

1 **Removal of oxyfluorfen from spiked soils using electrokinetic**  
2 **soil flushing with the surrounding arrangements of electrodes**

3 C. Risco<sup>1</sup>, H. Rubí-Juárez<sup>2</sup>, S. Rodrigo<sup>3</sup>, R. López Vizcaíno<sup>3</sup>, C. Saez<sup>1</sup>, P. Cañizares<sup>1</sup>, C.  
4 Barrera-Díaz<sup>2</sup>, V. Navarro<sup>4</sup>, M.A. Rodrigo<sup>1,\*</sup>

5 <sup>1</sup>Department of Chemical Engineering, Instituto de Tecnologías Química y  
6 Medioambiental, University of Castilla-La Mancha, Campus Universitario s/n, 13071  
7 Ciudad Real, Spain

8 <sup>2</sup>Facultad de Química, Universidad Autónoma del Estado de México, Paseo Colón  
9 intersección Paseo Tolloca S/N, C.P. 50120, Toluca, Estado de México, Mexico

10 <sup>3</sup>Department of Chemical Engineering, Facultad de Ciencias y Tecnologías Químicas,  
11 University of Castilla-La Mancha, Campus Universitario s/n, 13071 Ciudad Real, Spain

12 <sup>4</sup>Geoenvironmental Group, Civil Engineering School, University of Castilla-La  
13 Mancha, Avda. Camilo José Cela s/n, 13071 Ciudad Real, Spain

14  
15 **Abstract**

16 This work reports the results of a study in which the remediation of soil that undergoes  
17 an accidental discharge of oxyfluorfen is carried out by using electrokinetic soil flushing  
18 (EKSF). Two different electrode configurations were tested, consisting of several  
19 electrodes surrounding an electrode of different polarity (so-called 1A6C, one anode  
20 surrounded by six cathodes, and 1C6A, one cathode surrounded by six cathodes). A pilot  
21 plant scale was used (with a soil volume of 175 dm<sup>3</sup>) to perform the studies. During the  
22 tests, different parameters were measured daily (flowrates, pH, electrical conductivity and  
23 herbicide concentration in different sampling positions). Furthermore, at the end of the  
24 test, a complete post-mortem analysis was carried out to obtain a 3-D map of the pollution,  
25 pH and electrical conductivity in the soil. The results demonstrate that electrode

1 arrangement is a key factor for effective pollutant removal. In fact, the 1A6C  
2 configuration improves the removal rate by 41.3% versus the 27.0% obtained by the  
3 1C6A configuration after a period of 35 days. Finally, a bench mark comparison of this  
4 study of soil remediation polluted with 2,4-D allows for significant conclusions about the  
5 scale-up and full-scale application of this technology.

6

## 7 **Keywords**

8 Oxyfluorfen, herbicide, electroremediation, surrounded electrodes, pilot plant

9

## 10 **Highlights**

- 11 – The electrode arrangement has a crucial influence on the results attained by EKSF
- 12 – The 1C6A configuration is more efficient and overcomes 1A6C by 53%
- 13 – Dragging of herbicide by EOF and volatilization are efficient mechanisms in  
14 EKSF
- 15 – The pH in soil is well controlled by both the 1C6A and the 1A6C configurations
- 16 – The results of EKSF are not easily predictable because of the large number of  
17 parameters involved

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19 \* To whom all correspondence should be addressed: manuel.rodriigo@uclm.es

20

## 1 **Introduction**

2

3 Electrokinetic soil remediation is a very efficient technology for the removal of hazardous  
4 ions from soil. However, at the moment, there are few studies that focus on organic soil  
5 removal (Alcantara et al., 2010; Alcantara et al., 2012; Alshawabkeh et al., 1999a;  
6 Cameselle and Reddy, 2013; Hahladakis et al., 2013; Hahladakis et al., 2014; Lima et al.,  
7 2011; Lu and Yuang, 2009; Pazos et al., 2010; Reddy et al., 2011; Reddy et al., 2009;  
8 Ribeiro et al., 2011; Ribeiro et al., 2005; Weng, 2009).

9 For an optimal performance, the electrokinetic soil flushing (EKSF) process relies on a  
10 satisfactory electrode arrangement (Jeon et al., 2015; Kim et al., 2012; Kim et al., 2015;  
11 Rodrigo et al., 2014a). Until now, the most widely studied arrangement is facing two  
12 linear rows of electrodes with different polarities (Risco et al., 2016a). The advantages of  
13 this configuration are related to the expected better electric current distribution lines,  
14 which are also expected to produce a well-distributed pattern of electrokinetic flows  
15 within the soil and, hence, a very efficient drainage of pollution.

16 However, this is not the only possibility of placing electrodes in soil (Almeira et al.,  
17 2009; Alshawabkeh et al., 1999a; Alshawabkeh et al., 1999b; Peng et al., 2013), and  
18 configurations in which various electrodes surround a central electrode of the opposite  
19 polarity have also been tested, showing very interesting performances. At this point, it is  
20 important to remark that the recent literature indicates that the position of the electrodes  
21 sited in the soil is a key parameter in the remediation efficiency because it determines the  
22 direction and magnitude of the electrokinetic processes, and consequently, it influences  
23 the transport of pollutants. For this reason, different research works during the last few  
24 years have focused on the evaluation of the electrode configuration (Adams et al., 1997;  
25 Almeira et al., 2009; Jeon et al., 2015; Kim et al., 2012). The results obtained in these

1 studies indicate that the most effective electrode configuration (from a pollutant transport  
2 viewpoint) is a hexagonal configuration, that is, a ring of anodes with a central cathode,  
3 or vice versa, depending on the polarity of the pollutant. The number of electrodes and  
4 the electrode spacing used are directly related with the mass of the treated soil.

5

6 In a previous report of this group (Risco et al., 2016c), two of these configurations were  
7 applied in a soil that underwent a simulated discharge of herbicide 2,4-D. The study was  
8 conducted in a mock-up with a suitable size to fully understand the effect on the  
9 remediation of the different flows induced by the electric field. The results indicate that  
10 the pollutant was removed by electromigration, electroosmotic fluxes and volatilization.

11 In this work, we aim to expand our technology knowledge using a very different model  
12 of pesticide, the oxyfluorfen. This herbicide belongs to the diphenyl ether chemical group  
13 and has low water solubility (0.116 mg/L at 20 °C), low vapor pressure (0.026 mPa at 25  
14 °C), high K<sub>oc</sub> (log K<sub>oc</sub> = 3.46–4.13), and high K<sub>ow</sub> (log K<sub>ow</sub> = 4.86). As oxyfluorfen is  
15 not metabolized in plants and is subjected to very little translocation, photo-  
16 transformation is suggested as the only possible abiotic degradation process. Microbial  
17 degradation is not a major factor to be accounted for in this herbicide. The half-life in soil  
18 approximately ranges from 30 to 56 days, and the organic matter content of the soil seems  
19 to influence the oxyfluorfen persistence and activity (Sondhia, 2010; Sondhia and Dixit,  
20 2010). Finally, regarding its transport properties, it has been observed (Mantzou et al.,  
21 2014) that oxyfluorfen hardly moves into silty clay soil and exhibits low run-off potential.

