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Electrokinetic Remediation of PPCPs in Soil: Effect of operating parameters

Dissertação para obtenção do Grau de Mestre em Engenharia do Ambiente, Perfil de Engenharia de Sistemas Ambientais

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RESUMO

A reutilização de águas residuais tratadas, amplamente utilizadas para a irrigação de campos agrícolas, particularmente em regiões áridas e semi-áridas, é um aproveitamento importante de água que complementa os limitados e frágeis recursos hídricos naturais. Contudo, níveis consideráveis de produtos farmacêuticos e de cuidado pessoal (PPCPs) têm sido detetados nos efluentes e no solo agrícola irrigado com estas águas tratadas. Uma vez no solo, as plantas podem absorver, translocar e acumular estes contaminantes emergentes (CECs) em partes comestíveis podendo, subsequentemente, entrar na cadeia alimentar. Esta bioacumulação é preocupante pois alguns destes compostos atuam como desreguladores endócrinos.

O objetivo principal da presente dissertação foi estudar e otimizar o processo eletrocinético por forma a promover a degradação de CECs, usando como matriz um solo agrícola. A tecnologia desenvolvida foi avaliada em termos de eficiência de remediação e sustentabilidade. O solo utilizado foi dopado com uma solução fortificada contendo cinco CECs (16 mg/kg cada). Os compostos selecionados foram: sulfametoxazol (SMX), ibuprofeno (IBU), triclosan (TCS), cafeína (CAF) e atenolol (ATN). Utilizando varas de grafite como elétrodos, avaliou-se a viabilidade do processo eletrocinético (EK), testando três diferentes parâmetros: intensidade de corrente (CI), intervalos periódicos entre ON/OFF (Sw) e intervalos de reversão de polaridade (RP). Para o modo CI, foram testados 100, 50 e 10 mA, durante 24h ON no caso de CI-10 e 24h ON/OFF para CI-100 e CI-50. Para os sistemas Sw e RP (realizados com 10 mA), testaram-se intervalos de 6, 12 e 24h. Todas as experiências foram realizadas por um período de 7 dias, num microcosmos à escala laboratorial. Adicionalmente, dois testes complementares foram realizados como referência: controle inicial e controle após 7 dias, ambos na ausência de um campo elétrico de corrente contínua (DC).

Na experiência CI-50 foram atingidas elevadas percentagens de degradação para alguns compostos (97 ± 8% de SMX e 61 ± 5% de IBU), mas os elétrodos apresentaram sinais de corrosão após 24h de aplicação de 50 mA, demonstrando instabilidade no sistema. A experiência CI-10 apresentou a maior percentagem de degradação de TCS (56 ± 0%), mas o solo apresentou um gradiente de pH significativo (6,8-11,2). Os resultados da aplicação de corrente periódica durante 12h (sistema Sw) mostraram ser a opção mais viável, tendo em vista a degradação de CECs sem submeter o solo a alterações físico-químicas extremas. As eficiências de remoção na experiência Sw-12h variaram entre 36 e 72% (com RSD de 0 a 10%). Neste sistema, a eletrólise da água produziu um gradiente subtil de pH. As ténues alterações físico-químicas no solo, podem ter contribuído, até certo ponto, para a solubilização e/ou mobilização dos contaminantes em estudo. Estas variações podem assim ter promovido a remediação dos contaminantes por dois mecanismos de degradação: (i) reações eletroquímicas e (ii) biorremediação. O processo EK mostra-se como uma opção sustentável para a remediação de CECs em solos argilosos, diminuindo assim os riscos ambientais e para os humanos associados.

Palavras-chave: Remediação eletrocinética; atenuação natural; modo operacional; solo agrícola; produtos farmacêuticos e de cuidado pessoal

ABSTRACT

Reclaimed wastewater is an important source of water that complements the fragile and limited natural water sources, being widely used for irrigation of agricultural land, particularly in arid and semi-arid regions. Considerable levels of pharmaceuticals and personal care products (PPCPs), are found in effluents and in land fields irrigated with these “recycled waters”. Once in the soil, plants have the capacity to uptake, translocate and accumulate these compounds of emerging concern (CECs) in the edible parts of food crops. These can subsequently enter the food chain. This is of concern as some of these compounds act as endocrine disruptors.

The main objective of the present dissertation was to study and develop the electrokinetic process to promote CECs degradation using an agricultural soil as matrix. The developed technology was evaluated in terms of remediation efficiency and sustainability. For that, the soil was spiked with a 16 mg/kg solution containing five CECs. The selected compounds were: sulfamethoxazole (SMX), ibuprofen (IBU), triclosan (TCS), caffeine (CAF) and atenolol (ATN).

The feasibility of the electrokinetic (EK) process was evaluated by testing different operating modes, using graphite rods as electrodes. The main tested operating modes were: current intensity (CI); ON/OFF switch intervals (Sw); and reversed electro-polarization intervals (RP). For CI mode, 100, 50 and 10 mA were tested, for 24h ON in the case of CI-10 and 24h ON/OFF for CI-100 and CI-50. For Sw and RP systems (performed at 10 mA), periods of 6, 12 and 24h were tested. All experiments were carried out for a 7 day period, in a lab scale microcosms. Additionally, two complementary reference testes were done: initial control and control after 7 days, both without direct current (DC) electric field.

Experiment CI-50 showed high degrading percentages for some compounds (97 ± 8% of SMX and 61 ± 5% of IBU), but the electrodes were unstable and presented high signs of corrosion after 24h of 50 mA application. Experiment CI-10 presented the highest degrading percentage of TCS (56 ± 0%), but a significant soil pH gradient was observed (6.8-11.2). The results with periodic current application of 12h (Sw system) showed to be the most viable option for achieving the CECs degradation without submitting the soil to extreme physico-chemical changes. Removal efficiencies in experiment Sw-12h ranged between 36 and 72% (with RSD from 0 to 10%). Although. In this system, the electrolysis of water produced a subtle pH gradient. The slight physico-chemical changes promoted in the soil, may have enabled, to some extent, the solubilization and/or mobilization of contaminants under study. This may have enhanced the degradation of contaminants by two remediation mechanisms: (i) electrochemical degradation and (ii) bioremediation. The EK process shows to be a sustainable option for the remediation of CECs in clay soils, thus decreasing the environmental and humans associated risks.

Keywords: Electrokinetic remediation; natural attenuation; operating mode; agricultural soil; pharmaceuticals and personal care products

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ABBREVIATIONS AND SYMBOLS

Alpha	soil top layer
ATN	atenolol
Beta	soil bottom layer
C	centre sections
C18E	C18 endcapped sorbent
CAF	caffeine
CEC	cation exchange capacity
CECs	compounds of emerging concern
CI	current intensity
DAD	diode array detector
DC	direct current
d-SPE	dispersive solid-phase extraction
EC	electric conductivity
EDCs	endocrine disrupting compounds
EK	electrokinetic
EOF	electroosmotic flux
EU	European Union
FLD	fluorescence detector
GCB	graphitized carbon black
GC-MS	gas chromatography-mass spectrometry
GC-HRMS	gas chromatography high-resolution mass spectrometry
HPLC	high-performance liquid chromatography
IBU	ibuprofen
K_d	sorption coefficient
K_{ow}	octanol-water partition coefficient
L	left sections
LC-MS	liquid chromatography-mass spectrometry
LC-MS-MS	liquid chromatography tandem mass spectrometry
LD	limit of detection
LQ	limit of quantification

MLD	method limit of detection
MLQ	method limit of quantification
PPCPs	pharmaceuticals and personal care products
PSA	primary and secondary amine
QuEChERS	quick easy cheap effective rugged and safe
R	right sections
RP	reversed electro-polarization intervals
R_t	retention time
SMX	sulfamethoxazole
SPE	solid-phase extraction
Sw	on/off switch intervals
TCS	triclosan
UV	ultraviolet
WWTP	wastewater treatment plant

1. INTRODUCTION

Climate change and an increasing population trend brought up several challenges and concerns. Water stress is one of the many. Water scarcity and droughts are likely to increase in severity over the next years. This will have a direct impact on citizens and economic sectors who use and depend on water. Main pressures are forced by the agricultural sector, followed by urban and industrial sectors. Just in Portugal, in the year 2009, the relative water abstraction for the agricultural sector was 81%, 3 401 190 000 m^3, being the larger consumer compared to Urban and Industrial sectors (12% and 7%, respectively) (PNUEA, 2012).

The role of treated wastewater reuse as an alternative source for water supply has become embedded within international, European and national strategies. European Commission is working on to propose a Legal Instrument on Water Reuse in Europe, still in 2018, with the intend to overcome the lack of a coherent and comprehensive legislative framework within the European Union (EU), bridging and boosting water reuse among several member states. The legislation will focus on minimum requirements for water reuse in irrigation and aquifer recharge (European commission, 2018). As a support to the design of this legislation, a technical document has been published proposing minimum quality requirements for water reuse in agricultural irrigation and aquifer recharge based on a risk management.

Although the use of reclaimed water is an accepted practice in several EU countries enduring water scarcity issues (including Portugal), one of the main obstacles is the lack of harmonization in the regulatory framework regarding the management of health and environmental risks related to water reuse at EU level. In the Water Framework Directive (2000/60/EC), reuse of water is mentioned as one of the "supplementary measures" to achieve the Directive's quality goals. Moreover, Urban Wastewater Treatment Directive (91/271/EEC) stated "treated wastewater shall be reused whenever appropriate". Besides the lack of criteria at EU level, several member states issued their own regulations, or guidelines for different water reuse applications (Alcalde-Sanz and Gawlik, 2017).

Wastewater reuse is not only considered a reliable water supply to cover peaks of water demand, especially for agricultural irrigation, but also a method to reduce the use of additional fertilisers to crops growth (Alcalde-Sanz and Gawlik, 2017). However, some emerging organic contaminants, such as pharmaceuticals and personal care products are still present in these effluents (Xu *et al*., 2009a). These potentially harmful compounds may therefore be introduced into the terrestrial environment, if not effectively removed during the treatment (Chen *et al*., 2013).

Pharmaceutical and personal care products (PPCPs) have been extensively used for both personal health and cosmetic reasons as well as for veterinary purposes. They are part of the growing group of chemicals termed Compounds of Emerging Concern (CECs) (Alcalde-Sanz and Gawlik, 2017). After irrigation, the reclaimed water borne PPCPs, while flowing through the paths in the receiving soils are subject to volatilization, degradation, and plant uptake. Some PPCPs

are strongly sorbed by soil particles and organic matter, persistent in the top soil (0 – 30 cm) and recalcitrant to degradation, remaining in soils, whereas the highly mobile chemicals have the potential to move into aquatic systems (Qin *et al*., 2015). These contaminants, although at trace levels in the effluents, will probably accumulate in the soils if long-term irrigation occurs, which may result in environmental problems (Xu *et al*., 2009a), such as the contamination risk to soil, groundwater, surface water and dependent ecosystems, including crops to be irrigated. This poses not only a risk to the environment (including fauna and flora) but also to humans, through food chain.

To fast-track this contaminants and further removal, some techniques have been investigated and enhanced over the years. Electrokinetic (EK) remediation is an *in situ* or *ex situ* technology that already proved its value in contaminated soils with PPCPs (Guedes *et al*., 2014; Ferreira *et al*., 2017; Li *et al*., 2018), especially in fine-grain soil, overcoming the inaccessibility of these compounds comparing to other remediation techniques. Basically, the EK technique relies on the action of an electric field generated between inserted pairs of inert electrodes in the medium, by applying a low level direct current or a constant voltage, and several transport mechanisms and electrochemical reactions are induced (Acar and Alshawabkeh, 1993). The conditions thereby created are used as the cleaning agent.

1.1. Study objectives and research

The aim of this work carried out at RESOLUTION Lab., is to develop an *in situ* soil remediation process that decreases the risk of organic contaminants uptake by crops.

For that, the present dissertation proposes to answer the following questions:

a) Is the EK process a viable *in situ* technology for the remediation of different organic contaminants, without the use of enhancement agents?
b) Which operating parameters improve the PPCPs degradation rates, without promoting major changes in a clay agricultural soil?
c) How does an organic contaminant mobilize in the soil with and without EK?

To evaluate these questions, a microcosm capable of simulating *in situ* conditions was designed, and experiments were performed at a laboratory scale. The used design allowed to study the dispersion, through the whole soil, of five CECs, specifically belonging to the group of pharmaceuticals and personal care products, these being: sulfamethoxazole (SMX), ibuprofen (IBU), triclosan (TCS), caffeine (CAF) and atenolol (ATN). The selection of these analytes was based on the high frequency that these compounds are detected on treated effluent and also because they belong to different classes: nonsteroidal anti-inflammatory drug (IBU), antibacterial and antifungal (SMX), central nervous system stimulant (CAF) and a beta blocker (ATN), and present a wide range of physico-chemical characteristics (e.g. solubility and octanol-water partition coefficients, see Table 2.1.).

An agricultural clay soil used for organic tomato field plantation was considered. Experiments were carried out at room temperature in the mildest conditions to be as close as possible to a realistic situation. Microcosms were not exposed to direct ultraviolet (UV) radiation and a daily watering was maintained to preserve soil moisture content.

In total, twelve experiments were performed in duplicate, two controls (with no electric current) and ten applying the EK process. Three EK operating modes were tested: current intensity, periodic electric potential application and periodic electro-polarity reversal. The soil was spiked with 16 mg/L of each organic compound. All experiments were carried out for 7 days.

1.2. Dissertation structure

The present dissertation is organized in the following chapters:

I. Introduction – work scope and relevance, main objectives and structure;
II. Literature review – description of the central theme and relevant terms and previous work developed;
III. Materials and methods – description of materials used, characterization analysis, identification and data treatment methods;
IV. Results and discussion – presentation of results, hypothesis formulation and their discussion;
V. Conclusions – main outcomes;
VI. Future developments;
VII. References;
VIII. Annexes – includes a set of detailed data complementary to the main document and all abstracts presented as a result of this MSc study, either as oral or poster communications.

2. LITERATURE REVIEW

2.1. Pharmaceuticals and personal care products

Compounds of emerging concern (CEC) are a group of chemical compounds, not commonly regulated, that have been detected in drinking water, wastewater, or aquatic environment. The concern involves the knowledge gap around the substances concentrations that may pose (eco)toxicological risk.

CECs include groups of compounds categorized by their end use, such as pharmaceuticals and personal care products (PPCPs), and by their environmental and human health effects, such as endocrine disrupting compounds (EDCs).

PPCPs refer to products used by individuals for personal health/well-being or for cosmetic purposes. They consist on a wide range and diverse group of organic compounds, together with their respective metabolites and transformation products, a collection of thousands of chemicals, including, but not limited to, prescription and over-the-counter human drugs, veterinary drugs, diagnostic agents, nutritional supplements and other consumer products, such as fragrances, cosmetics, lotions and other personal care products (Daughton and Ternes, 1999). PPCPs include a large diversity of synthetic and naturally occurring compounds that are not commonly monitored or regulated in drinking water or aquatic environments (NH Department of Environmental Services, 2010).

EDCs are compounds that alter the normal functions of hormones resulting in a variety of health effects, defined by the International Programme on Chemical Safety (1998) as “exogenous substance or mixture that alters function(s) of the endocrine system and consequently causes adverse health effects in an intact organism, or its progeny, or (sub) populations.”. There are many PPCPs that act as EDCs. Some of the most popular groups are analgesics, antibiotics, anti-epileptics, β-blockers, lipid regulators, anti-inflammatory and hormones (Jones *et al*., 2001; Liu and Wong, 2013).

2.1.1. PPCPs contamination routes

PPCPs enter the environment (both aquatic and soil) due to a combination of activities, actions, and behaviour of industries and individuals. PPCPs are released all over the world from either a point- or diffused- sources, including, effluent, treated sewage sludge, landfill leachate, industrial effluent, combined sewer overflows, aquaculture and animal feed lots (Acar and Alshawabkeh, 1993; Daughton and Ternes, 1999; Beretta *et al.,* 2014). Figure 2.1 displays the sources, exposure routes, the spectrum of affected species by PPCPs and how they may be distributed. The speed of the passage and impact severity of PPCPs depends on the quality of water treatment (in wastewater treatment plants (WWTP)), compounds physico-chemical properties,

compound concentration (quantity), species affected and the fate they take once in the ecosystem, concomitantly, depending on the characteristics on the receiving environment/species (Jjemba, 2008).

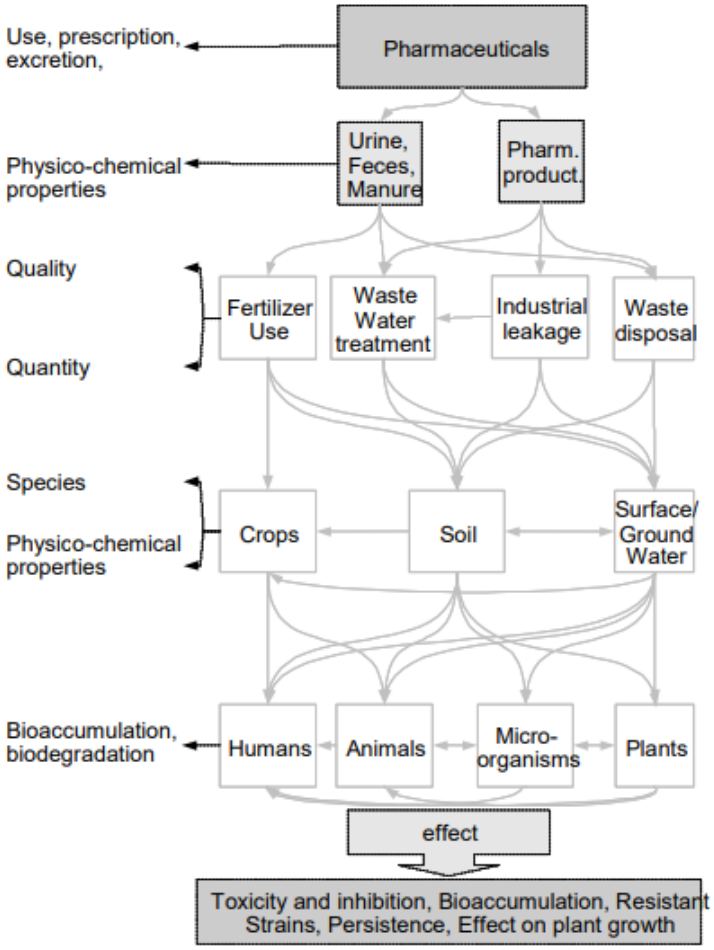


Figure 2.1. Possible pathways by which pharmaceutical and personal care products enter the environment and may endanger human health (from Vaňková, 2010).

According to the regulatory exposure modelling based on European and North American systems, the main pathways to environment are, primarily, WWTP effluent (to waterways) and, secondarily, terrestrial run-off (to soil) (Daughton and Ternes, 1999).

Human used PPCPs are generally excreted, entering the sewage system. Wastewater treatment processes were not directly designed to remove PPCPs from water. The processes that remove PPCP concentration from WWTP at some extent are activated sludge process, tertiary treatment with nutrients removal, membrane bioreactors, and advanced oxidation processes (Miao *et al.,* 2005; Ternes *et al.,* 2007; Tsang *et al.,* 2007; Reyes-Contreras *et al.,* 2011; Zhao *et al.,* 2014; Ávila and García 2015). But even with additional tertiary or complementary treatment steps, such as ozonation and/or powdered activated carbon adsorption to improve water quality, several PPCPs (and other compounds) may not be significantly removed (Reemtsma *et al.,* 2006). The

amount of PPCPs that passes the WWTP barrier may reach the environment, making their way up to the food chain.

