 0.66bcde

Table 2. Concentration ($\mu\text{mol kg}^{-1}$ DW plant biomass) of atrazine residues (ATR: atrazine; DEA: deethylatrazine; DIA: deisopropylatrazine) in maize tissues at the end of the EK-assisted phytoremediation experiment for the different treatments.

Values are given as the mean \pm standard deviation (n = 3). The different letters indicate significant differences ($p < 0.05$, Duncan's test) between soil treatments.

Atrazine dose (mg kg^{-1} soil)	Voltage (V cm^{-1})	ATR+DEA+DIA ($\mu\text{mol kg}^{-1}$ plant)		
		Root	Shoot	Total plant
5	0	174.4 \pm 1.3b	26.7 \pm 1.2ab	82.7 \pm 0.2b
	2	238.7 \pm 5.9c	29.5 \pm 1.4b	104.0 \pm 6.8c
	4	118.2 \pm 3.4a	22.4 \pm 3.6a	54.7 \pm 3.1a
10	0	146.2 \pm 4.9b	90.5 \pm 18.1a	108.4 \pm 13.7b
	2	131.9 \pm 8.9b	80.6 \pm 4.3a	95.8 \pm 5.6ab
	4	95.1 \pm 7.9a	86.7 \pm 1.5a	89.3 \pm 1.4a

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1 **Table 3. Atrazine and its metabolites (ATR: atrazine; DEA: deethylatrazine; DIA: deisopropylatrazine) remaining in the soil at the end**
 2 **of the EK-phytoremediation experiment (mean values expressed as % of the initial ATR soil concentration) and atrazine removal from**
 3 **soils.** The different letters indicate significant differences ($p < 0.05$, Duncan's test) between soil treatments.

	Control			Maize		
Voltage (V.cm ⁻¹)	0	2	4	0	2	4
Atrazine initial dose: 5 mg kg⁻¹						
ATR soil	81.14	54.54	25.72	62.66	32.81	26.20
(DEA+DIA)/ATR soil	7.32	10.91	24.49	6.31	45.99	44.75
Plant accumulation^a	-	-	-	2.92	3.75	1.83
Atrazine removal^b	18.86a	45.46b	74.28c	37.34b	67.19c	73.80c
Atrazine initial dose: 10 mg kg⁻¹						
ATR soil	60.54	61.63	56.55	37.10	13.19	46.96
(DEA+DIA)/ATR soil	5.52	5.61	4.93	7.87	33.29	10.77
Plant accumulation^a	-	-	-	1.41	1.34	1.10
Atrazine removal^b	38.46a	38.37a	43.45a	62.90b	86.81c	53.04ab

^a Accumulation of atrazine residues (ATR+DEA+DIA)

^b Calculated using only the amount of the parent atrazine remaining in the soil at the end of the experiment

FIGURE CAPTIONS

Figure 1. Trends in electric current for the maize and unplanted treatments. Data showed are mean values of treatments corresponding to 5 and 10 mg of atrazine per kg of soil. Error bars represent the standard deviation of six replicates.

Figure 2. Dry matter yields of root and shoot (g of dry biomass per pot) at the end of the EK-phytoremediation experiment for the different treatments. M5 and M10 corresponding to maize pots spiked with 5 and 10 mg of atrazine per kg of soil; V0: treatments without electricity; V2: treatments applying an electric field of 2 V cm⁻¹; V4: treatments applying an electric field of 4 V cm⁻¹. Error bars represent the standard deviation of three replicates. The different letters mean significant differences (p<0.05) between different treatments.

Figure 3. Atrazine residues concentration (μmol kg⁻¹) and distribution of the atrazine metabolites (ATR: atrazine; DEA: deethylatrazine; DIA: deisopropylatrazine) in roots, shoots and total plant at the end of the EK-phytoremediation experiment for the different treatments. V0: treatments without electricity; V2: treatments with an electric field of 2 V cm⁻¹; V4: treatments with an electric field of 4 V cm⁻¹. Error bars represent the standard deviation of three replicates. Different letters indicate significant differences (p<0.05, Duncan's test) between treatments corresponding to the same initial dose applied.