22 In this work, the effect of the electrode arrangements in EKSF is studied in a soil mock-  
23 up, and then, the remediation technology is applied for more than a month. The results  
24 are compared with a reference experiment in which the discharge is simulated but no  
25 treatment is applied. The results are also discussed with respect to the results obtained in

1 our previous works, which focused on the removal of 2,4-D (Risco et al., 2016a; Risco et  
2 al., 2016c; Risco et al., 2015), a pollutant with an expected higher water solubility and  
3 volatility and, hence, with very different expected results in terms of the efficiency of the  
4 EKSF treatment. For this reason, the comparison carried out in this work will provide  
5 relevant conclusions on EKSF technology.

6

## 7 **Materials and Methods.**

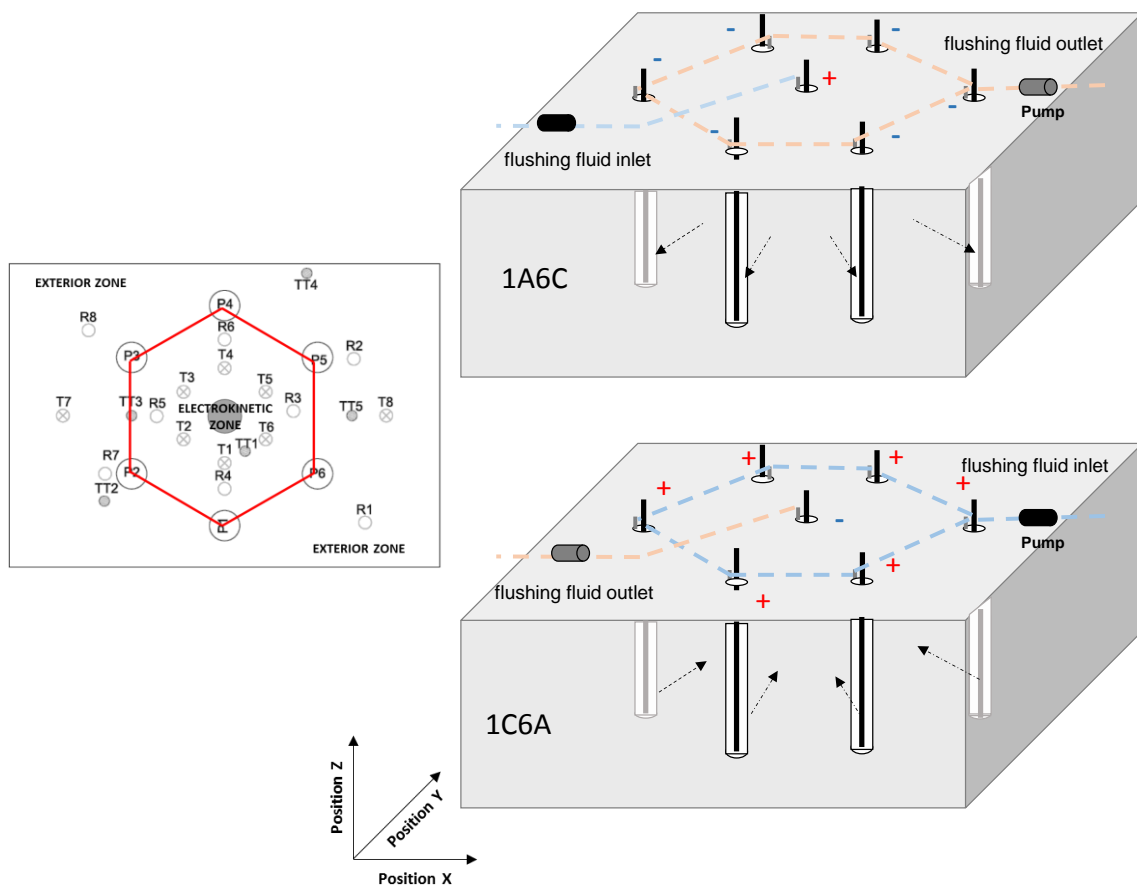
8 **Soil properties and flushing solutions.** Field soil from Toledo (Spain) was used in this  
9 study. This soil is characterized by its inertness, low hydraulic conductivity and lack of  
10 organic content. The mineralogical composition and the parameters used to classify this  
11 soil by the Unified Soil Classification System (USCS) are listed elsewhere (Lopez-  
12 Vizcaino et al., 2014a; Lopez-Vizcaino et al., 2014b)(Risco et al., 2016b). In addition,  
13 particle size distribution of the soil was measured by a laser diffraction particle size  
14 analyser (model LS 13320, Beckman Coulter) with an aqueous module. This analysis  
15 indicates that the soil are composed on these fractions: 4.9% clay, 68.2% silt and 26.9%  
16 sand, therefore it can be classified as a silty loam according with the texture classification  
17 of the United States Department of Agriculture (USDA).

18 Oxyfluorfen was used as the model of non-polar and hydrophobic herbicide. The  
19 commercial herbicide used was Fluoxil 24 EC (CHEMINOVA AGRO, S.A., Madrid,  
20 Spain) composed on 24% (v/v) Oxyfluorfen dissolved in aqueous solution by the  
21 emulsifier action of Calcium Dodecylbenzenesulfonate (surfactant included in a  
22 commercial solution).

23 **Experimental setup.** The electrokinetic experiments were conducted in two  
24 electrokinetic remediation plants, each of them consisting of an electrokinetic reactor, a  
25 power source and tanks of electrolyte. A layout of the two setups used is shown in Figure

1 1. The reactors were methacrylate prisms with a soil capacity of  $175 \times 10^3 \text{ cm}^3$  (LWH:  
 2  $70 \times 50 \times 50 \text{ cm}^3$ ). The electrodes (used for both the anodes and the cathodes) were graphite  
 3 rods with dimensions  $1 \times 1 \times 10 \text{ cm}^3$ , positioned in semipermeable electrolyte wells, using  
 4 the electrode configuration shown in Figure 1, in which six electrodes surround a central  
 5 electrode of different polarity (configuration 1A6C: anode surrounded by 6 cathodes;  
 6 configuration 1C6A: cathode surrounded by 6 anodes). The cathodic wells are connected  
 7 to  $100 \text{ cm}^3$  sewers to accumulate the fluid transported through the soil and facilitate  
 8 sampling. The reactor is designed to separate and collect the fluids through an outlet  
 9 situated on the side wall of the reactor. To monitor the flux of water and the temperature  
 10 evolution during the experiment, tensiometers, thermocouples and rhizon samplers (or  
 11 “rhizons”) were inserted into the soil. Figure 1 shows the instrumentation of the plant.