2.1.2. Occurrence in the environment and food chain

In 2013, Loos and co-workers published a comprehensive EU monitoring survey on the occurrence of emerging polar organic contaminants in WWTP´ effluents. In their study, 90 WWTPs across Europe were sampled (Portugal included), and 156 chemicals (i.e. "emerging" compound classes, pharmaceuticals and personal care products and veterinary (antibiotic) drugs) were analysed by solid-phase extraction (SPE) or liquid-liquid extraction (LLE), followed by liquid chromatography tandem mass spectrometry (LC-MS-MS) or gas chromatography high-resolution mass spectrometry (GC-HRMS), and four different toxicity assays were conducted on selected samples. A total of 125 target substances (i.e. 80% of the target compounds) were found at least once, in concentrations ranging from low nanograms to milligrams per liter (Loos *et al*., 2013). This creates a pathway for entry of these compounds into aquatic environments via WWTP effluent discharge to receiving waters (Reemtsma *et al.,* 2006), and into terrestrial environments via land application of biosolids (applied as a fertilizer to agricultural land) (Halling-Sorensen *et al.,* 1998; Ternes *et al.,* 2004) and wastewater reclamation (e.g. for irrigation of agricultural land) (Daughton and Ternes, 1999; Hirsch *et al.,* 1999; Durán–Álvarez *et al.,* 2014).

At low concentrations, many of these compounds raise considerable toxicological concerns, confirmed by Loos *et al.,* (2013) by vitro biodetection tools, as well as by significant toxicity induced by some of the tested WWTP effluents in aquatic organisms.

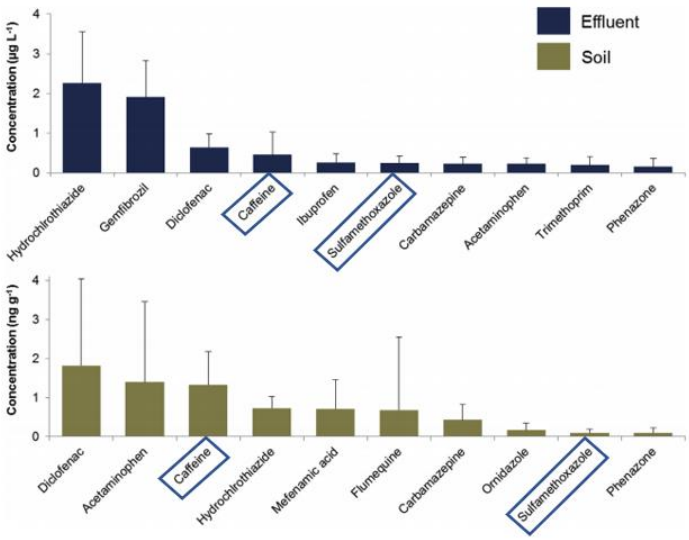


Figure 2.2. Top 10 of 78 pharmaceuticals (µg/L) found in WWTP effluent and in the receiving soils (ng/g) (adapted from Biel-Maeso *et al*., (2018)).

Biel-Maeso *et al.* (2018) conducted a study monitoring the occurrence of pharmaceuticals in soils irrigated with reclaimed wastewater (Figure 2.2). They measured the levels of a wide range of commonly used pharmaceutically active compounds (including IBU, SMX and CAF). Analysis of

target compounds showed total concentrations between 3 to 41 µg/L in effluents, and in surface soil samples were in the range of 2 and 15 ng/g, with predominance of analgesics and anti-inflammatories (maximum concentration = 10.05 ng/g), followed by antibiotics and psychiatric drugs (maximum concentration = 5.45 ng/g and 3.78 ng/g, respectively). Their distribution in soils was affected by heavy rain episodes, showing evidence of chemical leaching (concentrations were found in depth of 150 cm), and also their concentration dependeds on temperature, once in colder months compounds' concentrations were found to be higher, indicating persistence to biodegradation, comparing to higher temperatures in the summer, that contributed to an increase of microorganisms activity, responsible for the biodegradation of these contaminants.

Once in soils, PPCPs may become bioavailable to uptake by crop plants, entering this way into the food chain (Christou *et al.,* 2017; Wu *et al.,* 2010). The potential for PPCPs to enter the plant presents concerns for their phytotoxicity. In fact, accumulation of PPCPs through the food chain could also pose potential risks to species consuming plant parts, including humans (Wu *et al.,* 2010). These contaminants may have serious adverse health impacts, since human exposure to these chemicals has unknown long-term effects (Boxall *et al.,* 2012). Therefore, the uptake and bioaccumulation of PPCPs in the edible parts of food crops and their subsequent entry into the food chain has earned increasing attention.

Based on the wastewater reuse for vegetable crops irrigation, applied worldwide, Christou *et al.* (2017) reported that the long-term wastewater irrigation may result in the significant uptake of acidic PhACs (i.e diclofenac and sulfamethoxazole (SMX)) by plants and their subsequent bioconcentration in tomato fruits. The bioconcentration in the tomato reached its maximum in the last year of study (e.g. SMX concentrations in the fruit over the years ranged from 0.05 ng/g in the first year, to 1.0 ng/g in the second year, and 5.3 ng/g in the third year). This reveals that the concentration of the studied compounds in soil and fruits varied, depending on the duration of irrigation, as well as on the physicochemical properties of the studied compounds, highlighting the need for long-term (more than a single growing period) studies utilizing wastewater irrigation under field conditions (Christou *et al.*, 2017). Throughout the three years of the experimental period Christou *et al.* (2017) performed a public health risk assessment, results suggested that the daily consumption of tomatoes grown in field and irrigated for consecutive years with the tertiary treated wastewater containing a particular concentration of PhACs does not pose a health threat, due to the weight of tomato consumption for an adult or a toddler. More studies are needed to reach a definite conclusion for the classification of wastewater reuse as a safe practice regarding human health, particularly the potential sensitivity of subgroups of the population (i.e. pregnant, infants, elderly people, and chronic sufferers) and the simultaneous consumption of various other vegetables that may bioaccumulate higher contaminant concentrations.

Mendez *et al*. (2016) studied the fate of triclosan (TCS) when soil and crop plants were irrigated with reclaimed wastewater. They found out that in soils with no crops, the degradation of organic contaminants was dependent on the soil microbial activity. They also observed that with higher soil moisture levels and organic contents, a possible increase of microbial activity and diversity

influenced the time it took for the concentration to drop by half of the initial concentrations, promoting a low-level accumulation in soil. When crops are present, even at low TCS concentrations typically found in recycled waters, agricultural irrigation presents an additional exposure route for organic contaminants to humans, due to the bioaccumulation of TCS observed in all edible portions. For example, in long-term tomato studies, triclosan was translocated to fruits (<1 – 5 µg/L) (Mendez *et al.*, 2016). The concentrations detected in both onions and tomato fruits were below current human exposure limits. Still, TCS along with its degradation by-products, may be taken up by plants, posing a greater concern than triclosan concentrations alone (Mendez *et al.*, 2016).

Other studies with crops were evaluated, a study by Wu *et al.* (2010) demonstrated that plants are able to uptake PPCPs from soils irrigated with treated wastewater, although the plant uptake of these compounds depends on their physicochemical properties such as pK_a and octanol-water partition coefficient (K_{ow}), interaction with the substrate, and introducing pathways (Wu *et al.,* 2010). For example, among the compounds that these researchers studied, TCS was detected with the highest concentration in leaves from irrigation system and one of the two compounds were the most detected in ones' soy bean.

Experimental setups employing soil under real agricultural systems are imperative for evaluating PPCPs fate in the terrestrial environment, since soil is a living, dynamic system that influences the fate and bioaccessibility of organic contaminants.

2.1.3. Fate of PPCPs in the environment

PPCPs that end up in soil, through the application of reclaimed water irrigation, undergo processes of transport and transformation (Geological Survey (U.S.),1986; Jones *et al.*, 2001; EPA, 2006):

- volatilization (e.g., anaesthetics and fragrances);
- Respirable particulates contain sorbed drugs (e.g. medicated-feed dusts);
- Photolysis (depending on both direct and indirect reactions to UV light);
- Chemical oxidation (i.e. mineralization, the breakdown of chemical bonds);
- Sorption (encompassing absorption and solubilization processes);
- Hydrolysis (that result from the interaction of a chemical with water);
- Bioaccumulation (the uptake and retention of chemicals bioavailable to aquatic organisms, plants and potentially humans);
- Biotransformation and biodegradation (enzymatic transformation of a chemical as a source of energy, carbon and nutrients).

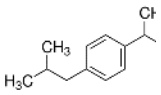
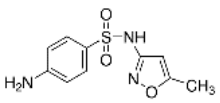
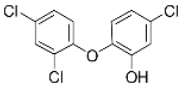
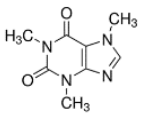
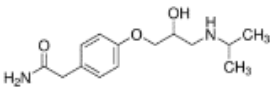
These factors affected the concentrations of PPCPs in the soil, being, sorption considered important once it influences the mobility and transport of hydrophobic organic compounds in the soil-water environment (Boxall, 2008; Durán–Álvarez *et al.,* 2014). Therefore, the tendency of

PPCPs to persist in soil or mobilize to groundwater may be indicated by the octanol-water partition coefficient (log K_{ow}) and sorption coefficient (K_d) of these compounds, being the least the coefficient, the most the tendency of PPCPs to move from soil into groundwater; whereas, volatilization and degradation are the processes that govern the elimination of these compounds from the soil (Karnjanapiboonwong and Todd, 2010).

2.1.4. Target contaminants of emerging concern

PPCPs removal efficiencies from the environment depend on their chemical and physical properties (e.g., chemical structure, aqueous solubility, octanol/water partition coefficient, and Henry's law constant) (Jones *et al.*, 2001). Table 2.1 presents the physico-chemical properties of the compounds under study.

Table 2.1. Physical-chemical properties of the studied compounds (Pubchem, 2018)

	Ibuprofen (SMX)	**Sulfamethoxazole (IBU)**	**Triclosan (TCS)**	**Caffeine (CAF)**	**Atenolol (ATN)**
Class	Analgesic, nonsteroidal anti-inflammatory	Bacteriostatic antibiotic	Antimicrobial disinfectant	Central nervous system stimulant	Beta-blocker
Chemical formula	$C_{13}H_{18}O_2$	$C_{10}H_{11}N_3O_3S$	$C_{12}H_7Cl_3O_2$	$C_8H_{10}N_4O_2$	$C_{14}H_{22}N_2O_3$
Chemical structure					
Molecular weight (g/mol)	206.29	253.28	289.54	194.19	266.34
Solubility in water (mg/L)	21 [(a)]	610 [(b)]	10 [(c)]	$2.16x10^4$ [(a)]	$1.33x10^4$ [(a)]
Henry's law constant (atm-cu m/mole)	$1.5x10^{-7}$	$6.4x10^{-13}$	$2.1x10^{-8}$	$1.1x10^{-11}$	$1.38x10^{-18}$ [(c)]
pKa (25 ºC)	4.91	1.6/5.7	7.90	0.7/14.0	9.6
Log K_{ow}	3.97	0.89	4.76	-0.07	0.16
Organic Carbon-Water Partitioning Coefficient	3.53	1.85	3.38 – 4.20	2.87 – 3.89 [(d)]	2.17 [(c)]

[a] at 25 ºC: [b] at 37 ºC; [c] at 20 ºC

[d] silt - sandy loam soils

[c] *Küster et al., 2009*

2.1.4.1. Ibuprofen

Ibuprofen (IBU) is a nonsteroidal anti-inflammatory drug with analgesic and antipyretic properties (González-Naranjo *et al.*, 2013).

Conventional WWTP are effective for easily biodegradable compounds such as IBU with elimination rates of around 90% (Loos *et al.*, 2013). Still, Loos *et al.* (2013), detected IBU at a frequency of 57%, belonging to the group of compounds found with the highest concentration, a maximum of 2.1 µg/L and an average of 80.5 ng/L.

Volatilization from moist or dry soil surfaces is not expected to be an important fate process due to the estimated Henry's Law constant. The pKa of IBU, indicates that this compound will primarily exist in the dissociated form in the environment. Ibuprofen will be mostly found in the anionic form at pH values of 5 to 9 (Toxnet, 2018). Studies by Lin and Reinhard (2005) in river water, demonstrated that IBU exhibited photodegradation. Once in the soil, the log K_{ow} indicates that this compound is moderately fixed to soil particles surface, thus expected to have slight mobility (González-Naranjo *et al.*, 2013). Due to this affinity to soil, it could be bioavailable for soil microorganisms or plants exposed to it and may reach groundwater by leaching. Hence, the contamination of IBU in soil matrix needs to be accounted (Yuan *et al.*, 2017; González-Naranjo *et al.*, 2013).

2.1.4.2. Sulfamethoxazol

Sulfamethoxazol (SMX) is a bacteriostatic antibacterial agent, belonging to a class of antibiotics known as sulfa drugs (sulphonamides). It is commonly used to fight infections in human and animals. Its broad spectrum of activity has been limited by the development of resistance (Drugbank, 2018).

SMX is only partially remediated in traditional wastewater treatment, and is persistent in the environment, since it is regularly detected in ground and surface waters. According to Loos *et al.* (2013), SMX was detected with a frequency of 83%, having its maximum concentration with 1.7 µg/L and an average of 280.0 ng/L.

Volatilization from moist or dry soil surfaces is not expected to be an important fate process due to the estimated Henry's Law constant. This compound will partially exist in the anion form in the environment according to the pKa1 and pKa2. Anions generally do not adsorb more strongly to soils containing organic carbon and clay than their neutral counterparts (Boethling *et al.*, 2000). Once in the soil, it is expected to have high mobility due to the estimated K_{oc}.

Sulfonamide antimicrobials are not readily biodegradable and persist in soils (Pubchem, 2018). The main processes of substance elimination in the environment, especially in waste water,

sediments, and soil are due to bacteria (Kümmerer, 2004). Radke *et al.* (2009) showed that in the tested river sediment (primary) biodegradation was much more important than abiotic processes, such as sorption or hydrolysis. It should be noted that the microbial capacity to degrade sulfamethoxazole could be a matter of concern if bacteria have developed resistance to this antibiotic (Martínez-Hernández *et al.,* 2016).

2.1.4.3. Triclosan

Triclosan (TCS) is a broad-spectrum antimicrobial agent used in multiple personal care products. It is believed to lead to the development of antibiotic resistance and is considered a persistent chemical in the environment (Karnjanapiboonwong and Todd, 2010).

Although TCS degradations in WWTP can reach the 90%, still a high amount of contaminant is likely to enter the environment (Loos et al. 2013). The TCS concentrations found by Loos *et al.* (2013) had a maximum of 4.3 µg/L and an average of 75 ng/L, and these results are in good agreement to other EU studies.

Among all PPCPs, TCS has the highest log K_{ow} (4.76), indicative of retention within the soil matrix, with the low water solubility at 10 mg/L. Once in soil, TCS is expected to have a low to no mobility, based upon the soil organic carbon-water partitioning coefficient (log K_{oc}) values, and will partially exist in anion form in the environment due to its pKa. It is non-volatile from moist soil surfaces, dry soils or water surfaces, based upon an estimated Henry's Law constant and the pKa (Pubchem, 2018).

Latch *et al.* (2005) performed experiments that proved that TCS rapidly photodegrades by direct photolysis once in an aquatic system (between 3 to 12% of the triclosan was converted to dioxin in the water), suggesting that sunlight could transform TCS to dioxin naturally. It is postulated that photolysis in natural waters leads to some of the TCS being coupled to humic substances. Indirect photolysis pathways, however, are not expected to be important. Because of its lipophilic nature and resistance to degradation, TCS in waterways is readily available for absorption and bioaccumulation by aquatic organisms in the environment (Adolfsson-Erici *et al.*, 2002).

In soil, TCS have a low leaching potential found in wastewater-irrigated soils (Gibson *et al.,* 2010). With an expected concentration gradient with depth due to the sorption potential of TCS in wastewater-irrigated soil (log K_{oc}, 3.0–3.4), the high pKa (7.9–8.1), and the calculated partitioning coefficient (log K_d=3.1) (Mendez *et al.,* 2016). Soluble TCS is likely to be uptaken by plans and degraded by microbial activity and diverse populations (Mendez *et al.*, 2016).

2.1.4.4. Caffeine

Caffeine (CAF) is a member of a group of compounds known collectively as purine alkaloids, i.e. naturally occurring chemical compounds derive from plant product, well known by the general

public, it is accumulated in tea, coffee and a few other plant species. This compound is also used in pharmacology as a supplementary substance in medicaments. CAF pharmacological effect is as a central nervous system stimulant (Pohanka, 2015).

CAF is one of the most relevant compounds frequently detected (93%) in EU effluent waters at significant concentrations (a maximum of 3.0 µg/L and an average of 191 ng/L) (Loos *et al.,* 2013), indicating that it is incompletely removed during the sewage treatment process. Because of its sizable input into sewage waters, mainly attributed to its massive consumption in daily life, CAF is regarded as a chemical marker for surface water pollution by domestic wastewater (Buerge *et al*., 2003).

In soils, CAF is expected to have low mobility in silt and loamy sand soils (Log K_{oc} of 2.87 – 3.89) and high mobility in sandy soils (Log K_{oc} value of 1.85). This compound is both a weak acid and a weak base. Although partial ionization to cation and anion forms may occur, electrochemical studies have found that the neutral form of CAF was predominant in the pH range of 5.5 to 9.0 (Pubchem, 2018). Cations generally adsorb more strongly to organic carbon and clay than their neutral counterparts suggesting that the cation form of CAF may have higher K_{oc} values than the neutral form. Volatilization of CAF from moist or dry soil surfaces is not expected to be an important fate process given the estimated Henry's Law constant. CAF is expected to persist in the water mainly due to its high solubility and low octanol-water partition coefficient.

A study by Buerge *et al.,* (2003) demonstrated the suitability of CAF as a quantitative anthropogenic marker for wastewater contamination of surface waters. On the other hand, CAF may work as an indicator of effluent discharge only under circumstances where biodegradation is not significant as it degrades rapidly in groundwater rich in bacteria (Knee *et al.,* 2010). In addition, in a soil contaminated with CAF, Martínez-Hernández *et al.* (2016) observed that in the first 48h the sorption process dominanted, still sorption rate decreased over time and biodegradation became the main process. This behaviour was observed also in SMX, in the same study.

According to Topp *et al*. (2006) CAF is readily biodegradable in soils, but the rate of this process varies depending on the soil texture, temperature (at 12 or 4°C mineralization of CAF in a loam soil was negligible), and moisture. For example, it is expected that CAF may be less readily bioavailable in soils that have higher clay and silt contents (Topp *et al*., 2006).

2.1.4.5. Atenolol

Atenolol (ATN) is a cardio-selective beta-blocker for management of hypertension (high blood pressure), angina pectoris, cardiac arrhythmias and myocardial infarction (heart attack) (Astrazeneca, 2017).

ATN cannot be classified as readily biodegradable and it is not expected to significantly adsorb to sludge solids during wastewater treatment. ATN is also unlikely to be significantly adsorbed into sediments and is water soluble. Therefore, ATN is expected to enter the aquatic environment

following sewage treatment, being highly susceptible to extensive degradation in aquatic environments (Astrazeneca, 2017).

ATN shows a low potential for bioaccumulation, as indicated by its low lipophilicity (log K_{ow} =0.16), a low potential for exposure of the terrestrial compartment via sludge (log K_{oc}=2.17), and a low affinity for sorption to sediment (Küster *et al.,* 2009). In natural sandy aquifer material, a significant pH-dependence on sorption is observed (Schaffer *et al.,* 2012). Volatilization from moist or dry soil surfaces is not expected to be an important fate process due to the estimated Henry's Law constant.

Little is known about ATN fate in the soil. Koba *et al.,* (2016) studied ATN degradation in soil (including clay soil) in an attempt to understand pharmaceuticals behaviour in soil matrix under near natural conditions, concluding that after 61 days this compound was almost completely degraded. Hu *et al.,* (2015) studied the adsorption of ATN on kaolinite (a clay mineral of low surface charge) at different conditions (e.g. solution pH, ionic strength, and temperature conditions) and compound concentration. The results showed ATN adsorption was almost instantaneous, suggesting a surface adsorption. The increase in ionic strength of the solution drastically reduced ATN uptake on kaolinite, and under solution pH below 5 or above 10 ATN adsorption was significantly reduced.

2.2. Electrokinetic process

2.2.1. Process overview

Electrokinetic (EK) remediation is also referred as electrochemical, electroremediation and other such terms in the published literature. A typical schematic *in situ* EK system is shown in Figure 2.4. The contaminated area is surrounded with a set of electrodes, possibly contained in wells or drains filed with a liquid electrolyte, then a low level direct current (DC), in the order of mA/cm^2, or a low potential gradient, in the order of V/cm, is applied (Akar and Alshawabkeh, 1993; Reddy and Cameselle, 2009). An electric field is formed inducing specific processes of transport, transfer and transformation. As a result, contaminants are mobilized and transported towards the electrodes (Reddy and Cameselle, 2009).