Figure 1

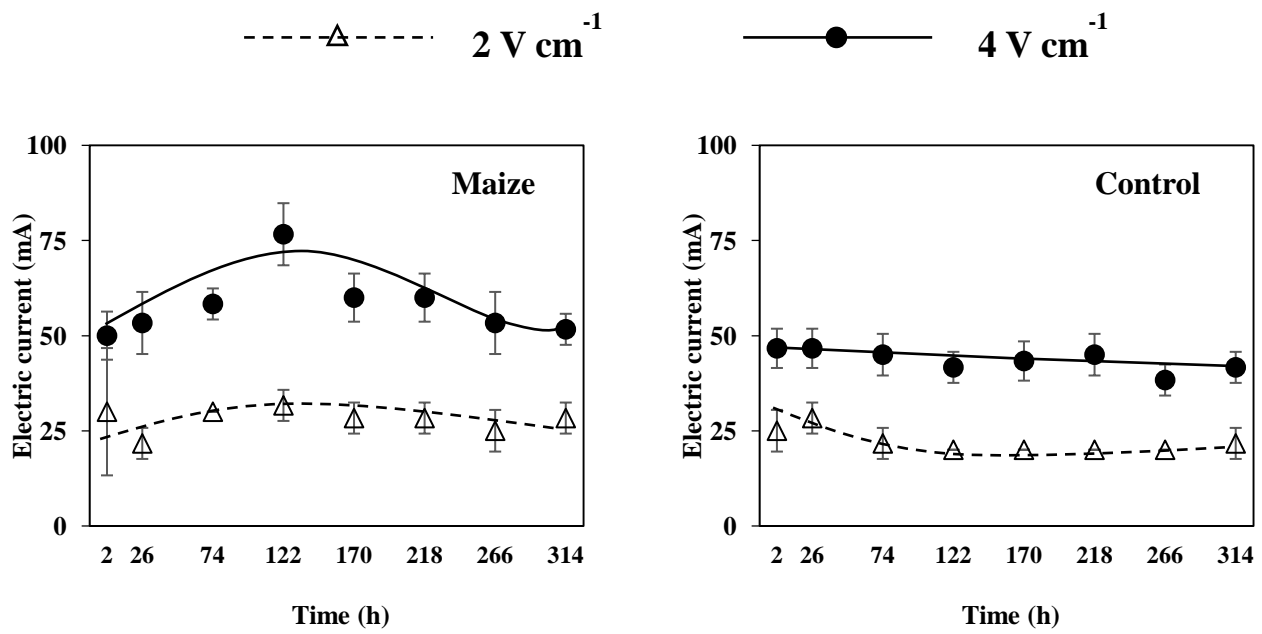


Figure 2

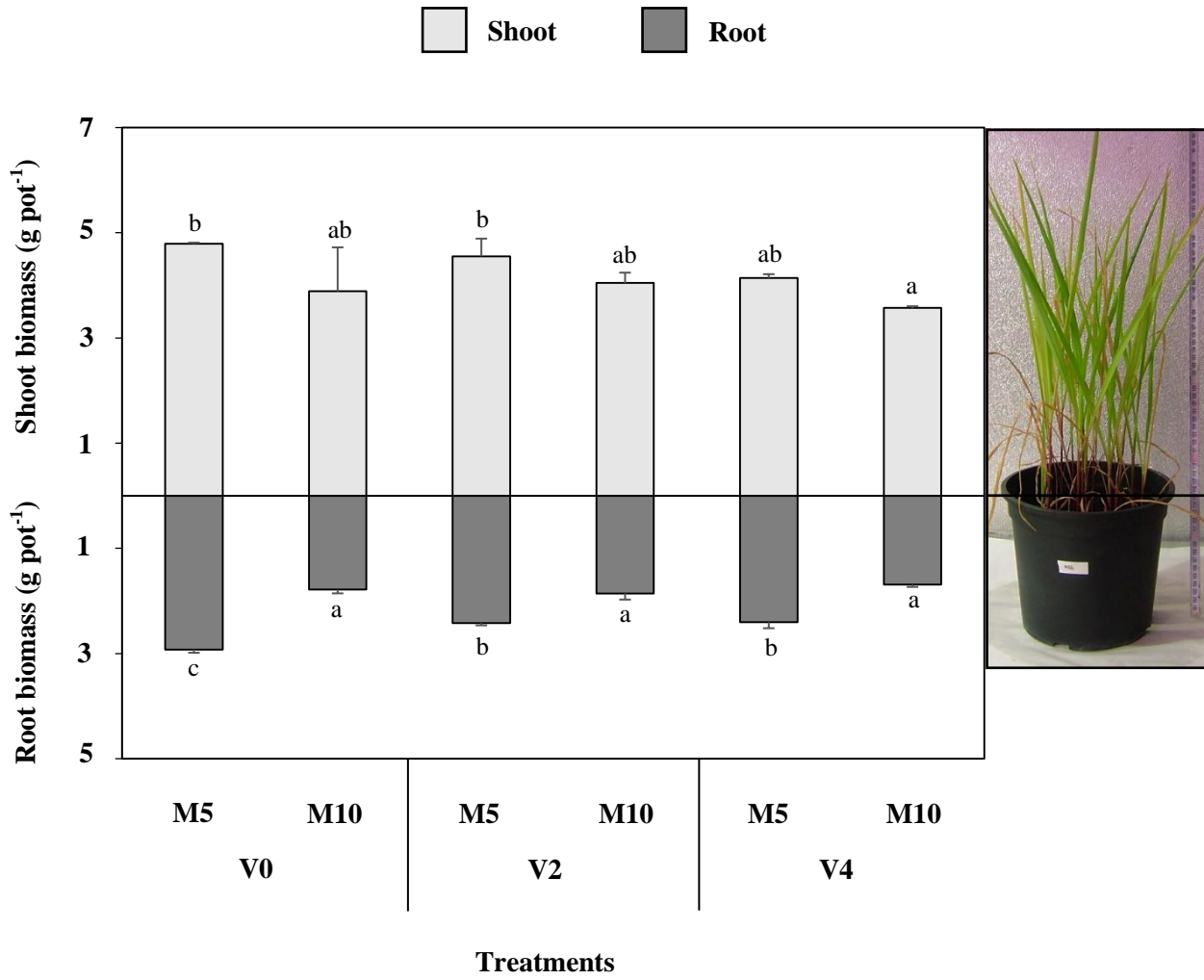


Figure 3

ATR
 DEA
 DIA