12



13

1 **Figure 1.** Diagram of the electrokinetic remediation plant and configuration of the  
2 instrumentation.

3  
4 **Experimental procedure.** The process of the preparation of the soil is important because  
5 of the complexity of natural soil. The process was divided into four different stages:

- 6 - installation of three layers of gravel with different particle sizes for mechanical  
7 and drain support;
- 8 - moistening the soil to 11% (natural water content condition);
- 9 - compaction of the soil in the electrokinetic reactor by compacting layers of a fixed  
10 thickness (5 cm) until achieving the natural density of the soil (approximately 1.4  
11  $\text{g cm}^{-3}$ );
- 12 - drilling of the electrolyte wells and instrumentation of the plant.

13 Once the plant was fully instrumented, the experimental procedure began with the  
14 pollution of the soil (simulating accidental spill). To do this, in the central point of the  
15 electrokinetic reactor, an accidental leak of  $6 \text{ dm}^{-3}$  of an aqueous solution of  $500 \text{ mg dm}^{-3}$   
16 of Fluoxil 24 EC (oxyfluorfen 24%) was simulated. After that, the electrolyte wells  
17 (water, pH 7.64 and  $0.391 \text{ mS cm}^{-1}$  of electrical conductivity) were filled. The level of  
18 the electrolyte wells were controlled by a level control system connected to the feed tank  
19 to adjust the volume of the water added to the soil. The test started when the power source,  
20 a 400 SM-8-AR ELEKTRONIKA DELTA BV, was turned on, applying a constant  
21 voltage gradient of  $1.0 \text{ VDC cm}^{-1}$ . This value was selected taking into account  
22 information obtained in the literature (Rodrigo et al., 2014b).

23  
24 **Analyses.** To characterize the EKSF treatment efficiency, the electrical current,  
25 temperature, pH, soil water content and oxyfluorfen concentration in electrolyte wells

1 were monitored daily, and at the end of the experiments, an in-depth sectioned analysis  
2 of the complete soil section was conducted. The pH and electrical conductivity were  
3 measured with an InoLab WTW pH meter and a GLP 31 Crison conductivimeter,  
4 respectively. The electric current was measured with a KEITHLEY 2000 Digital  
5 Multimeter. The temperature was measured with PT-100 thermocouples. To quantify the  
6 amount of oxyfluorfen in the liquid samples, an L-L extraction process in Eppendorf tubes  
7 (15 cm<sup>3</sup>) was used, using ethyl acetate as the solvent (ratio polluted soil/solvent = 0.7  
8 w/w). Both phases were vigorously stirred in a vortex mixer (VV3 VWR multi-tube) for  
9 2 minutes, and the organic phase was separated from water. The organic phase was then  
10 placed into tubes to be stripped with N<sub>2</sub> gas. A volume of 1.5 cm<sup>3</sup> of acetonitrile is then  
11 added and stirred for 3 minutes before being injected into the High Pressure Liquid  
12 Chromatography (HPLC). To quantify the amount of oxyfluorfen in the soil, an L-S  
13 extraction process was used. The L-S extraction process was carried out in Eppendorf  
14 tubes (15 cm<sup>3</sup>) using ethyl acetate as solvent (ratio polluted soil/solvent = 0.4 w/w). Both  
15 phases were vigorously stirred in a vortex mixer (VV3 VWR multi-tube), and the  
16 subsequent phase separation was accelerated by the use of a centrifuge rotor angular  
17 (CENCOM II P-elite) for 20 minutes and 4000 rpm. Then, liquid was stripped with N<sub>2</sub>  
18 gas, and acetonitrile was added before being injected into the HPLC. The HPLC used was  
19 Agilent 1100 (Agilent Technologies, Palo Alto, California, EEUU) with an UV detector  
20 with Acetonitrile (70%)/water (30%) as the carrying fluid at a flowrate of 0.25 cm<sup>3</sup> min<sup>-1</sup>  
21 using a column Gemini 5 μ C18 110<sup>a</sup> (Phenomenex, Ref. 00F-4435-YYO) with  
22 dimensions of 150x3.0 mm and a wavelength of 220 nm.

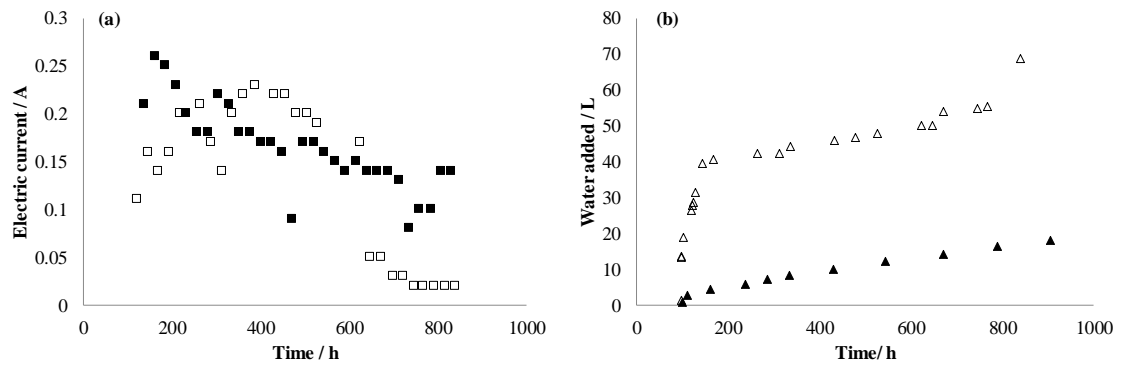
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## 24 **Results and Discussion**

25



1 Figure 2 shows the changes in the current intensity and in the volume of water added in  
 2 the anode wells during the two tests carried out to evaluate the performance of the two  
 3 ESKF strategies based on the placement of electrodes of the same polarity surrounding a  
 4 central electrode with a different polarity.  
 5

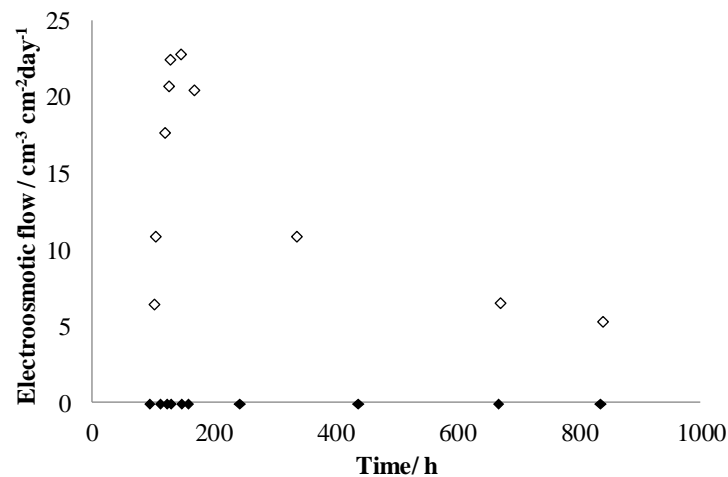


6  
 7 Figure 2. Changes in the (a) electric current and (b) volume of water added in the anode  
 8 wells over the two ESKF tests. Unfilled markers 1C6A, filled markers 1A6C.