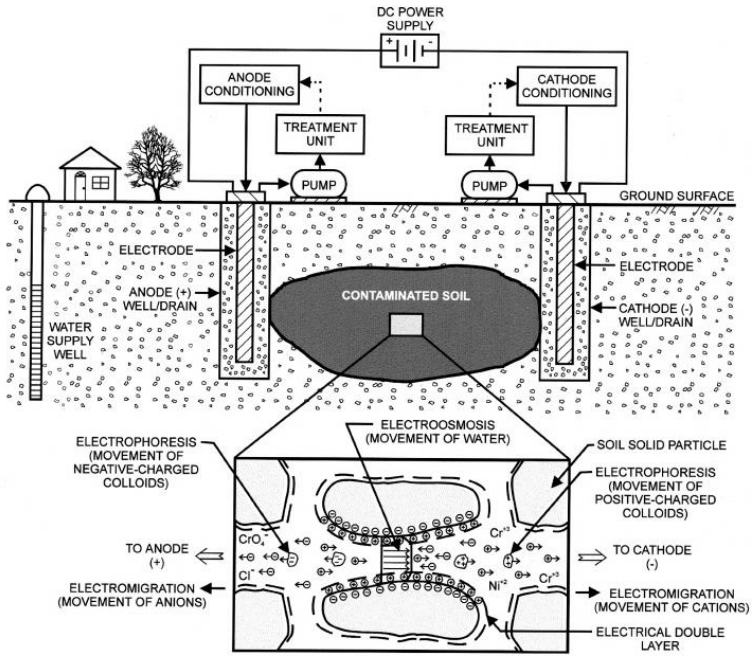


Figure 2.3. Schematic representation of electrokinetic *in situ* remediation system and main mechanisms (from Reddy and Cameselle, 2009).

The principle of electrokinetic remediation is to affect the transportation of contaminants allowing their removal, degradation, stabilization or immobilization from the contaminated matrix (Reddy and Cameselle, 2009; Pham and Sillanpää, 2015). Three main mechanisms are responsible for this mobilization, namely, electroosmosis, electromigration and electrophoresis. These mechanisms force the aqueous phase and ions to desorb from the porous surfaces and migrate towards the anode or the cathodes, depending on the speciation (Acar and Alshawabkeh, 1993; Acar *et al*., 1995). The soils for which EK is more efficient are those having clay minerals with high cation exchange capacity, low valency exchange cations, high surface charge density, and high surface area (Ribeiro *et al.,* 2015). These are the characteristics presented by clay soils. The efficacy of this remediation process depends on the characteristics of the contaminated media, such as buffer capacity, mineralogy and organic matter content (Virkutyte *et al.*, 2002; Reddy and Cameselle, 2009).

2.2.2. Electrokinetic transport and transfer processes

The transport of contaminants and water through the contaminated media towards the electrodes is due to the following, already referred, mechanisms: electroosmosis, electromigration and electrophoresis.

Electroosmosis is the movement of pore water (containing ionic and non-ionic species) relative to the stationary soil mass (fluid conduit) under the influence of an imposed electric field. This is known as electroosmotic flow (EOF). Generally, soil pores have negatively charged surfaces, and when exposed to a fluid the positive ions in solution, will be attracted to the negatively charged

soil surface, this region is termed ‘diffuse double layer’. Once an electric potential is applied this diffuse layer of cations around the soil particles is dragged and will cause the movement of the EOF toward the cathode soil compartment (Niroumand *et al.*, 2012; Yeung *et al.*, 1997; Virkutyte *et al.*, 2002), due to the net flow of cations. The parameter overriding the electroosmotic flow in a soil mass is defined by an empirical relation:

$$Q_e = k_e \times E \tag{2.1}$$

where Q_e is the velocity of electroosmotic flow (m/s), k_e is the coefficient of electroosmotic permeability (or electroosmotic permeability) ($m^2/(s{\cdot}V)$), and E is the electrical field intensity (V/m). It indicates that the velocity of water flow induced by electroosmosis is proportional to the electroosmotic permeability (Shang, 1997).

The Helmholtz–Smoluchowski theory, commonly accepted to interpret electroosmosis in soils says that the electrical force causes water movement in a liquid filled capillary. The electroosmotic permeability is derived based on the balance of the electrical and frictional forces between water and the wall of the capillary and is represented by Equation (2.2) (Shang 1997):

$$\mathrm{ke} = \frac{\mathrm{nE_w}}{\mu}\,\zeta \tag{2.2}$$

where n is the porosity of soil (dimensionless), E_w is the permittivity of pore water (F/m), μ is the viscosity of water ($N{\cdot}s/m^2$), and ζ is the zeta potential (V). The Helmholtz–Smoluchowski model suggests that the electroosmotic permeability is independent of the pore size, distribution or the presence of macro pores (Shang 1997). The effectiveness of the inducting motion is dependent of the conduit size (Acar and Alshawabkeh, 1993). Electroosmosis is best effective in fine-grained soils with low permeability, smaller conduits enable electrical double layers of small sizes to be effective, as the conduit size gets bigger the effectiveness of electroosmosis rapidly decreases (Virkutyte *et al.*, 2002).

The soil mass between the electrodes is treated in the same way and the whole bulk fluid moves at the same rate as the cation double layer (Pham and Sillanpää, 2015). Electroosmosis provides uniform pore water movement in most types of soil (Pham and Sillanpää, 2015), and facilitates advective transport of the solubilized contaminants toward the electrodes (Reddy and Cameselle, 2009). Its efficiency is defined as the quantity of water moved per unit of electricity (Ribeiro *et al.,* 2015). Still, water-saturated silts and low activity clays have the highest electroosmotic permeability, due to a high surface charge density, the zeta potential is typically negative (Acar *et al.,* 1993, 1995; Probstein and Hicks, 1993). Consequently, these types of soil show maximum electroosmotic flow and a higher ability to remove soluble organics (Probstein and Hicks, 1993).

Electromigration, also known as ionic migration, is the movement of dissolved ions and any other soluble charged species, available in the pore fluid towards the electrode of opposite charge. Induced with an applied DC electric field, the attraction and repulsion forces act, anions move towards the anode and cations towards the cathode (Virkutyte *et al.*, 2002; Niroumand *et al.*, 2012). The degree of electromigration depends on the mobility of the ionic species. The ionic

mobility is defined as the velocity of the ionic species under the effect of a unit electric field (Reddy and Cameselle, 2009). The movement of the ions in a liquid phase through a porous material is not linear, as it would be in a solution, here they must circumvent the particles or air-filled voids that obstruct their migration and go along the tortuous pores (Ribeiro *et al.,* 2015), known as tortuosity factor. Essentially, the reach of electromigration of a given ion depends on the conductivity of the soil, soil porosity, pH gradient, applied electric potential, initial concentration of the specific ion and the presence of competitive ions (Reddy and Cameselle, 2009). The electromigration transport is given by (Ribeiro and Rodríguez-Maroto, 2006):

$$J_m = -u \times c\Phi_e \tag{2.3}$$

where u and c represents the ionic mobility and concentration of species and Φ_e the gradient of electric potential.

The current efficiency of electromigration of a given ionic species is expressed as the proportion of electrical charge carried by the species of interest, relative to the amount of charge carried by all charged species in solution (Ribeiro and Rodríguez-Maroto, 2006), and is the major process of transport for polar organic molecules, ionic metals, ionic micelles and colloidal electrolytes. Electromigration is also part of the transport of hydrogen and hydroxyl ions generated near the electrodes due to water electrolysis reactions.

At lower concentrations of ionic species electroosmosis is the dominant process in EK, where soluble organic compounds are the target (Reddy and Cameselle, 2009). The relative contribution of electroosmosis and ion migration to the total mass transport varies for different soil types, water content, types of species, pore fluid concentration, and processing conditions (Acar and Alshawabkeh, 1993).

Electrophoresis is the transport of dispersed charged particles (cationic or anionic surfactant micelles, microorganisms, colloids, clay particles and organic particles) and bound contaminants relative to the stationary pore fluid under the influence of a spatially uniform electrical field (Niroumand *et al.*, 2012).

Compared to electromigration and electroosmosis, mass transport by electrophoresis is negligible in soil systems of low permeability such as clay, silty-clay and clay-loam. However, mass transport by electrophoresis may become significant in soil suspension systems and it is the mechanism for the transportation of biocolloids (including bacteria) and micelles (Reddy and Cameselle, 2009).

Electrokinetic treatment depends on some other interacting mechanisms, including diffusion, which is the movement of species under a chemical concentration gradient generated by ion migration and electroosmosis, is most present when the acidic and alkaline fronts, generated by electrolysis of water, meet (Ribeiro *et al.,* 2015) acting in the same direction of the acid front, towards the cathode; advection, caused by electroosmotic flow or any externally applied or internally generated hydraulic potential differences (Virkutyte *et al.*, 2002).

The DC electric field imposed on a system containing charged particles (e.g. a moist contaminated soil) induce simultaneous reactions other than the three main mass transport phenomena. One of the major processes is water electrolysis. This electron transfer reaction is based in the decomposition of water, which generates oxygen gas and hydrogen ions (H^+) due to oxidation at the anode and hydrogen gas and hydroxyl (OH^-) ions due to reduction at the cathode (Reddy and Cameselle, 2009) according to equations (2.4 – 2.5).

At the anode:

$$2H_2O \rightarrow O_{2(g)} + 4H^+ + 4e^- \quad (2.4)$$

At the cathode:

$$2H_2O + 2e^- \rightarrow 2OH^- + H_{2(g)} \quad (2.5)$$

The species input into the system at the electrodes and the species in the pore fluid will be transported across the soil by conduction phenomena. According to Acar *et al.* (1995), protons (H^+) are about twice as mobile as hydroxyl (OH^-), therefore the protons dominate the system and an acid front moves across the soil until it meets the hydroxyl front in a zone near the cathode where the ions may recombine to generate water.

Changes in soil pH start to show as a function of time and space (Yeung and Gu, 2011). The acid front created at the anode, by hydrogen ions production, decrease the pH near it, this front is carried towards the cathode by electromigration, diffusion, and pore fluid advection, desorbing an important amount of contaminants during the process (Guedes 2015; Ribeiro *et al.,* 2015). This effect not always means significant changes in soil acidification as it depends strongly on the characteristic of the soil. The migration of the protons may be hindered, particularly if the soil has a relatively high buffering capacity (Reddy and Cameselle, 2009). It is found that in high acid buffering soils, pH is not lowered near the anode due to buffering of the acid produced at the anode by carbonates present in the soil, but pH increases near the cathode as OH^- ions migrate easily (Reddy and Cameselle. 2009).

An alkaline front is formed by electrolysis that leads to a rapid increase in the hydroxide ion concentration, which in turn causes an increase in the pH near the cathode. This front is mobilized towards the anode by electromigration and diffusion (Virkutyte *et al.*, 2002; Guedes, 2015). This front has the potential to precipitate the ionic contaminants within the soil, if the electrical resistance increases drastically it may interfere negatively in the remediation process, by inducing a counteract front impeding the removal of contaminants (Yeung and Gu, 2011; Ribeiro *et al.,* 2015). As these two fronts meet, a rapid transition from low to high pH occurs.

Variations on soil pH depend upon the extent of transport of hydrogen and hydroxyl ions, as well as the geochemical characteristics of the soil. Reactions like absorption-desorption, chemical speciation, degradation and dissolution-precipitation of the contaminants are greatly affected by

electrolysis (Acar and Alshawabkeh, 1993). Additionally, soil pH changes affect the contaminant migration which may become stationary, and the magnitude and direction of the EOF which is decisive in the removal of non-charged organic contaminants (Yeung and Gu, 2011). Another important consequence of these acid and base fronts creation is on the microbial biota present in soil. These microorganisms, on which the biodegradation process depends, may suffer negative consequences when facing zones of the soil with extreme pH values, below 3 and above 9 or 10 (Juwarkar *et al.,* 2010).

2.2.3. Electrokinetic remediation strategies for soil

There are several remediation technologies for organic decontamination from soils, within two major treatment categories, namely biological and physicochemical (Pham and Sillanpää, 2015). The selection of proper soil remediation strategies is site-specific with various aspects for consideration. The electrokinetic processes have been applied in many different and complex situations from small scale to large scale remediation projects (Ribeiro *et al*., 2015).

Electrokinetic technology has been applied successfully in the remediation of inorganic contaminant and has been shown to be highly efficient in the removal of partially polar organic species. Volatile and soluble organic contaminants are quite easily removed by this technique (Pham and Sillanpää, 2015). However, hydrophobic and persistent organic compounds are difficult to remove from subsurface environments with traditional electrokinetic technology due to their low solubilities and slow desorption rates (Pham and Sillanpää, 2015). In these cases, in order to achieve an effective elimination or degradation of the persistent organic pollutants from soils, their solubility has to be enhanced (Cameselle and Reddy, 2012). Also, the combination with other processes and various operation modes is known to enhance decontamination Figure 2.4 outlines different electrokinetic processes for organic contaminated soil remediation.

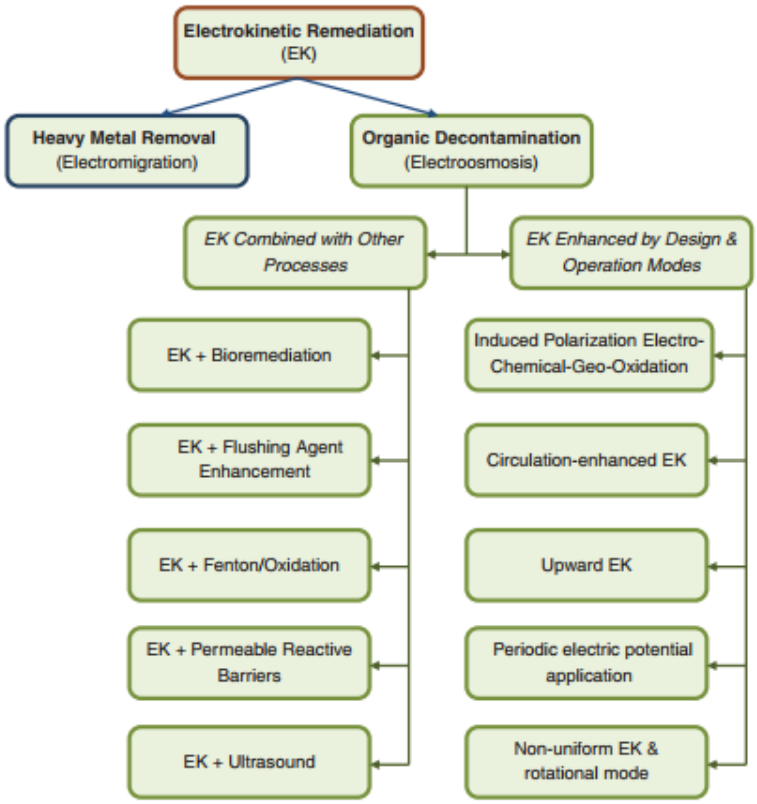


Figure 2.4. Electrokinetic remediation processes for organic decontamination (Pham and Sillanpää, 2015).

2.2.3.1. EK-Bioremediation

To achieve substantial biodegradation, microorganisms must be in contact with bioavailable contaminants, and this may require microbial movement. This is of great importance as soil bacteria are commonly immobilized *in situ* (attached to the surface in soil particles) turning bacterial transport inefficient in many soils if it is combined with a low hydraulic conductivity in soil micropores (Wick, 2009).

Electrokinetic bioremediation technology's main goal is to make compounds, nutrients, and electron acceptors bioavailable. Electrophoresis carries bacteria and charged particles to the positive electrode; nutrients and charged substances electromigrate according to the opposite charges they hold; and electroosmosis transports bacteria, contaminants, nutrients and electron acceptors towards the negative electrode (Wick, 2009).

Soil bacteria are like a colloid with a surface charge, able to move under DC field trough electroosmosis (dominant process in sands, sandy silts or sandy clays) or electromigration (dominant process in stiff clays and mixed clays) (Cauwenberghe, 1997; Cameselle *et al.,* 2013). With some substances traveling in opposite directions (i.e. EOF may create a flux counter to that of electromigration or electrophoresis) and others in the same direction, the probability of contact between substances through EK dispersion increases, consequently, achieving optimal

bioavailability and increasing the biotransformation rates (Wick, 2009). This is particularly important in fine-grained soils (e.g. clays) where hydraulic conductivity is extremely small.

Electrokinetic process combined with bioremediation can be economic viable because it does not require additional external microorganisms, and nutrient costs are reduced once their application can be uniformly dispersed over the soil contaminated volume or directed at a specific location. Still, there are some limitations to this process, including restriction of microbial population growth due to concentration of organic pollutants above the toxic threshold limits and, inhibition of the biodegradation process due to possible generation of by-products caused by organic pollutants degradation (Cauwenberghe, 1997; Virkutyte *et al.*, 2002). Also, the capacity of a habitat to deliver a compound will depend on the physical state of the chemical (eg. Dissolved or sorbed), its physical characteristics (hydrophobicity, effective diffusivity), its spatial distribution relative to microorganisms (bioavailable concentration/bioaccessible fraction), its EK transport and type of organisms involved.

2.2.3.2. Periodic electric potential application

Periodic electric potential experiments are found to result in sustained EOF and higher removal efficiency (Reddy and Saichek, 2004).

Reddy and Saichek (2004) hypothesised that by applying the electric potential in a periodic mode, or disconnecting the voltage periodically, would increase micellar solubilization and enhance EK efficiency. Studies were conducted to determine the contaminant mass removal by using a periodic voltage application. The voltage was applied according to a cycle of five days of continuous application followed by two days of ‘‘down time,’’ when the voltage was not applied. The periodic voltage effects were evaluated by performing four different bench-scale EK tests conducted using low voltage and high buffering (1.0 VDC/cm and 0.1 M NaOH), as well as high voltage and low buffering conditions (2.0 V/cm and 0.01 M NaOH). The results of these experiments confirmed positive effects of the periodic voltage application with which high amounts of contaminant removal can be achieved with higher voltage gradients (e.g. 2.0 V/cm). The high removal is attributed to the kinetic desorption and solubilization reactions and/or the pulsing mechanisms that were caused using this technique, like a pulsed electroosmotic flow, a pulsed surfactant molecular movement produced that generated a flushing action, increasing solubilization and physically mobilizing the PAHs, non-polar contaminants (Reddy and Saichek, 2004).

According to Cameselle and Reddy (2013), the periodic voltage application (1 V/cm; 5 days on, 2 days off) was used in an attempt to enhance the electroosmotic flow. In an experiment (referred as “periodic”), a periodic or pulsed voltage application of 1 VDC/cm was used. The periodicity consisted of a cycle of 5 days of continuous voltage application followed by 2 days of “down time.” The interval of time when the electric current is switched off allows contaminant transfer from the solid (soil) to the liquid phase (interstitial fluid), as well as diffusion of the contaminant through the

soil pores. Thus, the periodic voltage gradient application allows to achieve the dual objectives of generating high EOF while providing adequate time for mass transfer, diffusion, and contaminant removal. Experiments with periodic voltage application, showed a slightly lower EOF than the experiment with continuous application of a constant voltage of 1 V/cm, which induce a significant EOF (Cameselle and Reddy, 2013). The periodic mode was found to be effective as compared to continuous application of electric potential. It also has the additional benefit of saving electric power consumption.

2.2.3.3. Periodic polarity reversal

Periodic polarity reversal is considered a non-uniform EK system (i.e. the strength and direction of the electric field are changing with the distances between a set of electrodes) is intended to repeatedly pass contaminants through a degradation zone, while enhancing the removal efficiency of pollutants, reduce remediation time, helps to diminish the possibility of non-uniform potential and pH jumps in the soil system and reduces electrodes precipitation (Cauwenberghe, 1997; Virkutyte *et al.*, 2002; Huang *et al.,* 2012). During treatment process, the migration of organic contaminants is simultaneously driven by electromigration and EOF, and the main influencing factors on their migration velocity and direction are soil pH and electrode reactions. As the periodic polarity reversal strategy involves applying an electric field during equivalent time on both directions, the electroosmotic transport process also occurs in both directions along the soil for the same period (Mena *et al.,* 2016a). Under the condition of sub-acidity and neutrality contaminants mainly migrate towards the cathode with EOF; however, when the pH is relatively high, the main migration mode is electromigration and the pollutants will move towards the anode, in this way, neutralization of the soils can be easily achieved (Huang *et al.,* 2012). Therefore, periodic polarity reversal may accelerate bioremediation by mixing organic pollutants and bacteria in soil.