9  
 10 As it can be observed, there are important similarities and differences between the  
 11 performance of both configurations. For both arrangements of electrodes, the current  
 12 intensity increases rapidly in the mockups up to a maximum value, reached at 200 hours  
 13 in the case of the 1A6C and slightly later (at 400 hours) in the case of the 1C6A  
 14 configuration. In both cases, the maximum intensity attained is slightly over 0.20 A. Then,  
 15 the decrease in the intensity obtained in the 1C6A is more abrupt than in the 1A6C  
 16 configuration. In comparing the amounts of water demanded in the anodic wells to  
 17 maintain a constant level, it can be seen that the 1C6A demands more than three times  
 18 the volume of water required by the 1A6C configuration to keep the level of water in the  
 19 anode wells (68.7 vs. 18.0 dm<sup>3</sup>). In fact, this is a key point in the comparison of both  
 20 configurations. In the 1A6C configuration, there is no effective electro-osmotic flow, and  
 21 almost no water reaches the cathode wells, as observed in Figure 3, which shows the

1 electro-osmotic flow calculated with the volume of water collected at the cathodes in both  
 2 configurations. When comparing this value with the value added in the anode wells, the  
 3 significance of the water evaporation process can be noted. It can also be noted that the  
 4 electro-osmotic flow is strongly related with the profile of the intensity of the electric  
 5 current. In a previous work focused on the treatment of soil spiked with 2,4-D in the same  
 6 experimental device (Risco et al., 2016c), a similar conclusion was drawn. This result  
 7 means that controlling water flows in a strategy with several cathode wells, like the 1A6C  
 8 strategy, should be improved if an efficient technology is to be obtained. At this point, it  
 9 is important to take into account that, to try to avoid the failure of the EK processes  
 10 because of the lack of electrolyte continuity, water was added each day at the cathode  
 11 wells. The surplus water was taken at the end of each day (before being replaced with a  
 12 new volume of water), as will be discussed afterwards.

13



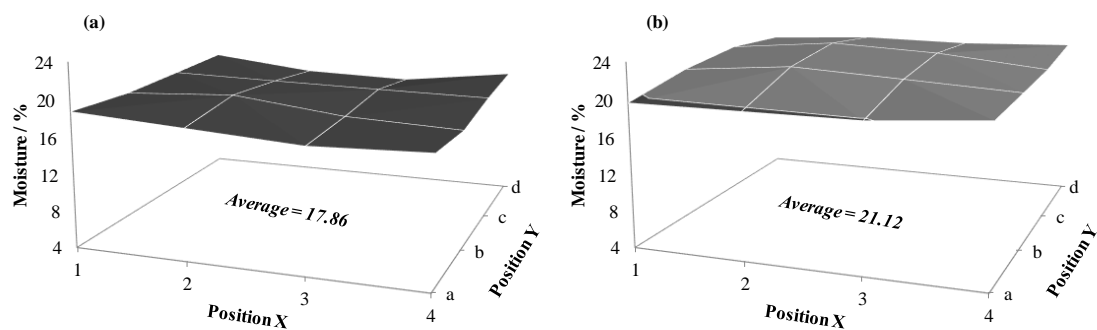
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15 Figure 3. Electroosmotic flow collected at the cathodes in the two EKSF tests. Unfilled  
 16 markers 1C6A, filled markers 1A6C.

17

18 This lack of water in the cathode wells does not correspond to the complete dryness of  
 19 the soil but just the opposite. In fact, it only means that water does not get into the well.

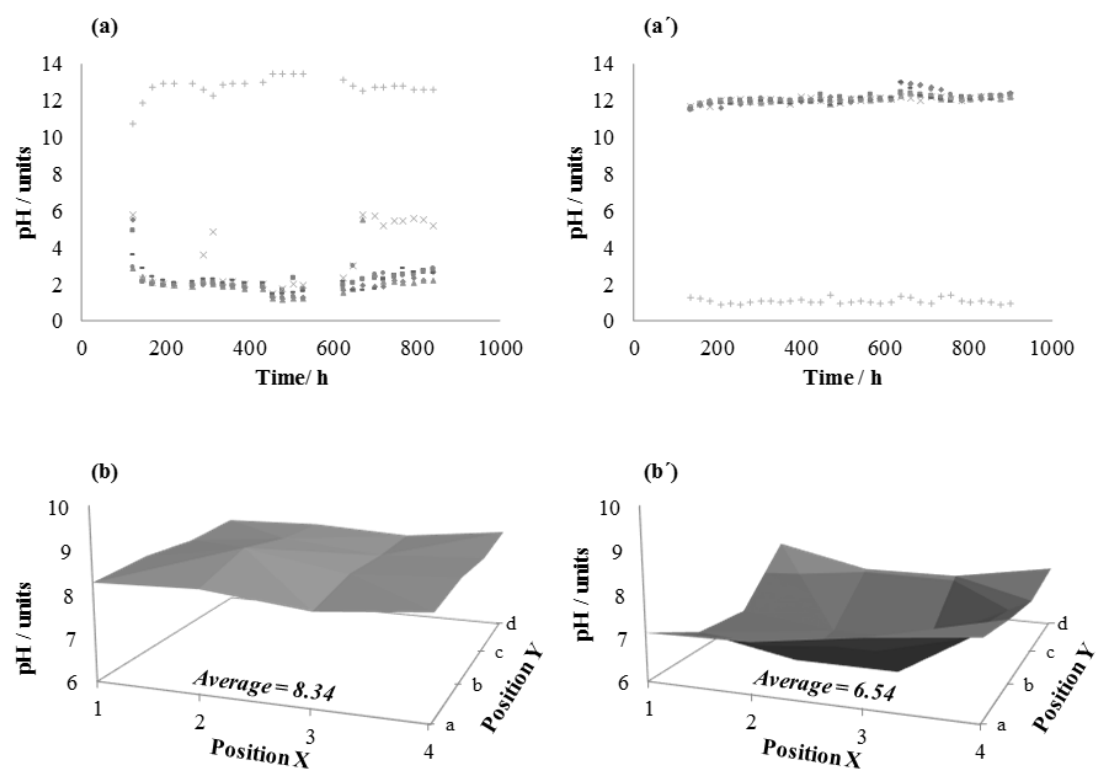
1 Figure 4 shows a 2-D plot of the water content of the soil after the treatment tests (average  
2 values of the samples in the same xy position at different z coordinates). It can be  
3 observed that there are no great differences between the water contents in the soil. The  
4 water content in the soil that undergoes the 1A6C strategy is higher than that shown by  
5 the 1C6A strategy. This soil water content is also greater than that obtained in the  
6 reference experiment after the same experimental time (9.9%). Hence, what is not  
7 promoted in the 1A6C strategy is the transport of water to the wells more than the drying  
8 of the soil. This can be a problem related to the improper distribution of electric current  
9 lines in this configuration to provide an adequate flow between the anode and each of the  
10 cathodes.  
11



12  
13 Figure 4. 2-D plot of the soil water content distribution after the two EKSF tests. (a) 1C6A  
14 and (b) 1A6C.

15  
16 One very important parameter in the EKSF processes is the pH, which is also directly  
17 related to intensity of the electric current. The pH is known to change in a different fashion  
18 (Lopez-Vizcaino et al., 2011) in both the anode and the cathode, as shown in Figure 5.  
19 However, despite these huge changes in the pH inside the cathode and anodic wells, both  
20 configurations are very effective in the neutralization of the pH fronts, and there are no  
21 extreme variations between the different zones of the soil, as shown in the 2-D maps

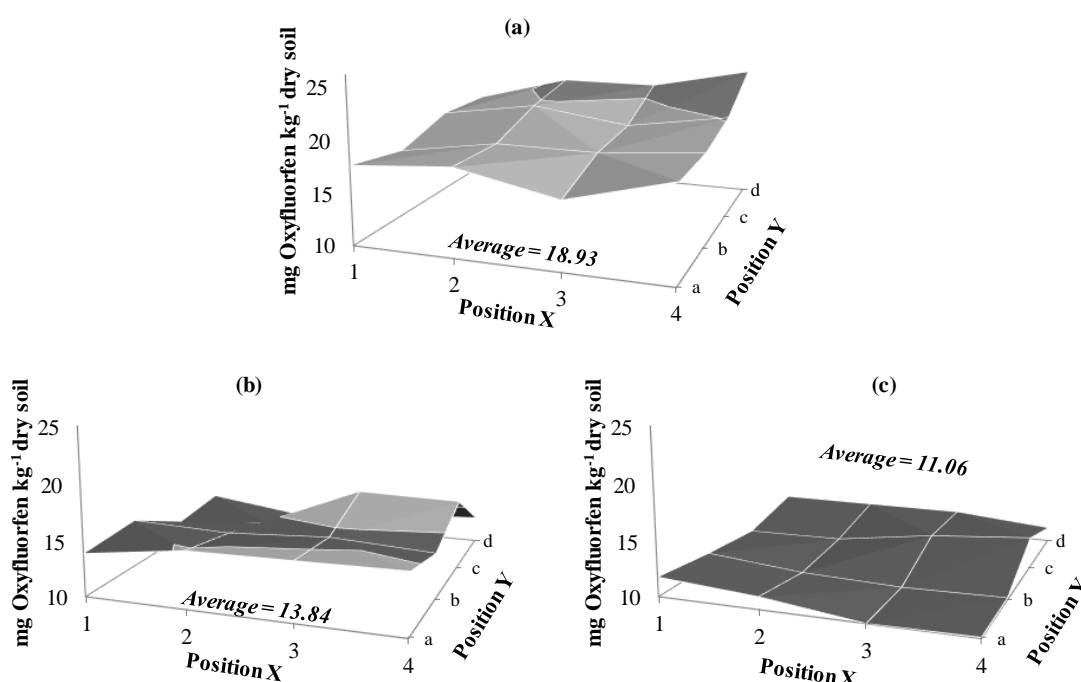
1 obtained after the postmortem analysis of the mockups, once the tests were over. The  
 2 changes are higher in the case of the 1A6C configuration, perhaps because of the lower  
 3 flow of water, which prevents neutralization. However, in both cases, the results are very  
 4 similar, and there are no large changes, such those obtained in the EKSF processes with  
 5 linear rows of anodes facing linear rows of cathodes (Lopez-Vizcaino et al., 2014a;  
 6 Lopez-Vizcaino et al., 2014b; Risco et al., 2016a).



7  
 8 Figure 5. pH changes during the electrokinetic remediation test measured in the  
 9 electrolyte wells (♦ P1, ■ P2, ▲ P3, x P4, – P5, ● P6, + P7) in both tests: (a) 1C6A and  
 10 (a') 1A6C. 2-D plots of the pH measured in the postmortem analysis of the soil after the  
 11 two tests: (b) 1C6A and (b') 1A6C.

12  
 13 Figure 6 compares, by using 2-D maps, the concentration of herbicide after the two EKSF  
 14 processes with different configurations of the surrounding electrodes with the  
 15 concentration remaining in the soil after the same experimental time in the reference test

1 without any EKSF remediation process after this spill. This test can be considered a blank  
2 experiment, and the differences between the two EKSF tests and the reference test allow  
3 us to understand the processes that are directly caused by an electric field applied between  
4 electrodes and to note the effect of processes not directly related to electrokinetics.  
5  
6



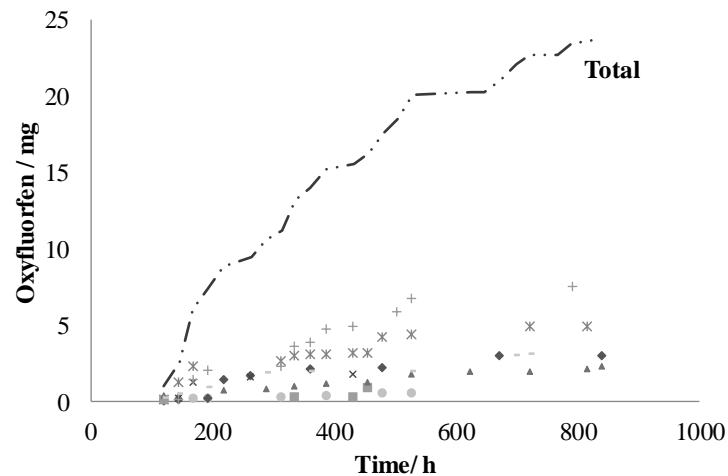
7  
8 Figure 6. 2-D plots of the concentration of oxyfluorfen: (a) reference experiment; after  
9 34 days of application of the EKSF: (b) 1C6A and (c) 1A6C.