Many authors studied these outcomes, such as Gray and Somogyi (1977), who suggested that electrode polarity reversal prevented the development of a pH gradient and a nonuniform electrochemical variation. This technique was studied as an alternative method to prevent excessive energy consumption and differential settlement, also by Chappell and Burton (1974), Wan and Mitchell (1976) and Kim and Han (2003).

Mena *et al.* (2016a) studied the optimization of the polarity reversal strategy for the synergistic combination of the EK and biological treatments, with the variation of intensity of the electric field (0.0 V/cm, 0.5 V/cm, 1.0 V/cm and 1.5 V/cm). They concluded that periodic changes in the polarity of an electric field has better results compared to electro-bioremediation. Soil pH and temperatures changes are kept within a suitable range compatible with the life of microorganisms. The application of the lowest electric fields resulted in low values of water transported by electroosmosis. Thus, the removal of nutrients from the soil due to the dragging with the water transported by the electroosmosis was lower than in the single electro-bioremediation technique.

However, it was considered that a nutrient replacement would be necessary. Hence, biological degradation was attenuated once extremes pH changes were also avoided by the periodic polarity reversal intervals, attaining an increase in microorganism's population. In this study, experiments with the highest values of electric field obtained better results at contaminant removal/degradation.

Harbottle *et al.* (2009) found out that in unsaturated soil, electrokinetics was induced significant a pH changes and when pH was controlled, using a regularly reversed electric field, moisture content increased. These were thought to hinder any electrokinetic enhancement of contaminant biodegradation. When both pH and moisture content were controlled by the same system, the recovery results indicated that the presence of the field had a positive effect on biodegradation of pentachlorophenol. Increased microbial activity and degradation of the contaminant were achieved. Negative impacts were found in experiments where pH or moisture content were not controlled, in the presence of a unidirectional field.

In order to avoid pH negative effects, polarity reversal intervals are applied because it avoids depletion of any nutrient and results in a proper pH distribution. Bi *et al.* (2011) articulated the polarity switching, eliminating significant pH variation from anode to cathode, but the conditions were still not favourable for plant growth compared to the control, especially with a longer period of electrical field application.

2.2.3.4. Induced polarization ElectroChemical GeoOxidation

ElectroChemical GeoOxidation process is considered the next generation in EK (Pham and Sillanpää, 2015). This geophysical process relies on the phenomena of Induced polarization naturally occurring conducting surfaces in soil and rock particles. Using a low-voltage, low-amperage alternating current or direct current passed between a set of electrodes driven into the ground (soil, sediment, sludge or groundwater) to address either organic and/or inorganic compounds. The electric field that is created induces redox reactions responsible for the decomposition of organic contaminants and/or the immobilization of inorganic constituents present in the contaminated matrix (Cauwenberghe, 1997). This technology does not require the use of catalysts for the redox reactions, benefiting the presence of natural catalysts, such as iron, magnesium, titanium and elemental carbon, that are present in almost all soils.

2.2.4. Strengths and limitations in the presence of organic contaminants

EK can be utilized for site remediation (*in situ*) under conditions where other remediation methods are normally limited. Facilitation on the recovery of ionic contaminants is one of the main characteristics of this remediation process, once pH shifts, ionic contaminants adsorbed in soil particles will desorb and be mobilized (Pham and Sillanpää, 2015). By applying an electric field instead of, for instance, strong acids, the electrolysis of water leads the contaminant removal,

thus the basic structure of the soil will remain controlled and its properties closer to the originals (Cauwenberghe, 1997). In fine-grain soils and/or low permeability (e.g. clay), hydraulic flow through fine pores is extremely limited, making these soils non-responsive to traditional technologies (e.g. soil flushing) (Cauwenberghe, 1997). Organic contaminants may be difficult to remove from soils. In some cases, if the contaminant is forced to migrate through a long and tortuous path, remediation process may not be completed, as stagnant zones may occur (Cauwenberghe, 1997).

All remediation techniques have their advantages and disadvantages, and Table 2.2 summarizes the strengths and limitations of the EK technique (Acar *et al.,* 1995; Cauwenberghe, 1997; Sharma and Reddy, 2004; Huang *et al.,* 2012; Guedes, 2015; Pham and Sillanpää, 2015).

Table 2.2. Strengths and limitations of the electrokinetic remediation process (Acar et al., 1995; Cauwenberghe, 1997; Sharma and Reddy, 2004; Huang et al., 2012; Guedes, 2015; Pham and Sillanpää, 2015)

Strengths	**Limitations**
Applicable both ex-situ and *in situ*, tough *in situ* has less land disruption favouring soil mild conditions	Limited solubility of contaminants in aqueous phase and weak desorption capacity from soil matrix. Necessity to apply enhancing solutions
Well suited for treating fine-grain or low permeability soils	Acidic condition can corrode some anode materials. Inert electrodes, such as carbon, graphite, or platinum, must be used so that no residue will be introduced into the treated soil mass
Versatile, can be used to enhance other treatment methods	Application of higher voltages results in process efficiency decreases. Excessive heat generated near the electrodes, may cause desiccation or cracking in the specimen
Substitute traditional technologies, because it achieves relatively uniform transport in inter-bedded clays and sands, even when the hydraulic conductivities vary by orders of magnitude	Some undesirable products (e.g., chlorine gas) may also be generated at the electrodes during the process because of electrolytic decomposition (redox) reactions of water
Shorting remediation time (no more than one month in the laboratory experiment)	Electrolysis reactions near the electrodes may cause changes in pH, possibly harming biodegradation process and change the solubility of the contaminants in the soil
Cost-effective (less expensive compared with using other traditional remediation technologies for treatment of per ton or cubic meter soil)	EK process is not efficient when the target ion concentration is low and non-target ion concentration is high, or when the target are non-polar organic contaminants
Removing organic contaminants from soils by direct EK technique: Immobilization and acidification of the soils near the anodes can be easily neutralized	Removal efficiency is significantly reduced if soil contains carbonates and hematite, as well as large gravel

2.2.5. Electrokinetics applied to PPCPs

Electrokinetic remediation technology has been applied in large scale for soils contaminated with heavy metals, other inorganic and organic pollutants. The latter, focusing in the removal of PAHs, chlorinated organic contaminants, chlorinated organic pesticides and herbicides from soil and others. It may be considered that the application of EK technique to remediate soils contaminated with PPCPs is still in the early stages, with few studied fulfilling this aim (Xuan *et al*. 2008; Xu *et al*. 2009; Yuan *et al*. 2013; Guedes *et al*., 2014; Ferreira *et al*., 2017; Yuan *et al*., 2017).

Guedes *et al*. (2014) studied EK remediation of six emerging organic contaminants considered endocrine disrupting agents, simulating an *ex situ* soil remediation at lab-scale. Two types of soils were tested (silty loam soil and sandy soil) in a closed 3 compartment EK reactor during a 4-day period, results showed that the electrokinetic movement of organic contaminants is mainly due to the EOF, and by controlling pH a better control over the mobilization of organic contaminants towards the cathode was attained, thus increasing the removal efficiency. At 10 mA, the silty loam soil (exp. B) pH ranged between 4.15 ± 0.12 at the anode and 7.65 ± 0.06 at the cathode end, and in the sandy soil (exp. F) from pH 3.95 ± 0.11 at the anode to 5.07 ± 0.15 at the cathode. At the end of all experiments the percentage of compounds degraded were between 52–66%. Concomitantly to other studies (Cameselle *et al*., 2013), Guedes *et al*. (2014) demonstrated that the soils characteristics will highly influence pH changes which in turn influences the EOF.

Ferreira *et al.* (2017) studied the efficiency of EK using soil suspension, by testing three cell schemes, 1 to 3 compartments (C) and the use of ion exchange membranes. The efficiency of contaminant removal after a period of 3 days, with a current density of 0.02 mA/cm^2, ranged between 44% and 100%. The 1 compartment cell showed to be the best option for homogeneous degradation rates of the contaminants under study, without significant soil pH variation since the beginning until the end (pH 5.1 ± 0.5, pH 5.5 ± 0.1, respectively). Compartmentalized cells showed compound mobilization to electrode compartment and pH variations from 3.55 to 4.74 (3C-cell) and a soil pH increase till 9.60 in the 2C-cell.

Yuan *et al*. (2017) studied the IBU degradation performance by EK coupled with RuO_2/Ni foam (RN) electrodes in a lab-scale cell system for 5-9 days. Results indicate that the degrading effect of EK in IBU is more evident than the removal effect, concluding that the remediation efficiency is highly dependent on the potential gradient, as it may abruptly enhance from 1 to 2 V/cm (remediation increased from 65.4 to 77.4%), but from 2 to 3 V/cm less improvement is noted (78.2%). A harsh pH change, ranging between 2.8 to 11.8 (anode-cathode, respectively) was observed. Among the removal mechanisms, electromigration was the most important for the mobilization of IBU. Their results showed that neither prolonging the treatment time nor increasing the electrode area could significantly enhance the IBU remediation efficiency. This demonstrated that the electrokinetic process coupled with binary metallic oxidation electrodes is a viable method for the remediation of IBU.

More recently Li *et al*. (2018) studied the removal of three antibiotics (tetracyclines) in soil using EK and a stationary cell. The average removal rates of the studied antibiotics were, after 7 days, between 34.5 and 39.5%; this was mainly attributed to direct or indirect electrochemical reactions as well as indigenous biological processes. The innovation on this study was that the fate of antibiotic-resistant bacteria and antibiotic resistance genes were also evaluated. The study concluded that, compared to the control without DC, the EK reduced the tetracycline resistance genes in a ratio between 12.4 and 61.2% (Li *et al*., 2018). These findings suggest that EK treatment is a promising technology for the removal of emerging contaminants such as antibiotics and more persistent ARGs in soil.

2.3. Analytical techniques

2.3.1. Solid phase extraction

Solid phase extraction (SPE) is a sample preparation technique most often used to prepare liquid samples and extract semi- or non-volatile analytes, but can also be used with solids that are pre-extracted into solvents. This sample technique enables the extraction, concentration, and clean-up of the analytes prior to their quantification (Sigma-Aldrich Co., 1998).

SPE is based on the partition of a solute between a mobile liquid phase (the matrix and various solvents) and a solid stationary phase. Many stationary phases have been developed, allowing more targeted extractions or adaptation for the extraction of a large number of chemicals of various types (Humbert *et al*., 2014).

The process provides samples, free of interfering matrix components, and concentrated enough for detection. A typical solid phase extraction involves five steps (Sigma-Aldrich Co., 1998):

1. Adsorbent selection;
2. Conditioning of the stationary phase and re-equilibration;
3. Sample loading (enrichment);
4. Remove unbound impurities to the sorbent (sorbent wash);
5. Elution step. The adsorbed target compounds are eluted in an organic solvent that leaves the retained impurities behind.

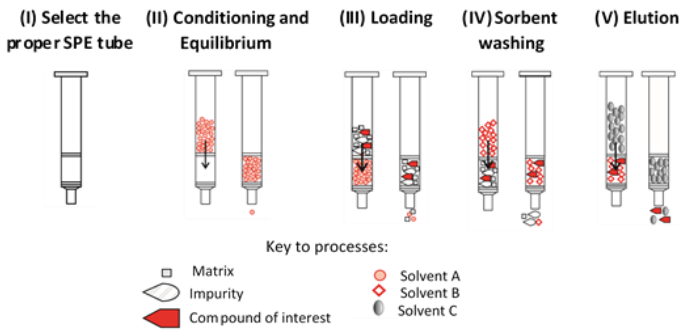


Figure 2.5. Schematic illustration of the basic steps of a solid-phase extraction (adapted from Sigma-Aldrich Co., 1998).

2.3.2. QuEChERS method

Quick Easy Cheap Effective Rugged and Safe (QuEChERS) method entails a few simple analytical steps, displayed in Figure 2.6, the procedure is based on a liquid partitioning with acetonitrile followed by a dispersive SPE clean-up with primary secondary amine (Anastassiades *et al*., 2003). The QuEChERS method simplifies the purification steps, and the major advantages of QuEChERS are its low solvent consumption (low cost), speed, high sample throughput and ability to obtain high recoveries for a wide spectrum of compounds (Vera *et al*., 2013).

Because of its flexibility and modifiable feature, QuEChERS technique became suitable not just for the determination of a wide range of chemical residues in food matrices, as originally did (Anastassiades *et al*., 2003), but also in matrices such as biological samples (Mattarozzi *et al*., 2016) and environmental samples (e.g. soils) (Padilla-Sánchez *et al*., 2010; Pinto *et al*., 2010).

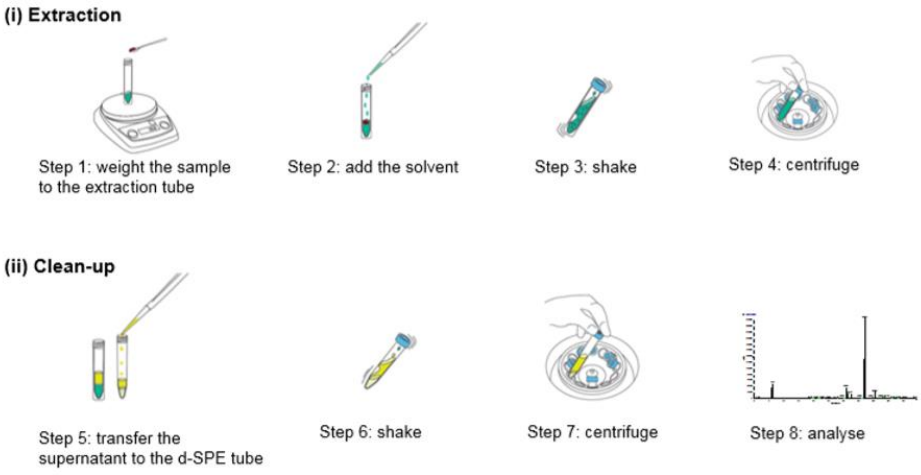


Figure 2.6. QuEChERS analytical procedure steps (from Guedes, 2015).

Samples are first extracted (Figure 2.6(i)) with an aqueous miscible solvent (e.g., acetonitrile) in the presence of high amounts of salts (e.g., magnesium sulfate), and/or buffering agents (e.g. citrate), causing the salting out effect which induce liquid phase separation (Vera *et al.,* 2013).

After the centrifugation, ideally the analytes of interest remain in the supernatant. This supernatant may contain excess of interferences such as organic acids, lipids, pigments, sugars, sterols, proteins and excess of water. In this case a clean-up (Figure 2.6(ii)) is required, using dispersive solid-phase extraction (d-SPE) a subsample of solvent extract is cleaned up (Vera *et al*., 2013). The d-SPE process consists in the addition, into an aliquot, of precise weights of the appropriate adsorbents (Table 2.3) to eliminate residual water and SPE adsorbents to extract interferences, retain the matrix components and enable the analytes of interest to stay in the acetonitrile phase after the centrifuge step.

Modifications to the original method can be made to ensure efficient extraction of pH dependent compounds (by using different buffers solutions) or addition of water to dry samples in order to obtain the necessary moisture (Pinto *et al*., 2010). Same is applied in the clean-up step, depending on the matrix components, the original dispersive SPE may be adapted or, according to Pinto *et al.* (2010) studies, it can be eliminated for soil samples, due to the absence of high content of lipid materials in the soil matrices. The latter are characterised by their mineral and organic matter fraction (manly composed by humic substances) (Vera *et al*., 2013).

Table 2.3. Salts and sorbents used to extract different types of interferences from sample in d-SPE (Phenomenex, 2012).

Adsorbents	**Purpose**
Magnesium sulfate ($MgSO_4$)	Removes excess water
Primary and secondary amine (PSA)	Removes sugars, fatty acids, organic acids, and anthocyanine pigments
C18 endcapped sorbent (C18E)	Removes fats, sterols and other non-polar interferences
Graphitized Carbon Black (GCB)*	Removes pigments, sterols, and non-polar interferences

* *Not for use with planar pesticides*

2.3.3. Chromatography

Chromatography is an analytical technique that has been classically defined as a separation process that is achieved by the distribution of substances between two phases, a stationary phase and a mobile phase. When the solutes distribute preferentially in the mobile phase they will move more rapidly through the systems than the ones distributed preferentially in the stationary phase. Thus, the solutes will elute in order of their increasing distribution coefficients with respect to the stationary phase (Ewing, 1997).

2.3.3.1. High-performance liquid chromatography

High-performance liquid chromatography (HPLC) has its origins in classical column chromatography. The separation of mixtures is carried out by passage of the sample through a column containing a stationary solid of a liquid mobile phase (with the help of a pressurized flow formed by a pump, increasing the separation velocities); components migrate through the column

at different rates due to different relative affinities for the stationary and mobile phases, based on adsorption, size or charge (Fifield and Kealey, 2000; Forgács and Cserháti, 2003).

This technique provides both qualitive and quantitative information: each compound in the mixture has its own retention time (i.e. the time from injection to top of peak, or, between the time they enter the chromatographic column and the time they exit), under a given set of conditions (Conklin, 2014, Meyer, 2004). Both area and height of each signal are proportional to the amount of the corresponding substance (Meyer, 2004).

An HPLC instrument require at least the elements seen in Figure 2.7:

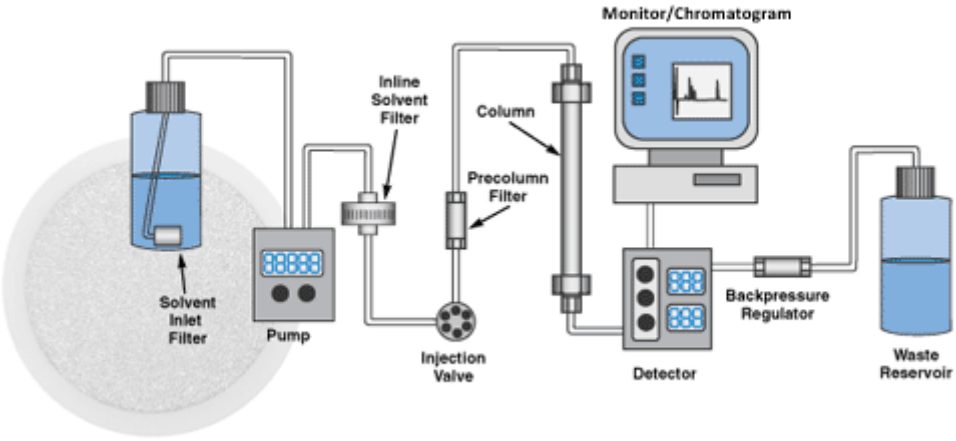


Figure 2.7. Schematic general configuration of a HPLC system components (adapted from Applied Porous Technologies, Inc., 2018)

A HPLC system can be divided into two different parts: one part is for separation, consisting of an injection device, a column and the mobile-phase delivery system, and the other part is for detection, including one or more detectors and a signal output device (Forgács and Cserháti, 2003).

A high-pressure pump takes the mobile phase from a reservoir through an injector. The mixture to be analysed is injected into the column, passes through the particle bed, (e.g. reverse-phase C18-packed) for component separation and, after separation, the separated mixture moves into the detectors, as a mobile phase, where the absorbance is monitored by one or multiple detectors (e.g. diode array detector (DAD) and fluorescence detectors (FLD)) and ends in a waste bottle (Forgács and Cserháti, 2003).

HPLC on soil matrix

Chromatography in its various forms is extremely important in the isolation and identification of complex mixtures found in the environment and in soil. It is applied to components that are isolated from soil by extraction. The extraction solution is important as it must be compatible with the chromatographic method and analyte detection method, for example, samples for HPLC must be soluble to some minimal extent in the eluent being used (Conklin, 2014).