10  
11 The results obtained with both strategies are sound, and they indicate that herbicides are  
12 efficiently removed from the soils. The 1A6C strategy is slightly more efficient than the  
13 1C6A configuration because of the lower remaining concentration in the soil after the  
14 test. Hence, the average concentration in the soil in the reference test decreases from the  
15 added 20.00 mg kg<sup>-1</sup> (this is the concentration expected in case a uniform distribution is  
16 attained after the simulated accidental discharge) down to 18.93 mg kg<sup>-1</sup>, which means

1 that, even in a soil without any treatment technology, the pesticide is partially removed.  
2 Evaporation and photolysis can help to understand this decrease, according to the  
3 literature (Alister et al., 2009; Das et al., 2003; Mantzos et al., 2014; Sondhia, 2010;  
4 Sondhia and Dixit, 2010). In this point, it is worth to take in mind that in comparing the  
5 vapor pressure of oxyfluorfen (0.026 mPa at 25°C) with other less volatile pesticide like  
6 chlorsulfuron ( $3 \times 10^{-6}$  mPa at 25°C) evaporation of oxyfluorfen can be even 10000 times  
7 higher. Biological oxidation or phytoremediation are ineffective with this herbicide. In  
8 comparing the results obtained in the reference test with those shown in the two 2-D maps  
9 of oxyfluorfen (after the EKSF processes), there is a clear effect on the removal caused  
10 by the application of the electric field. Thus, there is a decrease in the average  
11 concentration, down to 13.8 (1C6A) and 11.1 (1A6C) mg kg<sup>-1</sup> after 35 days of treatment.  
12 This result indicates an improvement of 27.0% and 41.3% with respect to the soil not  
13 undergoing EKSF, respectively. This observation indicates that the electric field applied  
14 in both configurations is clearly inducing removal mechanisms of the herbicides  
15 contained in the soils.

16 Data obtained from the rhizons (Figure 1) provide information about the evolution of the  
17 concentration over the tests. Unfortunately, the 1A6C configuration leads to a system in  
18 which no water can be collected at the electrode wells and rhizons, and hence, there is no  
19 possibility of measuring the herbicide on the line. Water was added each day in the  
20 cathode wells to avoid a lack of electrolyte continuity (pH of this water changes abruptly  
21 once added). The surplus water was taken at the end of each day (before being replaced  
22 with a new volume of water) and contained a high concentration of oxyfluorfen, and it is  
23 the value registered as taken in the cathode wells (dragged to the cathodes). In the case of  
24 the 1C6A strategy, Figure 7 shows that, according to the 2-D concentration plot, there are  
25 no relevant differences in the amount of herbicides obtained in each sampling point and

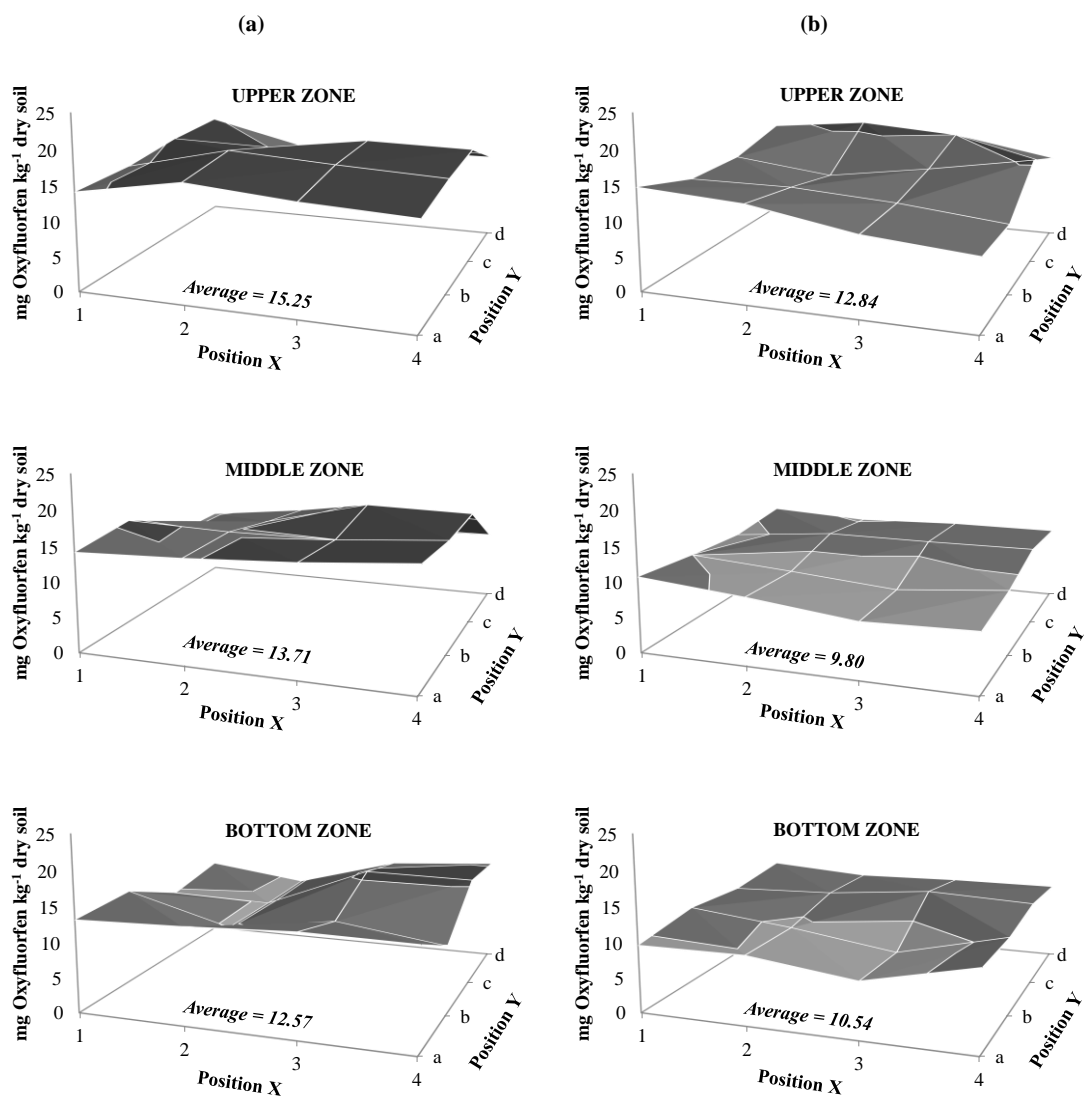
1 that the herbicide extraction rate decreases with time at each sampling point. The first  
2 observation can be easily related to the flat herbicide distribution pattern observed in the  
3 2-D map. On the other hand, the latter observation may be explained because of the  
4 decrease in the concentration of the herbicide in the soil during the tests.