Detection of components after separation is either by optical, spectrophotometric, or electrical methods. For HPLC, by chromatographing target analytes (i.e. through a calibration study, using standard compounds), a list of retention time (R_t) values can be prepared and used to "identify" the components in an unknown mixture (Conklin, 2014).

Identification by R_t values may not be sufficient for absolute identification. Therefore, true identification occurs when HPLC (or other chromatography techniques such gas chromatography (GC)) are coupled to a spectrometric and spectroscopic method such as mass spectrometry (i.e. GC-MS or LC-MS techniques), infrared spectrometry, or ultraviolet or visible (Conklin, 2014). These techniques may be of great use to proceed tentatively to identify a by-product.

3. MATERIALS AND METHODS

3.1. Chemicals and solvents

The organic compounds used in the present dissertation were SMX (analytical standard), IBU (≥ 98%), CAF (≥ 90%), ATN (≥ 98.5%) acquired from Sigma-Aldrich (Steinheim, Germany), TCS (≥ 97%) from Labesfal.

The water used for analyte extractions and analytical determinations was deionized and purified with a Milli-Q plus system from Millipore (Bedford, MA, USA). All used solvents were acquired from Sigma–Aldrich (Steinheim, Germany), Panreac (Barcelona, Spain), Merck (Darmstadt, Germany), Carlo Erba (USA), J.T.Baker (Germany) or Fluka (U.S.A). Solvents involved in the handle and process of the samples, particularly Methanol (MeOH), acetonitrile (ACN) and acetone (ACE), were acquired from Sigma–Aldrich, J.T.Baker (Germany) and Carlo Erba (USA) and, were gradient HPLC grade. Formic acid from Fluka was also HPLC grade. For the extraction method, magnesium sulfate (≥97%) from Sigma–Aldrich (Steinheim, Germany) was also used.

3.2. Soil sample

The soil samples were collected in October 2017 in São Nicolau, Santarém, Portugal (39°12'42.6"N 8°42'41.5"W), at an organic tomato field plantation (Figure 3.1), managed by Marco Nunes productions, that supplies biologic tomato for Compal, S.A. (broader designation for *Companhia de Conservas Alimentares, S.A.).*

A manual sampling method was applied for collecting surface soil samples between 0-15 cm. First, a manual removal of coarse elements, roots, and tomato remains from previous crops was carried out. Then 70 kg of soil were collected, between 0-15 cm depth, using a mattock and a stainless-steel shovel, guaranteeing that the depth measurement for the sample began at the top of the soil horizon.

The soil was then transported to *Instituto Nacional de Investigação Agrária e Veterinária, I.P., UEIS Sistemas Agrários e Florestais e Sanidade Vegetal Ambiente e Recursos Naturais, ex Estação Agronómica Nacional (Solos),* to their sample preparation laboratory. As the soil sample was already dried (no rain and high temperatures preceded the sampling), the sieving procedure was carried out immediately through a No. 10 (2.0 mm) IS Sieve to separate the coarse elements from the fine earth fraction (< 2 mm).

Then, to ensure that the sample was as representative as possible of the soil, the bulk were mixed, and 200 g where collected for soil characterization, at *ex Estação Agronómica Nacional (Solos)*, using its standard methods.

Figure 3.1. Location of the soil sampling and photograph of the field; São Nicolau, Santarém, Portugal (39°12'42.6"N 8°42'41.5"W).

3.3. Electrokinetic experiments

3.3.1. Electrokinetic experimental set-up

Experiments were performed in a rounded corner glass cell (140 x 140 mm), that included a perforated acrylic tray (130 x 130 mm) shown in Figure 3.2(a). This tray was developed at the FCT FabLab – Association of Digital Manufacturing Laboratories, using the laser CO_2 equipment (EPILOG MINI 25) to shape the acrylic plate (cutting parameters: 11 % of speed, 100% power and frequency at 5,000 Hz). Design and layouts were done with CAD and Graphic design software (AutoCAD 2016 and CorelDRAW 2017), and its dimensions are presented in Figure 3.2(b). The tray consisted of a plate with grid, and support pins. The plate was created by using Line and Fillet command, 130 x 130 mm square with a curve to suit the glass complex (radium: 30 mm). Then, the grid with squares of 5 x 5 mm was created and by using the rectangular array tool multiplied by a set of 18 columns x 18 rows with a specific spacing between object of 1 x 1 mm. Four tray support pins were created by using the Line command, same goes for the 4 support holes parallel at the grid, 5 x 2 mm.

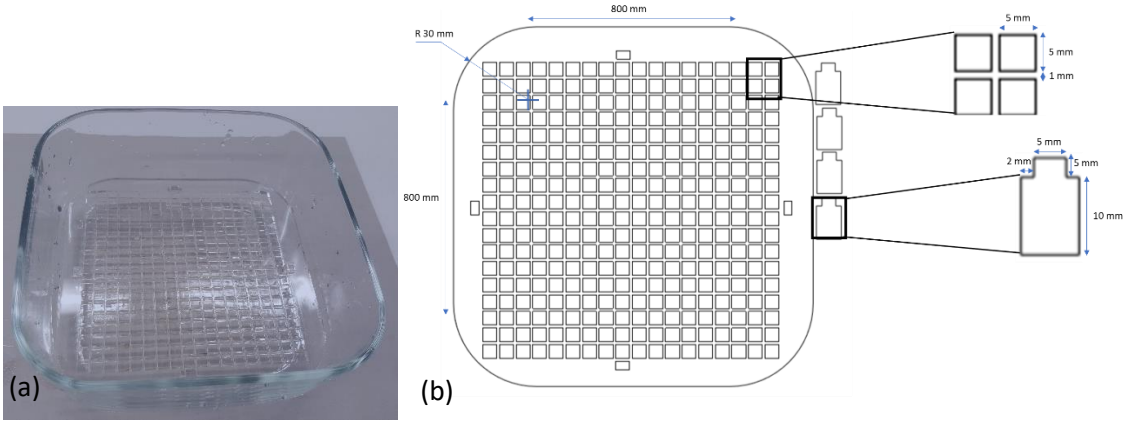


Figure 3.2. System used in the experiments: (a) microcosm with acrylic tray and (b) grid design details.

Four graphite rods were used as electrodes (99.9995% metals basis; length 80 mm, diameter 3 mm; AlfaAesar), two as anode and two as cathode. A power supply (Hewlett Packard E3612A, Palo Alto, USA) was used to maintain a constant DC. The cell scheme is presented in Figure 3.3(a).

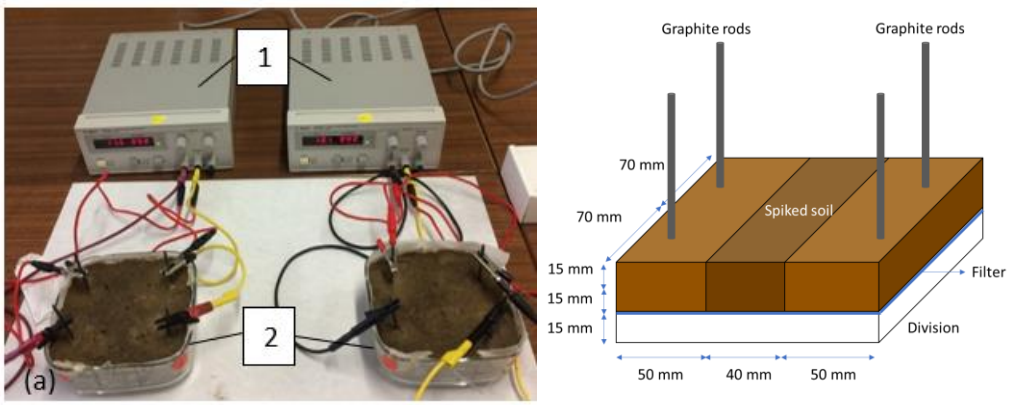


Figure 3.3. Microcosms scheme (a) Experimental set-up: 1) Power supply, 2) Compartment cells; (b) Compartmental divisions of the cell

3.3.2. Experimental design

In these experiments the main tested operating conditions were: current intensity (CI); ON/OFF switch intervals (Sw); reversed electro-polarization intervals (RP) according to Table 3.1. For CI mode, 100, 50 and 10 mA were tested for 24h ON in the case of CI-10 and 24h ON/OFF for CI-100 and CI-50. In Sw experiments, 6, 12 and 24h of ON/OFF intervals were tested (respectively, Sw-6h, Sw-12h and Sw-24h; Table 3.1). In the RP experiments 6, 12 and 24 h were also used in which the DC was applied for 6, 12 and 24h, then the DC was turned off for the same times, and when DC application re-started a polarization reversion was applied (RP-6h, RP-12h and RP-24h; Table 3.1). All experiments with DC were operated for a 7 day period.

Two control experiments were also performed. Experiment C-t0 was used as a reference test to assess contaminants' recoveries after system irrigation with the spiked water. Degradation percentages were evaluated according to the obtained recoveries. Another control was performed for 7 days without DC application, to assess natural attenuation (C-t7). All experiments, controls and EK ones, were carried out in duplicate.

The EK experiments were carried out at the mildest conditions as possible, meaning that experiments were conducted at room temperature with no pH control, with minimum interference in the parameters to maintain conditions as close as possible to a realistic situation. Still all microcosms were watered periodically to maintain the moisture of the soil. The microcosms were also protected from direct exposure to UV light.

In total, 600g of soil (dry weight) were placed in the top of the acrylic tray coated with filter paper to prevent soil leaking but allowing possible water leaching to pass through. Prior to the beginning of the experiments, the soil in the centre of the microcosm (Figure 3.3(b)), approximately 200g of soil, was irrigated with spiked deionized water containing till five contaminants: SMX, IBU, TCS, CAF, ATN, at 16 ppm. In experiment CI-50, the spiked solution was leaked on top of the whole soil surface (not only in the central compartment as the remaining experiments). The highest concentration (16 ppm) was used to allow to assess contaminants mobilization within the soil, even in cases of high degradation efficiencies, and to test the limits of the technique by using a highly contaminated matrix.

Table 3.1. Experimental parameters applied to each assay (n=2)

Experiment	PPCPs (N.º)	PPCPs (ppm)	Spiked mass (g)	Current (mA)	ON (h)	OFF (h)	Polarity reversal	Tested parameter
C-t0	5	16	200	0	-	-	-	Recovery
C-t7	5	16	200	0	-	-	-	Natural attenuation
CI-100[§]	3	8	200	100	24	-	-	Current intensity
CI-50[θ]	3	8	600	50	24	24	-	
CI-10	6	16	200	10	24	-	-	
Sw-6h	6	16	200	10	6	6	-	Switch ON/OFF
Sw-12h	5	16	200	10	12	12	-	
Sw-24h	5	16	200	10	24	24	-	
RP-6h	5	16	200	10	6	6	6	Reversed electro-polarization
RP-12h	5	16	200	10	12	12	12	
RP-24h	5	16	200	10	24	-	24	

[§] *Experiment aborted after 24h;* [θ] *Whole soil spiked; performed in ON/OFF mode*

Current intensity, voltage drop between the working electrodes, and soil temperature were monitored throughout the experiment.

At the end of the experiments, soil, filter paper and leached water were collected. The soil was divided as follows:

- horizontal cut - separating the top layer (α sections) from the bottom layer (β sections);
- two transversal cuts - separating left (L) centre (C) and right (R) sections;
- median cut - separating the sections from 1 to 6.

This allowed the attribution of an alphanumeric code, depicted in Figure 3.4. These divisions led to a total of 12 soil fractions, which ensured a proper analysis of the contaminant dispersion and/or degradation. In all soil sections, moisture content, pH, electric conductivity (EC) and organics contaminants concentration were determined according to the analytical procedures described in section 3.4.

The pH and EC were determined in the leached water. The filter paper and leached water were also extracted for organic contaminants determination according to the analytical procedures described in section 3.4.

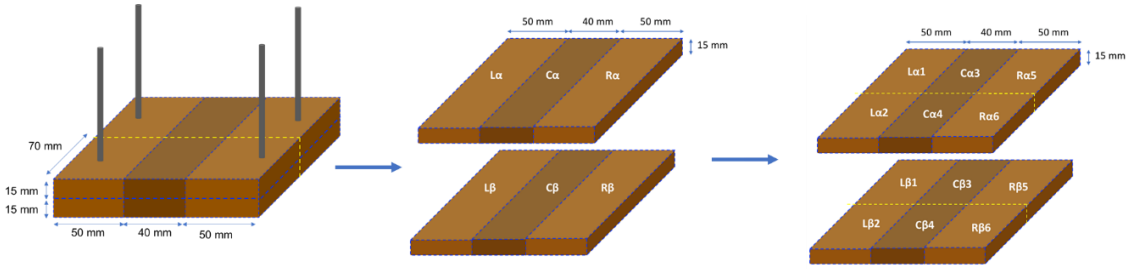


Figure 3.4. Soil division procedure at the end of each experiment.

3.4. Analytical methodologies

3.4.1. Humidity, pH and conductivity

The moisture was determined gravimetrically in soil samples. The gravimetric method calculates soil moisture by the difference between the fresh weight and dry weight of a given soil sample. Basically, a fresh weight subsample taken from each soil section for each experiment was weighed and placed into a goblet and then oven dried at 50 °C for at least 24h (till constant weight) and then left for 24h till room temperature. After samples are weighed (dry weight) and moisture content calculated.

The pH and conductivity were measured from the soil samples as follows: 2 g of the dried soil samples were suspended in 10 mL of deionized water, stirred for 1h using magnetic bars (approximately 100 bpm) allowing the sediment to settle for another hour. Measurement of the

parameters was made in the supernatant phase, within the next 3 h. The pH value was measured using a pH meter (Metrohm-Solitrode with Pt1000) and EC was measured using a conductivity meter (Horiba-LAQUAtwin).

3.4.2. Organic contaminants extraction

3.4.2.1. Soil

Organic contaminants concentration was determined using a fractionated serial extraction, QuEChERS method (adapted from Pinto *et al.,* 2010). Basically, 2.5 g of wet soil (collected immediately after the end of the experiments) were weighed into a 15 mL polypropylene centrifuge tube. Then 1.5 ml of deionized water were added to the soil and mixed in a Vortex for a few seconds (approx. 15 sec). After, 2.5 mL of acetonitrile were added and agitated vigorously in the Vortex for 1 min. Subsequently, 1 g $MgSO_4$ was added and immediately vigorously shaken (manually) for 6 seconds followed by vortex agitation for 30 seconds. Samples were then centrifuged at 5,000 rpm for 5 minutes (20 ºC). The supernatant (organic aliquot phase) was collected and filtrated through polytetrafluoroethylene syringes filters (previously passed through acetonitrile) and transferred to a vial. All samples were stored at −18 ºC until analysis. HPLC was used to analyse organic compounds present in each sample. All soil sections were extracted in triplicate.

3.4.2.2. Leached water

Leached water extraction was performed by SPE, using Sep-Pak C18, 100 mg, cartridges. The SPE cartridges were conditioned by washing with 3 × 1 mL of methanol, followed by re-equilibrium with 3 × 1 mL of Milli-Q water. For organic compounds enrichment, the samples were acidified to pH 2, using nitric acid, before extraction. The aqueous samples, maximum volume of 20 mL, were passed through the cartridge at a flow-rate of approx. 1 mL/min by applying a moderate vacuum. After that, the cartridges were dried for approx. 5 min by vacuum. The retained analytes were eluted sequentially with 1 mL of methanol. Samples were transferred to a vial and kept at −18 ºC until analysis.

3.4.2.3. Filter paper

At the end of the experiments, the filter paper was divided into lateral and bottom section and extracted three times by sonication (UAE). The extraction procedure was adapted from Ribeiro *et al.* (2011). Basically, the filter was extracted three times using 50 mL of acetone for 10 min. In order to remove the particulate matter, the extracts were filtered through MFV-5 glass microfiber filters (diameter of 47 mm, pore size of 0.5 µm) from Filter-Lab (Barcelona, Spain). All the extracts were collected, as one. Samples were then concentrated using 250 and 50 mL pear-shaped

evaporating flasks on a rotavapor, Büchi RE 111 (40 ºC /moderate vacuum) at 40 ºC till approximately 2 mL. Samples were transferred to a vial and kept at −18 ºC until HPLC analysis.

3.4.2.4. HPLC analysis

The determination of the organic compounds was performed by high performance liquid chromatography with diode array and fluorescence detectors (HPLC–DAD–FLD). HPLC analysis was performed on 1260 Infinity II LC Systems (Agilent technologies, USA) equipped with 1260 Infinity II Quaternary Pump (G7111B) with an operating pressure of up to 600 bar, up to 10 mL/min, and a 1260 vial sampler (G7129A). The diode array detector (G1315B) and the fluorescence detector (G1321A) were from Agilent 1100 Series. Analytes separation was carried out using Chromolith High Resolution RP-18 column with 100 mm x 4.6 mm from Merck (Darmstadt, Germany and an Onyx SecurityGuard C18 cartridges (5 mm × 4.6 mm) from Phenomenex (Torrance, USA) were used. The UV wavelength was set to scan from 220 nm to 400 nm. Target compounds were measured at 275 nm for CAF (channel DAD A), 282 nm for SMX and TCS (channel DAD B), and 220 for IBU and ATN (channel FLD A). All operations and data analysis were processed by the LC OpenLab software.

All HPLC runs were performed at a constant flow of 0.5 mL/min, in gradient mode. The two eluents used were composed of a given percentage of Mili-Q water/Acetonitrile/Formic acid (eluent A: 94.5/5/0.5; eluent B: 5/94.5/0.5). The formic acid was diluted 50% in water. All eluents were filtered through Nylon 66 membranes (pore size of 0.45 µm; Bellefonte, PA, USA). The gradient run was set to: 3 min 5% B, after 95% B until 20 min, then 97% B from 20-22 min, where it was held constant until 25 min, then to 5% B until 27 min. Post run equilibrium was carried for 2 min. The oven was set to 36 °C.

Prior analysis, 200 µL of sample extracts were mixed with 100 µL of eluent A (2:1) in a vial with insert and analysed.

3.4.3. Method validation

3.4.3.1. HPLC calibration curve and limits

Individual stock solutions of the organic compounds for calibration purposes were prepared at 8000 mg/L and 5000 mg/L in methanol:acetone (60:40, v:v) and stored at −18 ºC. Working solutions were prepared by the adequate mixture and dilution of the stock solutions into methanol:eluent A (2:1).

In total, 9 calibration solutions (1.0; 1.5; 2.0; 2.5; 5.0; 7.5; 10.0; 12.5; 15 ppm) were used. A statistical analysis (regression analysis - Linear regression) was done to determine the adjust between compound concentration and the respective compound area of the peak, the calibration

curves are explicit in Table 3.2. The regression equation used is defined by the formula $y = mx + b$, y represents the area, m the slope, x is the concentration of the compound (ppm) and b is the y-intercept.

Table 3.2. Calibration curves acquired for SMX, IBU, TCS, CAF, ATN

Compound	Calibration curve *	R^2
SMX	$y = 117.830x + 0.5981$	0.9998
IBU	$y = 10.985x + 0.1298$	0.9997
TCS	$y = 39.795x + 5.6251$	0.9992
CAF	$y = 80.367x + 1.0581$	0.9995
ATN	$y = 12.256x + 0.1472$	0.9995

**where y is the area (count) and x the concentration (ppm) of the compound in the sample*

The limit of detection (LD) and the limit of quantification (LQ) are the smallest amount of the compound that can be detected and quantified in the HPLC method. Table 3.3 shows the limits obtained for each compound. The LD were calculated through the residual standard deviation (S_x) multiplied by 3, for each compound. The LQ is the value of the LD multiplied by 3.

Table 3.3. Limit of detection and quantification of SMX, IBU, TCS, CAF, ATN

Compound	LD * (ppm)	LQ ** (ppm)
SMX	0.24	0.73
IBU	0.28	0.84
TCS	0.48	1.45
CAF	0.39	1.17
ATN	0.39	1.16

**LD=3s_X, where s_X is the residual standard deviation **LQ=3LD*

3.4.3.2. Methods recoveries and limits

Recovery assays were performed to validate the extraction method. The process of quantification is done by a comparison between the concentration that is expected (real value, i.e., known concentration added in the present sample) and the concentration that is obtained (obtained value). The exact method of calculation is determined by the following equation: $\text{Recovery } \% = \frac{obtained\ value - real\ value}{real\ value} * 100$. Samples not spiked were also extracted and the extract was spiked with the organic compounds under study (S_{samle}) to evaluate the matrix effect. Matrix effect was calculated by comparing the response obtained for the standards directly injected in the mobile phase ($S_{solvent}$) and the response for the same amount of standard added to the already extracted sample (S_{sample}).

Recoveries were between 80 and 120% in all cases. Matrix effect varies between -2 to +18%. Repeatability presented values between 8.3 and 29%, whereas intermediate precision was

between 5.4 and 16%. The method limit of quantification (MLQ) and detection (MLD) are presented in Table 3.4.

Table 3.4. Methods limits of detection and quantification of SMX, IBU, TCS, CAF, ATN.

Compound	QuEChERS (mg/kg d.w.)		SPE (mg/L)		UAE (mg/L)	
	MLD	MLQ	MLD	MLQ	MLD	MLQ
SMX	0.36	1.10	0.07	0.22	0.04	0.11
IBU	0.42	1.26	0.08	0.25	0.04	0.13
TCS	0.72	2.18	0.14	0.44	0.07	0.22
CAF	0.59	1.16	0.12	0.35	0.06	0.18
ATN	0.59	1.74	0.12	0.35	0.06	0.17

3.5. Statistical analysis

Statistically significant differences among samples for 5% level of significance (95% confidence interval, $p<0.05$) were evaluated through one-Way ANOVA Tukey's multiple comparisons test, using GraphPad Prism software (version prism 7).

For all experiments, pH, EC and moisture content, organic contaminants degradation percentages and distribution within the microcosm were comparatively examined, in order to validate the results obtained.

For the pH, EC, and moisture content the comparisons were carried out following three variables: (i) comparing to soil initial values (C-t0); same experiment, different soil sections; (iii) different experiments, same soil section.

Compounds degradation percentages were analysed in two variables: (i) same compound, different experiments; (ii) different compound, same experiment. Compounds mobilization percentages were analysed in three variables: (i) same compound, same experiment, different soil sections; (ii) same compound, different experiments, same soil section; (iii) different compounds, same experiment, same soil section. For statistical purposes, samples presenting values below MLD or MLQ (not detected, n.d.) were analysed has being zero.

Cases that did not have SD associated (e.g. one lost sample), were not considered while evaluating statistical differences.

4. RESULTS AND DISCUSSION

4.1. Soil characterisation

In this work the surface soil was collected from an organic tomato plantation. Soil characterization can be found in Table 4.1.The soil has a clay textural class. Clay soils usually contain a large surface area, a high water holding capacity, poor percolation and a high buffering capacity. They are usually very fertile soils and present a good nutrient bonding as they have a high cation exchange capacity, once clay minerals are negatively charged, then chemically active.

An initial chromatographic screening of the soil was carried out (n=6) and none of the here studied organic compounds were detected (<MLD).

Table 4.1. Soil characterization*

Parameter	**Value**
Particle size distribution (%)	
Clay (ϕ < 0.002 mm)	**61**
Silt (0.002 < ϕ < 0.02 mm)	**29**
Sand (0.02 < ϕ < 2 mm)	**10**
✓ **Textural class: Clay**	
Exchangeable cations (mg/kg)	
Ca	**2245**
Mg	**402**
Na	**688**
K	**250**
pH (H_2O)	**8.06**
Electrical conductivity (mS/cm)	**0.71**
Organic carbon (g/kg)	**27**
N organic (g/kg)	**1.48**

*Kindly provided by *Instituto Nacional de Investigação Agrária e Veterinária, I.P., UEIS Sistemas Agrários e Florestais e Sanidade Vegetal Ambiente e Recursos Naturais, ex Estação Agronómica Nacional (Solos).*

4.2. Soil spiking

The soil spiking method was drawn after three attempts. (i) Initially the soil spiking method aimed a simulation of a contaminated aged soil and for that, a mass of soil equivalent to the amount needed for the central compartment (about 200 g) was spiked with a 8 ppm solution (1:1 w:v; different spiking volumes were initially tested, data not shown). The soil was then placed in a mechanical shaking for 2h and then stored in the fridge for 3 days. After the 3 days, a microcosm was assembled with the spiked soil being used in the central compartment of the microcosm and

clean and dry soil was placed in the lateral compartments (experiment CI-100), Figure 4.1(a) presents the visual difference observed between lateral soil compartments and central compartment due to their water content differences. Due to this and having in mind that the final aim of the work being carried out at RESOLUTION Lab is to develop an in situ soil remediation process that decreases the risk of organic compounds uptake by crops, (ii) it was considered that by simulating the irrigation of an agricultural soil with a spiked solution on the beginning of the experiment it would allow to assess the viability of the applied remediation technology thus allowing the experimental set-up to be as close as possible to a real situation in which irrigation is carried out with water containing organic compounds, and so, in experiment CI-50 the spiked solution was leaked on top of the whole soil surface. (iii) Later, aiming at assessing contaminants mobilization due to EK, it was decided that for the following experiments the spiking procedure would be carried out only in the central compartment.

In all studies, and due to the high water holding capacity of clay soil, no leaching was observed.

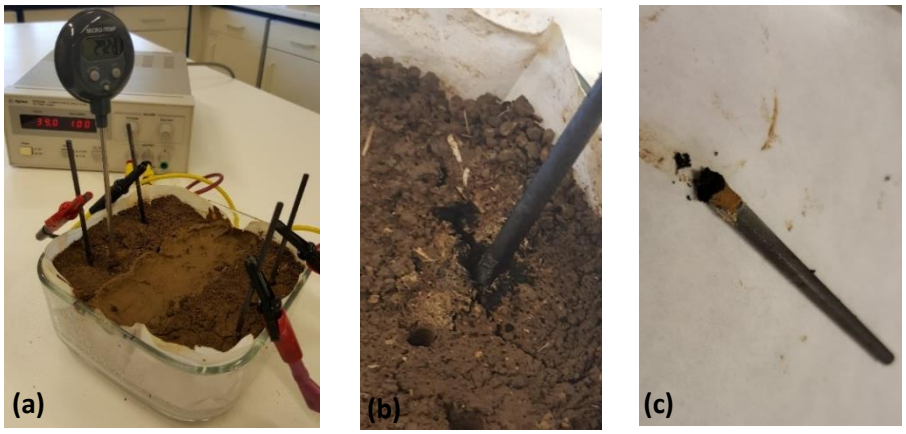


Figure 4.1. First trial EKR (CI-100) (a) microcosm at time zero (b) microcosm at time 24h (c) sample of a corroded electrode

4.3. General EK results

An initial experiment was performed using 100 mA (CI-100). After 24 hours all electrodes showed signs of corrosion and a steeply soil temperature increase (from 16 to 27.2 °C) was observed in the first 24 h (Figure 4.1). As a result, this experiment was aborted, and new current evaluations were performed at 50 and 10 mA.

In the CI-50 (50 mA) significant electrodes corrosion was still observed, together with a drying and slightly compaction of the soil around the anodes as it can be seen in Figure 4.2 (lighter soil portion around the electrodes of the left side of the figure). Due to the electrodes corrosion, it was decided to change the operating parameters of this experiment to an ON/OFF system, to asses if it would allow to increase electrode's life expectancy. Still, at the end of the experiments, the electrodes showed signs of extreme corrosion.

The formation of a circle of a reddish-brown was observed around the electrodes (anodes) after 1 day of the beginning of the experiments. This effect has already been observed in previous studies (Ferrarese and Andreottola, 2010). In addition to the change in the oxidation state of, probably, iron and other metals from the soil natural content, a further iron supply deriving from the anode corrosion may intensify the clogging around the electrodes (Röhrs *et al.*, 2002). To confirm this, a soil analysis should be performed for the quantification of metal species in all soil sections, e.g. quantification through Atomic Absorption Spectrometry.

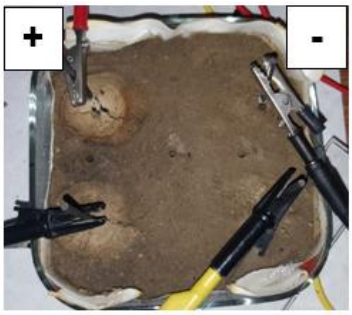


Figure 4.2. Experiment CI-50, Ion Fe formation and mobilization at the electrodes (anodes (+) in the left side; cathodes (-) in the right side)

The use of an electrode that is effective, commercially and widely available and at a reduced cost is part of the goal. Electrode durability was also included as an indicator to make the remediation process cost effective. Having this in mind, CI-50 experiment allowed to acknowledge the need to adjust DC intensity to lower values, due the persistent corrosion of the electrodes and an unwanted thermal increase effect. The thermal effect is less energy efficient and dries the soil faster. It is important to maintain a good soil moisture content along the days, as it highly influences EK efficiency. In the specific case of organic contaminants, their removal by EK from the soil is mostly carried out by electroosmosis (Guedes *et al.*, 2014). As observed by (Sivapullaiah *et al*., 2015) the low voltages (5 V) induces water flow initially, and a voltage increase to 10 V improves flow by almost 30 times. Still, prolonged application of higher voltages (e.g. 20 V) does not necessarily improve the electroosmotic flow, due to pH increase at cathode. Having all this in mind, a decision was made to use lower currents for the following experiments, and 10 mA (0.03 mA/cm^2) was adopted as the best option (Guedes *et al*., 2014).

4.4. pH

Without applying a DC, after a 7 day period the soil pH did not show significantly diverging trends contrasting to the natural pH value of the investigated soil ($pH_{C\text{-}t0}$ = 7.3±0.2), remaining between 7.3 and 8.0 (no statistical differences, p>0.05).

From all experiments the current intensity tests (CI-50 and CI-10) are the only assays that show statistical differences (p<0.05) from C-t0 and C-t7 (Table 4.2). In the soil sections Rα and Rβ of

CI-50 pH increased around 4.1 pH units, and in CI-10 Rα soil compartment it increased about 3.8 pH unit, being these final values statistically different from soil initial pH (p<0.05). The application of 50 mA also resulted in high pH changes in the soil, with a maximum pH amplitude occurring in CI-50 comparing to the application of 10 mA (CI-10). It resulted in a rapid acidification of the soil section L (anode compartment) and a major alkalinisation of the R section (cathode). CI-50 attained the most acidic conditions in the left compartment (Lα,β) corresponding to the anode section ($pH_{CI\text{-}50;L\alpha1}$=5.4 and $pH_{CI\text{-}50;L\beta1}$=5.2) followed by the central compartment (Cα,β) with pH closer to the initial, and the right compartment (Rα,β), that corresponds to the cathode section, presenting the most alkaline conditions ($pH_{CI\text{-}50;R\alpha6}$ = 12.2 and $pH_{CI\text{-}50;R\beta6}$ =11.6), see Table 4.2.

It would be expected that a higher current result in higher pH variations. Nonetheless, CI-50 and CI-10 had similar pH behaviour along the study, due the ON/OFF systems used in CI-50. Still, CI-10 pH presented less sharp variations, especially in β layer, and statistics prove that a jump in α layer, between L and R compartment still exist, with significant differences in most sections comparing to α5 and α6 (p<0.05).

By comparing CI-10 (running for 24h ON) and Sw system, a pattern is observed, as the longer the duration of current application, the greater is the change (increase/decrease) of soil pH. Therefore, between experiments with 10 mA, the pH changes are more pronounced when the current is kept permanently on until the end of the experiment (experiment CI-10). Comparing CI-50 and Sw-24h, the 10 mA ON/OFF also presented lower pH variations comparing to 50 mA ON/OFF used in CI-50, showing statistical differences in α5 section (p<0.05).

When Sw and RP systems were employed, pH variations turn out to be subtler not showing statistical differences comparing to soil initial pH (7.3±0.2). Comparing any Sw and RP experiments, no statistical differences were observed for soil pH (p>0.05).

All these pH changes can be explained by the electrolysis of water at the anode, that generates hydrogen ions, causing a soil pH decrease along the microcosms as the acid front starts to be driven towards the opposite electrode via electromigration and electroosmosis. And, at the cathode, the electrolysis of water generates hydroxyl ions and an alkaline front starts to be formed, moving through electromigration towards the anode end. In the central compartment, and because the ionic mobility of H^+ is 1.8 times higher than the mobility of OH^-, the pH fronts should meet in the soil at approximately two-thirds of the distance from the anode compartment where the ions may recombine to generate water and consequently maintaining pH close to neutral (Ribeiro and Rodríguez-Maroto, 2006). This was not observed in these experiments after 7 days. The systems were being irrigated with deionized water that presents a pH of 3.86±0.04, which might have slightly influenced the pH. Still, the more significant factor is the soil buffering capacity which may counteract the H^+ ions being formed through electrolysis. Lukman *et al*. (2013) stated that high pH environment might be explained by the presence of calcite in the soil minerals which increases its buffering capacity. It is expected that the carbonates will neutralize the H^+ ions generated at the anode which suppresses the development and migration of an acid front near the anode (Reddy *et al*., 1997; Lukman *et al.*, 2013).

Table 4.2. pH in the different soil sections for all experiments (experiment C-t0, pH_{CT0} = 7.3 ±0.2 [§])*.

		pH [1]								
Soil comp.	**Soil section**	**C-t7**	**CI-50**	**CI-10**	**Sw-6h**	**Sw-12h**	**Sw-24h**	**RP-6h**	**RP-12h**	**RP-24h**
Lα	**α1**	7.96	5.36 [A,c,d,f,g]	6.82 [h,i]	8.48 [a]	7.51	8.43 [a]	8.02	8.38 [a]	8.07 [a]
	α2	7.64	5.88 [B,c,d,f,g]	7.11 [h,i]	7.39	7.31[b]	7.94	7.35	8.74	7.95
Cα	**α3**	7.90	7.04 [c,d,f,g]	8.31 [h,i]	8.55	8.00	8.20	7.99	8.07	8.40
	α4	7.87	8.60 [a,b,c,d,e,g]	9.17	8.46	8.22	8.24	7.61	8.09	8.31
Rα	**α5**	7.79 [c,h]	11.50 [§,C]	11.3[§,H]	9.25	9.16	8.45 [c,h]	7.54 [c,h]	7.91 [c,h]	8.42 [c,h]
	α6	7.29 [d,i]	12.20 [§,D]	11.1[§,I]	8.12 [d,i]	9.06 [d]	8.14 [d,i]	8.17 [d,i]	8.05 [d,i]	9.13 [d]
Lβ	**β1**	7.57	5.23 [§,d,E,f,g]	6.94 [h,i]	8.08 [e]	7.42	8.45 [e]	8.13 [e]	8.10 [e]	8.42 [e]
	β2	7.62	6.39 [d,f,g]	7.09 [h,i]	7.43	7.44	8.42	7.48	8.40	7.92
Cβ	**β3**	7.93	7.09 [d,f]	8.37 [h,i]	8.49	8.07	8.31	7.89	8.05	8.48
	β4	7.69	8.14 [a,d,e,g]	8.12 [h,i]	8.48	7.87	8.27	7.35	8.26	8.41
Rβ	**β5**	7.80	10.40 [§,F]	9.10	8.68	8.58	8.10	8.30	7.99	8.51
	β6	7.81 [g]	11.60 [§,G]	9.19	9.27	8.56 [g]	7.98 [g]	7.85 [g]	7.96 [g]	8.77 [g]

Statistical analysis: Multiple comparisons were statistically performed at p<0.05 (95% confidence interval); data that has lowercase letters is compared statistically with the accordingly capital letter; [§] values are compared to C-t0 soil pH.

[1] SD values can be seen in Appendix 4

***** *Experiment CI-100 was aborted, results are not shown*

The pH changes affect soil surface properties such as ion exchange capacity, ion (cation and anion) adsorption capacity, and magnitude and sign of the zeta potential (Sivapullaiah *et al*., 2015), as well as they negatively affect the activity of microbial flora and the plants growing at the electrodes´ areas (Cang *et al.,* 2011, 2012).

One EK parameter that allows to avoid, or at least minimize, pH negative effects is the ON/OFF systems and the electro-polarization reversion, in defined time intervals. However, if EK is applied for longer periods of time than the 7 days here studied, the ON/OFF system could affect more the soil pH, and this should be taken into consideration. On the other hand, the RP systems should more easily counteract the pH changes (as we are reversing the reactions occurring in each electrode section), as well as the migration of other soil ions. For example, the migration of nutrients should be minimized, and RP system should make their distribution along the soil column more equitable (parameters not studied in this dissertation).

Comparing to other works, the pH variations here obtained follow the same patterns, and differences can be found when different EK set-ups are used. For example, Guedes *et al.* (2014) studied EK remediation in two types of soil, experiments were carried out in a laboratorial cell simulating an *ex situ* soil remediation (closed 3 chamber EK reactor). One of the soils presented a silty loam texture (with 53.4% clay) and, in experiment B, 10 mA without pH adjustment was performed, being these DC and soil conditions more similar to the experiment characteristics of the soil and parameters in the present dissertation. The pH had the same tendency, a decrease in the anode compartment and an increase at the cathode. But, as the experimental set up used by Guedes *et al*. (2014) is a closed system cell with electrolytes, the pH variations were higher, in the soil section closest to the anode, pH 4.15±0.12, comparing to the ones obtained in CI-10 (6.24 - 7.11)[1]. The pH variation obtained in CI-10 after 7 days are lower than the ones obtained in experiment B at the end of 4 days by Guedes *et al*. (2014). As referred in section 2.3.5, Guedes *et al*. (2014) study also showed that soils characteristics highly influence pH changes which in turn influences the EOF, and this should be accounted.

On the other hand, experiments conducted with an open system simulating *in situ* remediation, as studied in the present dissertation, with ON/OFF every 8h for 15 days reported lower pH variations, being the soil less acidic at the anode compartment and a more neutral soil pH at the cathode (Couto *et al.*, 2015). Comparing to the original soil pH of 6.58, the pH slightly decreased in the anode compartment (pH between 5.94 and 6.35) and increased in the cathode compartment (pH between 6.95 and 7.49).

Comparing to RP systems, concordant results were also achieved by Mena *et al.* (2016a), which applied daily polarity reversals and observed a “zig-zag” shape in the variation of the pH values corresponding with the daily change of the anodic and cathodic electrode, thus avoiding the extreme pH fronts throughout the soil.

[1] Guedes *et al.,* (2014) pH values were statistically compared with the pH data of the present study, using GraphPad Prism software, t-test at 95% confidence interval

4.5. Voltage drop and soil conductivity

In all experiments voltage drop varied between 6.7 and 10.7 V when 10 mA were applied and between 11.9 and 66.1 V when 50 mA were used. The application of a higher current (CI-50) presented, as expected, higher voltage than in experiments conducted with 10 mA, e.g. 17.7 V comparing to 7.7 on CI-10). This is a direct result of Ohm's law, the amount of electric current flowing through a conductor is directly proportional to the voltage imposed on it, accounting that initial soil EC (medium resistance) is the same in all experiments. Therefore, when the current increases so does voltage. In certain experiments (e.g. CI-50) a voltage increase was detected during the same application along each day, which might be explained by the water content on the soil that decreases along the 24h, as the soil dried due to room temperature or due to water migration (analysed in more detail in section 4.6). Therefore, the microcosm was irrigated every 24h to increase soil moisture and decrease system resistance. The other factor that affected voltage drop was related to the corrosion and damage of the graphite rods, which resulted in a circuit resistance increment, being this more obvious in the CI-50.

Table 4.3 shows the EC of all soil compartments. Experiment CI-50 showed the highest EC of all experiments in Rα6 section, 2.62 mS/cm, with statistical differences (p<0.05) compared to the initial EC of soil (at approximately 0.67±0.15 mS/m) and C-t7 (with no current applied) and every α6 section of the experiments with DC application.

As the experiments kept running, the resistance in the soil starts to increase due to the depletion of ions from the soil, especially on the central soil sections. Electrical conductivity of CI-50 and CI-10 variation presented the same pattern. High EC at Lα compartment, followed by a decrease in the Cα compartment and rising again in the Rα compartment. This may be explained by the generation of ions due to electrolysis reactions in the electrodes sections as well as to the electromigration towards the electrodes. This electromigration causes the EC decrease in the central compartments, although without statistical differences (p<0.05).