5  
6 Figure 7. Herbicide collected at the different sampling points distributed across the soil  
7 mock-up undergoing the 1C6A strategy. \* R1, ● R2, ◆ R3, ■ R4, ▲ R5, x R6, + R7, -  
8 R8.

9  
10 Coming back to the results of the postmortem analysis, a very interesting piece of  
11 information can be obtained from the 3-D plot of both EKSF processes because this plot  
12 provides information about potential differences in the concentration in the vertical axis  
13 (z-axis according to Figure 1). Figure 8 shows a three-graph plot (each plot corresponding  
14 to one layer of soil) for each of the electrode arrangements studied. There are no great  
15 differences between the plots, and the shape of the curve is maintained in the three  
16 horizontal layers monitored. Surprisingly, a higher concentration is measured in the top  
17 layer, and this fact suggests that draining the herbicide (which consists of micelles) using  
18 gravity is not a very favored process and leads to a concentration gradient. On the other  
19 hand, the uniform distribution in each layer indicates the easiness of transport of this

1 pesticide after an accidental discharge (at least within the time and size used in the  
 2 experimental tests), which contrasts what it is stated in other works about the mobility of  
 3 oxyfluorfen (Mantzios et al., 2014; Sondhia, 2010; Sondhia and Dixit, 2010). The mobility  
 4 in the horizontal plane seems to be contradictory to observation in the z-axis, but it may  
 5 be explained in terms of the current distribution lines generated during the EKSF process  
 6 because these vertical gradients are not observed in the blank tests (data not shown).



7  
 8 Figure 8. 3-D plots of the concentration of oxyfluorfen after the postmortem analysis.  
 9 (a) 1C6A and (b) 1A6C.

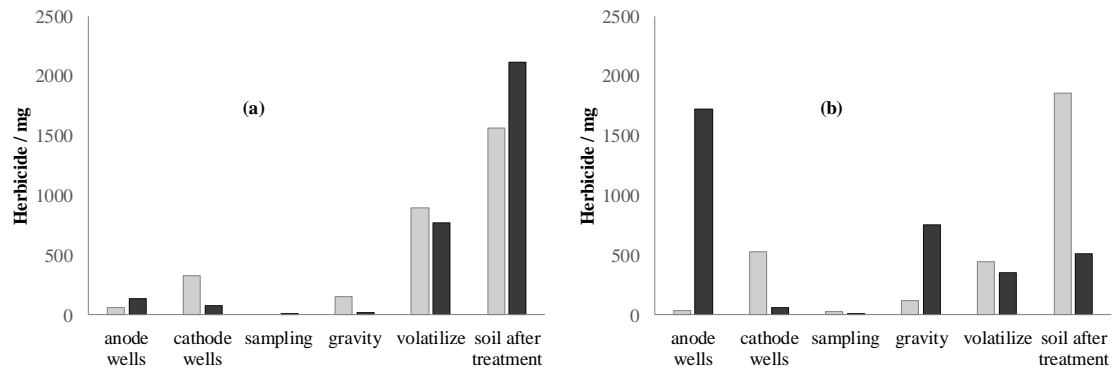


1 Though the remediation tests started only 2 days after the discharge, the distribution of  
2 pesticide in the soil is almost uniform, and the treatment does not affect the flat  
3 distribution patterns of the herbicide but just the concentration remaining in the soil. This  
4 observation was also noted in previous works of our research group with pesticides (Risco  
5 et al., 2016a; Risco et al., 2015) and with other organics (Lopez-Vizcaino et al., 2014a;  
6 Lopez-Vizcaino et al., 2014b). This result suggests the importance of reacting rapidly  
7 once an incidental spill is detected in order to prevent the uncontrolled diffusion of  
8 pollutants, which makes remediation more difficult and costly.

9 To conclude this discussion about the effects of the electrode arrangements on the  
10 removal of oxyfluorfen by EKSF, it is important to check the mass balances of the  
11 herbicide and water during the tests. The study presented in this work is a part of a more  
12 general study about the treatment of soils polluted with pesticides with different  
13 strategies, and the same electrode configurations were previously studied for the removal  
14 of pesticide 2,4-D from soils. Comparing the main results in order to check the influence  
15 of the nature of the pesticide on the development of EKSF process, can provide very  
16 valuable conclusions because of the very different transport characteristics of both  
17 pesticides. Thus, Figure 9 shows the distribution of the herbicide in the end of the  
18 experiment and compares it with the distribution of 2,4-D obtained after the same tests  
19 (in the same operation conditions) in order to obtain feedback about the influence of the  
20 characteristic of the pollutant molecule on the performance of the EKSF process (Risco  
21 et al., 2016c). The initial amount of pesticide spilled in the soil in both cases was 3000  
22 mg. The adsorption of both pesticides in the soil was tested, checking that is nil.

23

24



1

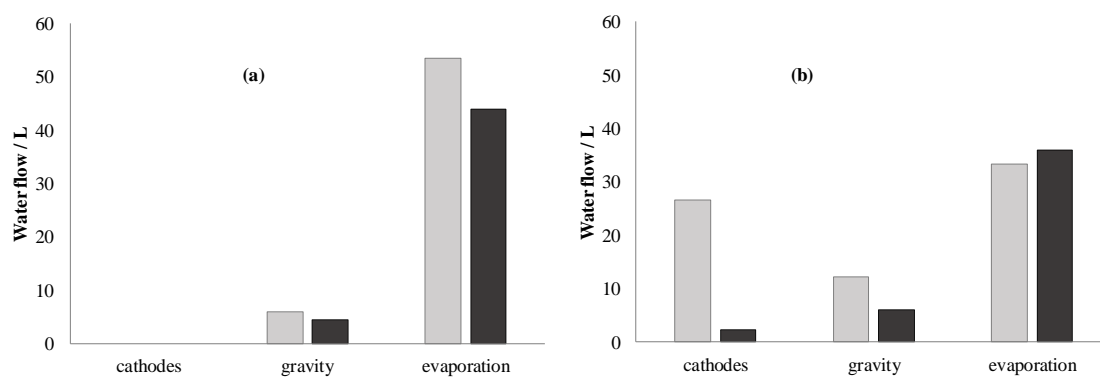
2 Figure 9. Distribution of oxyfluorfen (grey) and 2,4-D (black) after the application of  
 3 EKSF with the 1A6C (a) and 1C6A (b) strategies.

4 The results demonstrate that there is a huge influence of the characteristic of the pollutants  
 5 on the primary mechanisms affecting the transport of the pesticide in the soil. Transport  
 6 by electro-osmotic flow (collected in the cathode wells) is the primary EK mechanism for  
 7 the removal of oxyfluorfen, obtaining an 85.2% and 94.2% of the total removal of  
 8 oxyfluorfen by electrokinetic mechanisms with 1A6C and 1C6A configuration,  
 9 respectively. However, transport by electromigration (collected in the anode wells) is the  
 10 primary EK mechanism for the removal of the ionic 2,4-D (64.2% with 1A6C and 96.8%  
 11 with 1C6A configuration, in respect of the total removal of 2,4-D by electrokinetic  
 12 mechanisms). This transport mechanism is especially important in the 1C6A  
 13 configuration, and it leads to a very efficient process for the removal of the anionic  
 14 herbicide 2,4-D. The concentrations of oxyfluorfen collected at the anode wells can be  
 15 explained in terms of the electrophoresis of the micelles of this pollutant; as expected,  
 16 because of the steric limitations, this process is not as important as electromigration in  
 17 the case of 2,4-D. However, EK processes are not the only mechanisms to consider in  
 18 order to understand the performance of the EKSF with the 1A6C or 1C6A configurations.  
 19 Volatilization plays a very important role in the results, and this volatilization is higher  
 20 in the case of the 1A6C arrangement (around 28%) than in the case of the 1C6A

1 configuration (around 13%). This result is observed in the remediation of both pesticides  
2 studied (the oxyfluorfen and the 2,4-D). In addition, the volatilization of both pesticides  
3 is comparable, and the volatilization of oxyfluorfen is slightly higher than that of 2,4-D.  
4 This result is in agreement with the comparable values of the vapor pressure of both  
5 compounds at room temperature (that is, 0.026 mPa at 25°C for oxyfluorfen and 0.020  
6 mPa at 25°C for 2,4-D).

7 The water mass balances are shown graphically in Figure 10. The evaporation flows are  
8 similar in both systems, and they include the most important water flows measured in the  
9 soil mockups. There are no big differences between the results obtained in the tests with  
10 the two pesticides studied when the same arrangement is used. In comparing both  
11 configurations, the evaporation in 1A6C is slightly greater than the evaporation of 1C6A.  
12 This result is in agreement with the observed higher volatilization of herbicide and  
13 indicates that the capillary barrier is less effective in the case of the 1A6C configuration.  
14 Gravity fluxes are less important than evaporation. In addition, the gravity fluxes  
15 measured in the test with oxyfluorfen were slightly higher than those attained in the  
16 remediation of the soil containing 2,4-D (Risco et al., 2016c). Regarding the volume of  
17 water collected in the cathodes (associated with the electro-osmotic flux), in 1A6C, no  
18 water was collected (except for the volume collected during an unexpected event due to  
19 a valve failure registered during the 2,4-D test, which is not shown in the figure). On the  
20 other hand, the volume of water collected in the 1C6A configuration is very different in  
21 both tests, and it is much higher in the case of the remediation of soil polluted with  
22 oxyfluorfen.

23



1 Figure 10. Distribution of water during the remediation test of soil polluted with  
 2 oxyfluorfen (grey) and 2,4-D (black) after the application of EKSF with the 1A6C (a)  
 3 and 1C6A (b) strategies.

4 To know more about this point, the electrical conductivity and soil water content in the  
 5 four tests (two configurations with the two pesticides) are compared in Table 1.  
 6

7  
 8 Table 1. Average electrical conductivity and soil water content in different remediation  
 9 tests

Configuration/ herbicide	electrical conductivity mS cm <sup>-1</sup>	Soil water content %
Configuration: 1C6A; herbicide: 2,4-D	0.252	23.50
Configuration: 1A6C; herbicide: 2,4-D	0.222	28.84
Configuration: 1C6A; herbicide: oxyfluorfen	0.140	17.76
Configuration: 1A6C; herbicide: oxyfluorfen	0.123	21.06

10  
 11 Although all the tests started with the same value of water content (11%), the increase  
 12 experienced in the case of the 1A6C arrangement is higher than that in the case of the  
 13 1C6A configuration, and it is 48.5% higher in the case of 2,4-D and 30.0% higher in the  
 14 case of oxyfluorfen. The main difference is observed in the electrical conductivity, which  
 15 is almost double in the 2,4-D experiment compared to the oxyfluorfen experiment. This

1 result can explain the lower EO flux because of the smaller width of the Debye layer  
2 associated with the higher electrical conductivity of the system.  
3 Hence, the results obtained with the application of the two configurations studied in this  
4 work demonstrate that it is not easy to predict the performance of the system because of  
5 the very large number of associated parameters. However, the technology seems to be  
6 efficient, and high removals of oxyfluorfen (or 2,4-D) can be attained. Likewise, the  
7 contribution of non-electrokinetic processes is quite relevant. In fact, the removal by  
8 volatilization indicates that collecting this gaseous flow in order to attain a highly efficient  
9 is mandatory and thus, complete treatment of the soil should be studied in the future.

10

## 11 **Conclusions**

12 From this work the following conclusions can be drawn:

13

- 14 – Oxyfluorfen can be successfully removed from soil using EKSF, with the  
15 arrangement of electrodes consisting of several electrodes surrounding one  
16 electrode of different polarity. It can attain a 27 or 41% improvement in the  
17 removal of oxyfluorfen (vs. natural volatilization) after 34 days of treatment using  
18 1C6A and 1A6C configurations, respectively.
- 19 – Very different results are obtained between the 1C6A and 1A6C configurations.  
20 The second is more efficient than the first. The main mechanisms involved in the  
21 remediation of the soil are dragging by electro-osmotic flux and volatilization.  
22 Compared to the reference experiment, 1C6A improves removal by 18.5% versus  
23 the 12.9% improvement obtained in the 1A6C test, by electrokinetic transport  
24 mechanisms, after a 35-day-long treatment. However, the pesticide volatilization  
25 is favored in EKSF with 1A6C (29.9%) versus 1C6A configuration (14.9%).

- 1       – Comparing results with those obtained in the remediation of 2,4-D with the same  
2       electrode arrangements shows that the differences in the main transport  
3       mechanisms can be explained in terms of the very different characteristic of 2,4-  
4       D and oxyfluorfen.
- 5       – Both the 1C6A and the 1A6C configurations may attain good control of the acidic  
6       and basic fronts and prevent the acidification or basification of soil. Hence, the  
7       negative consequences that can be associated with this undesired process can be  
8       avoided in full-scale applications.

9

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