In general, and when no RP was performed, conductivity decreased from Lα compartment to Rα compartment as it was observed in Sw-12h experiment, Table 4.3. This might be explained by the generated ions at the electrodes. In the L sections of experiments of CI and Sw, anode compartments, more H^+ ions are produced, which consequently resulted in higher EC. On the other hand, the presence of OH^- might lower the conductivity, given the capability of forming compounds with other ions (Reddy *et al.,* 2011), as observed in R soil sections.

Table 4.3. Electric soil conductivity ($EC_{C\text{-}t0}$=0.67±0.15[§])

		Conductivity (mS/cm)[1]								
Soil comp.	**Soil section**	**C-t7**	**CI-50**	**CI-10**	**Sw-6h**	**Sw-12h**	**Sw-24h**	**RP-6h**	**RP-12h**	**RP-24h**
Lα	**α1**	0.72	1.46	1.55	1.05	1.13	0.81	0.58	0.76	0.71
	α2	0.73	1.02	1.54	1.38	1.35	1.15	0.43	1.03	1.12
Cα	**α3**	0.70	0.21 [a]	0.16	0.41	0.38	0.28	0.68	0.70	0.63
	α4	0.73	0.25 [a]	0.17	0.50	0.47	0.31	0.64	0.74	0.68
Rα	**α5**	0.71	0.84 [a]	0.84	0.27	0.29	1.03	0.75	0.51	0.50
	α6	0.69 [a]	2.62[§,A]	0.62 [a]	0.90 [a]	0.31 [a]	0.85 [a]	0.67 [a]	0.62 [a]	0.45 [a]
Lβ	**β1**	0.58	0.84 [a]	1.04	0.60	1.06	0.58	0.60	0.68	0.73
	β2	0.58	0.81 [a]	1.20	0.89	0.99	0.85	0.43	0.80	1.04
Cβ	**β3**	0.59	0.15 [a]	0.92	0.33	0.38	0.36	0.62	0.58	0.48
	β4	0.58	0.14 [a]	0.20	0.41	0.48	0.31	0.56	0.66	0.50
Rβ	**β5**	0.57	0.41 [a]	0.23	0.56	0.26	0.74	0.58	0.45	0.45
	β6	0.56	1.06	0.26	0.34	0.33	0.20	0.64	0.62	0.50

Statistical analysis: Multiple comparisons were statistically performed at p<0.05 (95% confidence interval); data that has lowercase letters is compared statistically with the accordingly capital letter; [§] values are compared to C-t0 soil EC.

[1] SD values can be seen in Appendix 5

***** *Experiment CI-100 was aborted, results are not shown*

The duration of each DC application also affected the EC. For example, when ON/OFF was performed for 6 and 12 hours (Sw-6h and Sw-12h, respectively), the longer periods attain higher changes in electrical conductivity, for instance variation from Lα compartment to Rα are $EC_{SW\text{-}12h}$= 1.09 to 0.29 mS/m and $EC_{SW\text{-}6h}$= 0.97 to 0.45 mS/m, respectively, although without statistical differences (p>0.05).

Results attained at experiments with periodic polarity reversal were more similar between soil sections, and closer to initial soil EC, due to the periodic change of the anode to cathode, and vice-versa.

4.6. Soil temperature and moisture content

Temperature was not controlled during the EK experiments, and a measurement of soil temperature was carried out during the experiments. Besides experiment CI-100 (as referred in section 4.2), no major temperature changes were observed in the soil. The majority of experiments were conducted with the soil temperature being very similar between all experiments, approx. 15 °C. In this study, temperature values did not exceed the optimal value for the development of microbial populations (Mena *et al.*, 2016a) and for the EK remediation to proceed without restrains, regardless the electric field applied. The uniform temperature allows a more efficient use of the energy. A soil saturated in moisture favours the transportation of current instead of the electric heating.

Due to EOF and soil drying along the experiments, moisture variations can occur when EK experiments are performed. Still, in the here tested conditions, no statistical differences were observed at end of the experiments (Table 4.4). This is a consequence of the irrigation that was performed every 24h. Still, the experiment conducted with 50 mA (CI-50) and the experiment conducted with 10 mA applied for 24h (CI-10), present a trend of moisture increase from the L to the R sections (anode to the cathode), being this a possible indication of EOF developing towards the cathode end. This trend is more obvious in the top layers (α). Still, no statistical differences were observed (p>0.05).

In experiments with longer durations higher differences may be expected if no irrigation is performed. In the experiments performed by Mena *et al.*, 2016a, moisture showed decreases in the central compartment, after two weeks under 1.5 V/cm with RP every 24h. Low moisture contents could affect EK remediation performance, by decreasing system conductivity, as well as possibly affect the biological communities in soil, thus decreasing biological remediation efficiencies (Mena *et al.*, 2016a). Therefore, moisture control of the soil (through periodic irrigation), as the one performed here, should be considered in the EK soil treatments. In all studies, and due to the high water holding capacity of clay soils, no leaching was observed.

Table 4.4. Moisture content in percentage for each experiment (Moisture content for C-t0 = 17.7±3.7%; C-t7 = 17.3±2.7%).

		Moisture content (%) [1]								
Soil comp.	**Soil section**	**C-t7**	**CI-50**	**CI-10**	**Sw-6h**	**Sw-12h**	**Sw-24h**	**RP-6h**	**RP-12h**	**RP-24h**
Lα	**α1**	17.9	12.1	14.6	15.5	16.6	20.4	20.0	22.4	14.5
	α2	18.1	12.7	14.4	12.8	16.1	20.8	20.5	21.9	13.1
Cα	**α3**	17.8	14.5	15.2	12.9 ^{B}	16.3	20.9	22.0 ^{b}	22.5 ^{b}	15.6
	α4	17.7	14.6	16.3	14.8	15.9	19.2	22.0 ^{d}	22.7 ^{d}	13.1 ^{D}
Rα	**α5**	17.1 ^{a}	16.6	18.3	15.4 ^{C}	19.0	24.7 ^{c}	18.5	22.8	16.5
	α6	17.3 ^{a}	15.5	18.4	14.9	17.1	21.4	19.4	22.4	15.6
Lβ	**β1**	26.3 ^{A}	16.5 ^{a}	15.0 ^{a}	15.9 ^{a}	15.7 ^{a}	20.5	15.7	19.0 ^{a}	16.0 ^{a}
	β2	16.7 ^{a}	14.3	15.4	13.6	16.1	19.0	19.2	19.9	14.7
Cβ	**β3**	17.0 ^{a}	15.0	15.1	13.1	15.5	18.0	17.5	20.8	16.5
	β4	16.3 ^{a}	14.6	15.6	15.2	15.8	20.4	17.0	20.9	14.4
Rβ	**β5**	16.6 ^{a}	17.5	17.1	15.7	17.1	18.0	15.4	21.6	18.0
	β6	16.3 ^{a}	17.9	17.6	15.7	15.1	21.5 ^{a}	15 .0	20.5	17.2

Statistical analysis: Multiple comparisons were statistically performed at p<0.05 (95% confidence interval); data that has lowercase letters is compared statistically with the accordingly capital letter; § values are compared to C-t0 soil EC.

[1] SD values can be seen in Appendix 6

***** *Experiment CI-100 was aborted, results are not shown*

4.7. Organic contaminants removal

4.7.1. Total degradation

The amount of contaminants not detected, comparing to the initial concentrations, was considered as degraded. The degradation percentage of organic compounds in all experiments can be seen in Table 4.5 (statistical differences to $p<0.05$ are presented in Appendix 7 and 8).

C-t7 was done to assess the natural attenuation in 7 days. The test was performed with the same setup used for the other experiments but without current application. Between all compounds SMX was more susceptible to natural attenuation, 64±8%, followed by IBU with 49±6%, ATN with 47±8%, TCS with 20±8% and, CAF with 6±0%. The degradation of TCS and CAF in C-t7 presented statistically significant differences ($p<0.0001$, $p<0.0002$), comparing to the other compounds (Appendix 7). Natural attenuation is generally described as a range of physical and biological processes. This mechanism can be classified as (i) destructive attenuation, which include biodegradation (where microorganisms break down target substances) and chemical reactions, and ii) non-destructive attenuation, including sorption, dilution and volatilization (EPA, 2012). In account to the compounds studied, volatilization from moist soil surfaces was not expected given compounds estimated Henry's Law constant. Also, photodegradation is not a relevant fate process since the experiments were conducted in indoor circumstances and protected from direct UV radiation. Therefore, biodegradation is considered as being the main mechanism responsible for organic compounds degradation of the parent compound (Kimura *et al*., 2007; Xuan *et al*. 2008; Robinson and Hellou 2009; Xu *et at.,* 2009b).

When EK was applied, different degradation behaviours were observed among the EK experiments according to the applied conditions. In all EK experiments the degradation trend was similar to the C-t7, SMX > IBU ≥ ATN > TCS > CAF.

When the spiking was performed in the whole cell compartments, CI-50, high remediation values for SMX and IBU were achieved, up to 97±8% and 61±5% were degraded, respectively. TCS presented the lowest remediation of the three, with 34±5%.

When the spiking was performed in the central compartment, contaminants presented different degradation behaviours among them according to the different operating parameters tested. The constant application of 10 mA (CI-10), allowed to achieve the highest degradation values for SMX, ATN and TCS, 85±1%, 69±6% and 56±0%, respectively. CAF experienced better degradations in experiment Sw-12h, 36±9%, showing significant differences from all experiments ($p<0.05$) with the exception of CI-50. IBU does not show statistical significant degradation percentages among the different EK experiments, but its highest degradation using 10 mA was achieved in Sw-12h, 57±8%. The lowest degradation for SMX was attained in Sw-6h experiment, with 63±4%. IBU, CAF and ATN had the lowest degradation percentages in RP-6h, with significant difference ($p<0.05$). In RP-6h, IBU presented a degradation of 43±8%, ATN with 39±8% and CAF with no

degradation being observed. For TCS the worst operating parameters were the ones used in RP-12h system where no degradation was observed.

Table 4.5. Degradation percentages and standard deviations (mean ± SD) of the organic contaminants in all conducted experiments.

	Degradation (%)				
Experiment	**SMX**	**IBU**	**TCS**	**CAF**	**ATN**
C-t7	64 ± 8	49 ± 6	20 ± 8	6 ± 4	47 ± 8
CI-50	97 ± 8	61 ± 5	34 ± 5	*	*
CI-10	85 ± 1	47 ± 4	56 ± 0	13 ± 13	69 ± 6
Sw-6h	63 ± 4	45 ± 8	41 ± 4	7 ± 14	55 ± 2
Sw-12h	72 ± 10	57 ± 8	44 ± 3	36 ± 9	65 ± 1
Sw-24h	74 ± 6	55 ± 1	31 ± 1	7 ± 11	60 ± 6
RP-6h	64 ± 11	43 ± 8	21 ± 18	WD	39 ± 8
RP-12h	68 ± 6	51 ± 3	WD	WD	49 ± 11
RP-24h	70 ± 20	47 ± 7	1 ± 10	4 ± 9	44 ± 15

** CAF and ATN were not analysed in experiment CI-50*
WD – Without degradation

Comparing to natural attenuation, an increase in the degradation percentage was generally observed in the experiments in which CI and Sw were applied, using 10 mA (Figure 4.3). These differences were statistically significant for SMX in CI-10, for TCS in CI-10, Sw-6h, Sw-12h, for CAF in Sw-12h and ATN in CI-10 (p<0.05, for adjusted p values see Appendix 8). Still in some cases, the use of current decreased degradation of the compounds being this statistically significant for TCS in RP-12h (p>0.05).

The compounds with lowest biodegradation were, as referred before, TCS and CAF (C-t7, Table 4.5). By applying Sw system, TCS degradation doubled (in Sw-6h and Sw-12h) and CAF degradation increased by 30% in Sw-12h, with statistical relevance (p<0.05, Appendix 8). The ON/OFF system (Sw) presented better results comparing to electro-polarization reversal (RP) that showed to have a detrimental effect on the degradation of all compounds comparing to C-t7 (Figure 4.3). For example, TCS degradation in Sw-12h was improved by 24%, whereas when polarity reversion is applied less 25% of this compound was degraded (RP-12h), being this statistically different (p<0.0001). The change from Sw to RP showed to be particularly relevant for CAF, that showed the best degradation in Sw-12h (36±9%) and no degradation in RP-12h (Table 4.5; p<0.0001).

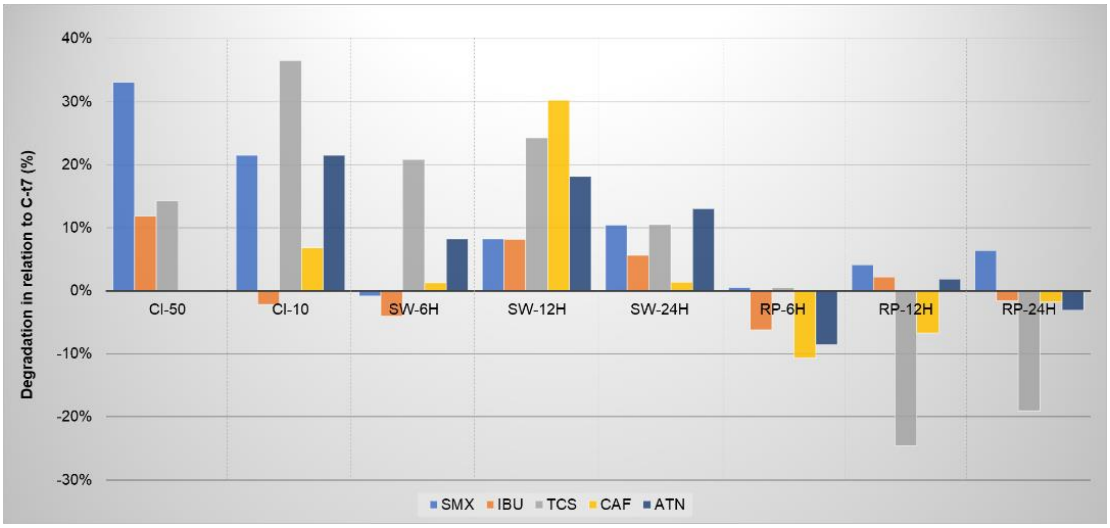


Figure 4.3. Percentage of compound degradation in relation to control experiment (C-t0). CAF and ATN were not analysed in experiment CI-50.

4.7.2. Organic compounds soil distribution

Figure 4.4 represent the mobilization profile of each compound at the end of the respective experiment. Compounds mobilizations percentages and respective RSD can be found in Appendix 9.

All experiments showed higher compound concentrations in the central compartment and higher mobilization of contaminants in layer α. This is due to the soil spiking procedure that was done in the central compartment and, as in fine-grained soils hydraulic conductivity is extremely small, it leads to an almost stagnant water in the nano- and micropores (Wick, 2009).

In C-t7, as no DC field was applied, it was to be expected that the central compartment (Cα and Cβ) exhibited the highest compound concentration. All compounds are found in residual concentrations at the L and R compartments (from 6 – 12%). Organic compounds' concentration in the L and R compartment suggests that there is dispersion, probably influenced by the small hydraulic mobility through the daily water irrigation, which dragged contamination. Another factor that may have influenced this dispersion is the division and sampling at the end of the experiments, as no physical separator was used between the L, C and R soil sections, a manual division was carried out, and operator error should be considered. The same should be accounted for the bottom soil section (β). In depth between 8 to 23% of organic compounds were detected in Cβ (Figure 4.4). SMX and IBU showed higher leaching capacity than the remaining contaminants. Presenting high concentrations in Cβ compartment than other organic compounds. This can be considered as a trend since this occur in all experiments (SMX concentration in layer β ranges between, 11 - 31% and IBU concentration at layer β between, 11 - 32%; whereas TCS concentration in layer β diverge between, 6 – 15%; and ATN concentration in layer β between, 5 - 9%, with statistical differences, $p<0.05$). Although CAF is the compound that presents the highest solubility and lowest log K_{ow} (2.16×10^4 mg/L and -0.07, respectively), it was not detected

in the β layer. Martínez-Hernández *et al*. (2016) evaluate the role of sorption and biodegradation in the removal of 5 organic compounds, having shown that CAF displayed the fastest initial sorption velocities (h = 2055 µg/kg/h) which may explain the here obtained results.

When an electric field is applied to the soil, organic compounds are expected to be solubilized and transported to the electrodes through several transport, transfer and transformation processes. Predominantly by electroosmosis but also through diffusion and electromigration, once the electric field promotes the electrolysis of water, H^+ form at the anode and move towards the cathode and OH^- ions formed at the cathode travel towards the anode, attracting as well other charged species/ions, as detailed in the literature.

Experience CI-50 was the only experiment in which the spiked solution was leaked on top of the total soil surface (not only in the central compartment as in the remaining experiments), having in common with other experiments the application of an electric field, though with higher current intensity. This generates a combination of differences that clearly affect the mobilization results and should be taken into account in the subsequent analysis. SMX and IBU presented the highest concentrations at the L compartment (a total of 65% and 92%, respectively and both without significant differences between layer α and β, but with significant differences between the two compounds, $p<0.05$) as for concentrations at the Cα and Rα, these compounds were below MLD. At the cathode end, lower concentrations are found, 22% (SMX, Rβ) and 3% (IBU, Rβ), although without statistical differences. RSD associated with these compounds are very low. TCS is more evenly distributed in the three compartments and in both layers (α, β), without statistical differences, giving a total of 38% at the L compartment (anode), 28% in the central compartment and 34% at the cathode. These differences may be explained by compounds different solubilities and pKa (Table 2.1). SMX and IBU present pKa (1.6/5.7 and 4.91, respectively) below soil pHs in all compartments (Table 4.2). Contrary, TCS has a pKa of 7.9, which is equal or higher than soil pH in the central and left compartments (Table 4.2). This means that SMX and IBU are mainly in their ionisable form which increases their solubility and facilitates their electromigration towards the anode compartment (Lα,β). Whereas TCS is protonated in the L and C compartments, mainly migrating towards the R compartment, where it may suffer deprotonation, thus electromigrating towards the anode end. This may have hindered TCS degradation in the CI-50 experiments, that was only 34±5%, comparing to SMX and IBU (97±8% and 61±5%, respectively). Nevertheless, it is important to acknowledge the high RSD associated to TCS concentrations within the different soil sections (e.g. Lβ contaminant concentration of 23% with an RSD of 60%) except Lα compartment with a contaminant concentration of 15% and an RSD of 3%.

When spiking was carried out only in the central compartment, the dispersion followed the same trend when unidirectional current was applied. In CI-10, higher concentrations were found at the L compartment than in the R compartment for SMX (a total of 33%, no statistical difference between layer α and β), IBU (a total of 39% with significant differences between layer α and β, $p<0.05$) and TCS (a total of 16% without statistical difference between layer α and β). At the R compartment, SMX and IBU present the same pattern, with no statistical differences; 6% of

contaminant concentration in Rα section, and Rβ with values below MLD; both with an RSD of 3%. TCS was also found at the anode with higher concentrations than cathode compartment, with a total of 16% at the anode and 11% at the cathode compartment, both with no statistical differences between layers. RSD for TCS goes up to 43%. ATN mobilized in higher concentrations towards the R compartment (10% in the Rα and 3% in Rβ) than the L compartment, no statistical differences between R and L sections.

According to the literature, it is expected that the periodic DC application (Sw experiments) would enhance solubilisation and desorption of the contaminant due to the “down time” that allows contaminant transfer from the soil to the interstitial fluid, as well as diffusion of the contaminant through the soil pores (Cameselle and Reddy, 2013). Thus, inducing higher mobilization of organic compounds than constant current application, because organic compounds become more susceptible to the pulsed EOF. But even with Sw system providing time for mass transfer, diffusion, and contaminant removal, the EOF towards the cathode is expected to be slower in comparison to continuous application of constant voltage.

Experiment Sw-6h has the highest mobilizations from central to lateral compartments. The compound concentration in C compartment increase from Sw-6h > Sw-24h > Sw-12h, including CAF, with a representativeness of 27% in Lα, 51% in Cα and 22% in the Rα sections, although with no statistical differences between same sections (L and R) of different compounds. Sw-6h shows the highest RSD range, till 109%.

When polarity reversal is applied the direction of the electroosmotic transport changes periodically, occurring along the soil during the same amount of time. Therefore, a symmetrical redistribution of volume of water and contaminants for both directions would be expected. With pH amenity induced by the polarity reversals, some contaminants have high probability to solubilize in the pore fluid and therefore more likely to disperse. TCS and ATN showed similar distribution for both directions. However, TCS it is also the compound that has higher RSD associated.

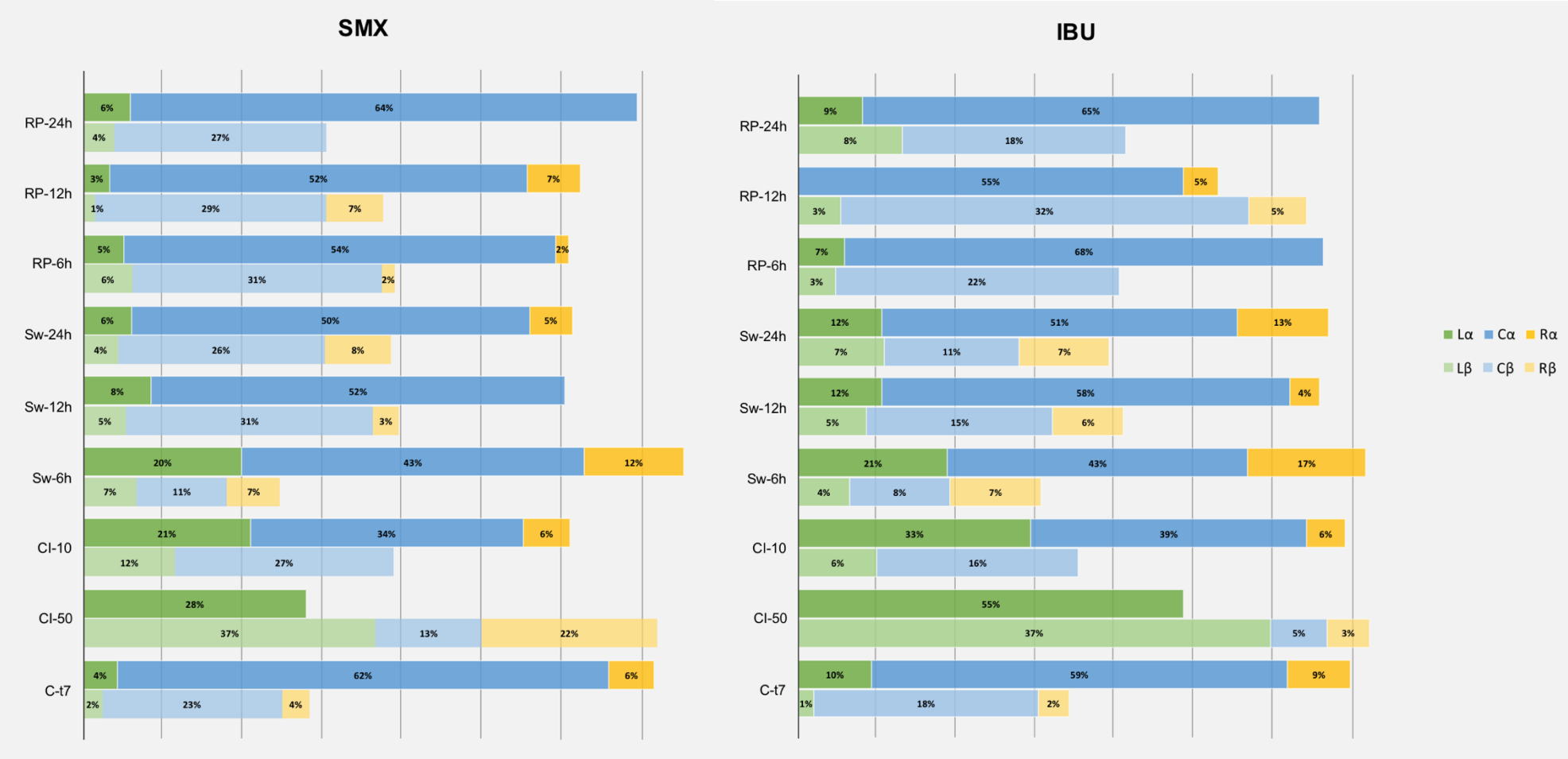


Figure 4.4. (a) SMX and IBU distribution within soil section for al experiments, normalized to final organic compound concentration.

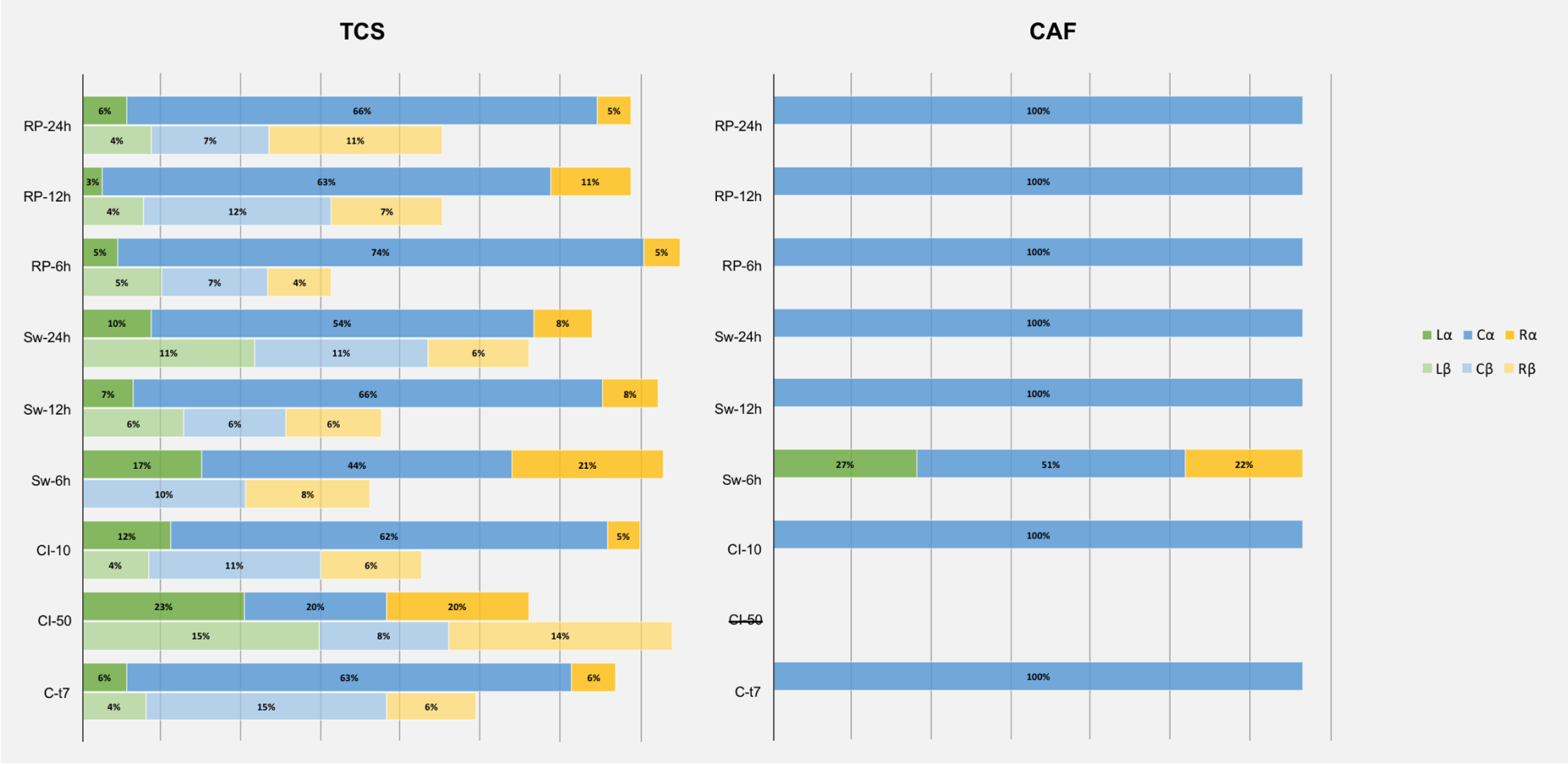


Figure 4.4. (b) TCS and CAF distribution within soil section for al experiments, normalized to final organic compound concentration.

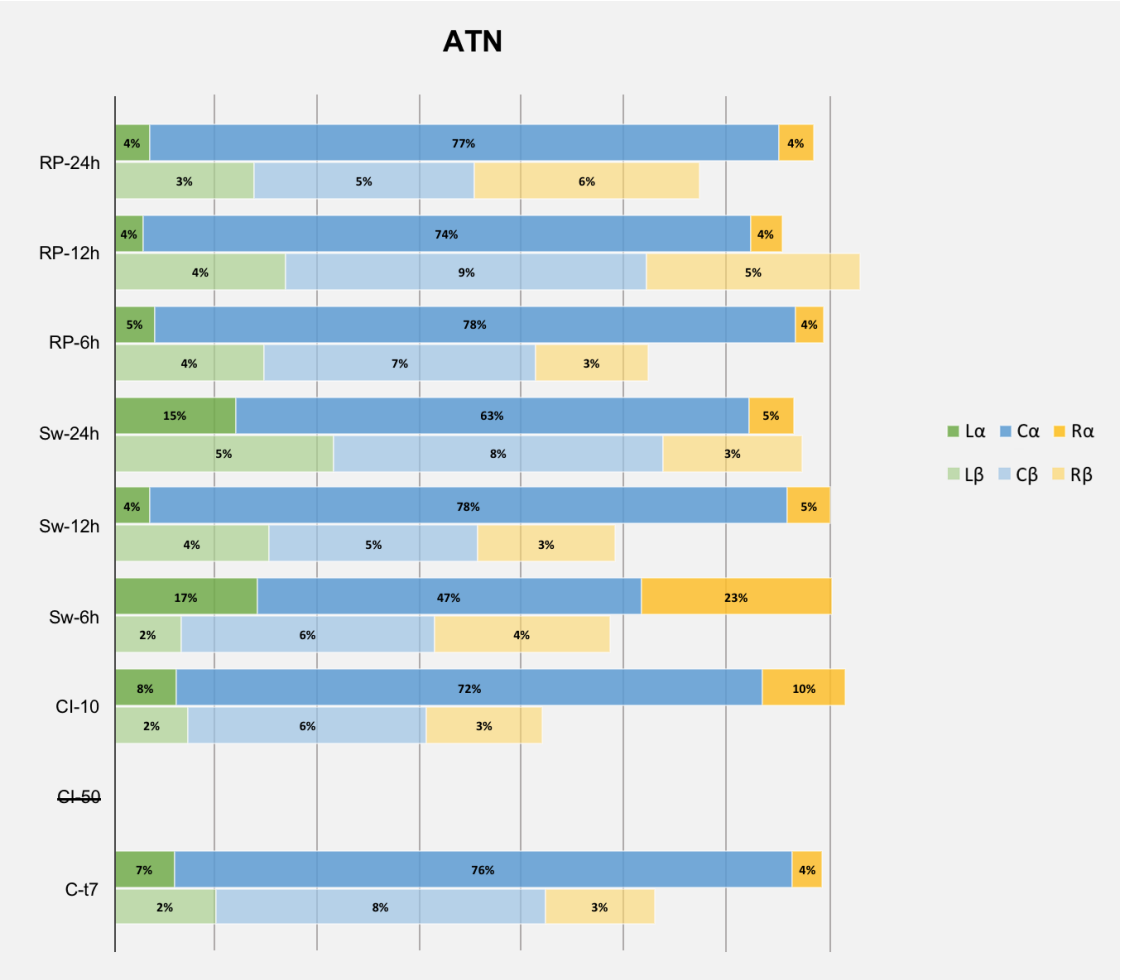


Figure 4.4. (c) ATN distribution within soil section for al experiments, normalized to final organic compound concentration.

The experiment with no current showed small RSD, for instance, TCS RSD vary between 0 – 5%, an analogous observation for the remaining contaminants can be done. The moment that an electric field is applied to the soil, higher RSD are observed, taking CI-10 for example, TCS mobilizations present RSD up to 43% (see Appendix 9).

Although the compound RSD sometimes reaches extremely high values at a given section, as observed especially in Sw-6h experiment, for example 17% of ATN is found in the Lα compartment with an $RSD_{L\alpha}$=109%, the mass balance performed showed that the total degradation percentages of organic compounds have very low RSD associated, between 0% and 20% (e.g. Sw-6h, ATN degraded 55% with an RSD=2%, see Table 4.5). These high RSD are potentially associated with organic compounds distribution along the two experimental replicates as the microcosm were manually prepared by (i) putting 600g of soil in the cell and a manual press was performed to even the soil height along the microcosms and (ii) manual irrigation. This may influence soil compaction and water distribution within the two different microcosms which in turn may have influenced the organic compounds mobilizations (distribution within the different 12 soil sections). This may have resulted in high RSDs for the organic compounds concentrations in sections R, C and L (both α and β) as contaminants electromigration and electroosmosis depend on factors such as porosity, flow path radius, pore width, as well as the physico-chemical properties of the solid and the liquid phases.

4.7.3. EK removal of organic contaminants

Analysing how EK process affects the remediation of CECs, it can be suggested that the process occurs by two degradation mechanisms (i) electrochemical reactions and (ii) EK enhanced biodegradation.

Overall, the processes induced by electric field are divided into two categories: (1) electrokinetic transport (including electroosmosis, electromigration, electrophoresis and diffusion), that favour the mobility and contact of substances; electrokinetic mass transfer, where pH changes leads to geochemical reactions that induces sorption/desorption of contaminants from soil particle surface (affected by the migration of H^+ and OH^- ions produced by electrolysis reactions), precipitation/dissolution of contaminants (significantly influencing the removal efficiency); and (2) electrochemically induced chemical reactions by (2.a) direct anodic oxidation, where the pollutants are adsorbed on the anode surface and destroyed by the anodic electron transfer reaction and (2.b) indirect oxidation in the liquid bulk which is mediated by the oxidants that are formed electrochemically. Such oxidants include chlorine, hypochlorite, hydroxyl radicals, ozone and hydrogen peroxide (Klavarioti *et al.,* 2009). These chemical reactions are accountable for the destruction of immobile organic contaminants within the soil matrix (Ferrarese and Andreottola, 2010, Reddy and Cameselle, 2009). By EK transport processes, these oxidants advance through the soil and react with the organic contaminants resulting in complete degradation or in smaller molecules, usually less toxic that the original ones. These simpler molecules are easier to be degraded by the indigenous microorganisms in the soil. The use on CI and Sw, in which a unidirectional DC is applied,

may have allowed a better transport of the oxidants through the soil column thus improving organic compounds degradation. The RP, may have counteracted the oxidant mobilization through the constants polarity reversals, thus decreasing the organic compounds oxidation, as observed in the RP experiments (Table 4.5, Figure 4.3).

In clay soils, as the one used in this study, oxidation-reduction reactions present an important contaminant removal process. Pamucku (2009), presented that the transformations occurring when a low-intensity electric field is applied to a soil can induce the surface of clay particles to act as micro-electrodes (due to the double layer), inducing redox reactions in the organic contaminants further from the electrodes. As the donated/accepted electron pass across the electrical double layer, the available species are converted into others through redox reactions (Pamukcu, 2009). This may influence central compartment degradations. Experiments that present high compound concentration at lateral compartments (like Sw-6h) account for the 1st hypothesis, mobilization occur towards lateral compartments where degradation takes place. In the experiments that have less compound concentration at L and R compartments, like Sw-12h, low mobilization is implied, thus accounting for the 2nd hypothesis: these compounds degrade at the central compartment by the effect of particles acting as micro-electrodes, thus achieving similar total degradations, taking TCS, for example, experiments Sw-6 and Sw-12h show similar total degradation percentages (41% and 44%, respectively, see Table 4.5).

To confirm these hypothesis, it would be necessary to ensure one of the following measures:

1) Ensure analytical procedures that require soil extraction, over the time duration of experiment, to create a profile of contaminant mobilization and concentration in each section - which in the scale performed it was not feasible. If an extraction (with replica) per section in the α layer was to be collected, in 24h less 10 g of each compartment (L, C and R) would be accountable for the final purpose and over a 7 day period it would account 70 g (12%) of the 600 g, which could severally impact the results;
2) Collect the interstitial fluid - this would require a representative volume for that purpose. In the experiments here performed the volumes were not representative or not existent and therefore not doable;
3) Use of the new technologies for organic compounds detection in the matrices;
4) Evaluate the soil redox potential in each section of the microcosms.

Graphite rods enhance redox reactions, especially when iron species are present (Ferrarese and Andreottola, 2010), potentially increasing the percentage degradations seen in the vicinity of the electrodes (visible in CI-50, Figure 4.2). Still, direct oxidation has its limitations regarding the electrodes corrosion, which can deactivate the electrode and reduce their lifetime (Laine and Cheng, 2007), thus presenting a second cause of rod corrosion, which was highly affecting these EK experiments, namely in the 100 and 50 mA. Nevertheless, this reaction is extremely efficient for the mineralization of organic compounds in fine-grain soils (Ferrarese and Andreottola, 2010).

On the other hand, the chemical destruction of organic contaminants can occur by chemical reduction, when a reductive chemical process results in less toxic compounds so they can be easily degraded by the microorganisms into the soil (Cameselle *et al*., 2013).

In C-t7 it was shown that the indigenous microorganism community of the soil is able to degrade the here studied organic contaminants, with TCS and CAF being the compounds with the lowest biodegradability. When a low current is applied (10 mA), it is expected that it serves as a stimulator of biodegradation (EK-biostimulation) by: enhancing contaminant bioavailability through EK mobilization; increase of bacteria mobility; EK-induced mass transfer and transport of ionic electron acceptors and nutrients; and electrochemical production of limited electron donors (H_2) and acceptors (O_2) (Reddy and Cameselle, 2009; Harbottle, 2003).

According to the literature (Reddy and Cameselle, 2009; Reddy and Saichek, 2004), the unidirectional electric field (used in CI and Sw experiments) should favour the contact between substances and increase the biotransformation rates. Electrophoresis carry bacteria and negatively charged particles to the positive electrode; electromigration of nutrients and charged substances migrate according to the opposite charges what they hold; and electroosmosis transport bacteria, contaminants, nutrients and electron acceptors towards the negative electrode.

DeFlaun and Condee (1997) performed experiments at bench-scale model aquifers to test electrophoresis as a tool for bacterial dispersion in situ for the remediation of trichloroethylene. In this study, a unidirectional movement of four different motile and nonmotile strains where observed to the anode only. This is in contrast to findings by Wick *et al*. (2004), which showed that electrophoresis accounted for less than 20% of all bacteria moved in the tested system (for PAH removal) and electroosmosis was found to be the predominant transport mechanism in clay soil (up to 90%). Wick *et al*. (2004) observation is in good agreement with the observation that *E. coli* moved in capillaries exclusively by electroosmosis at electrical field strengths of >0.3 V/cm over a wide range of pH values and ionic strengths tested by Liu *et al.* (1999). The same researchers found that bacterial motility is the predominant mode of motion at voltages below 0.2 V/cm, with bacteria moving at different mean speeds toward anode and cathode, due to the superimposed effects of EOF, electrophoresis, galvanotaxis, and random motility. The microbial community in this study account only the indigenous ones (no additional bacteria was added), and the dispersion of these microbes is considered to be homogeneously distributed, having a high catabolic potential. This means that the degradation of the contaminants added onto the soil is dependent on the physical state of the its chemical (e.g. dissolved, sorbed) and physical characteristics (e.g. hydrophobicity, effective diffusivity), and its spatial distribution relative to microorganisms (bioavailable concentration/bioaccessible fraction), its EK transport and type of organisms involved. Near the electrodes, community changes are attributed to electrokinetically induced changes of soil pH and physicochemical structure and it may negatively affect biodegradation in the electrode sections (Lear *et al.,* 2004; 2007). In the electrode sections, it is expected that electrochemical degradation is the main degradation mechanism of the organic compounds.

Taking into consideration that EOF is the main bacteria transport mechanism, and that EOF is preferential transported towards the cathode experienced in unidirectional systems, it is affected when polarity reversal technique is applied. Although there is lack of evidence of a significant EOF developed in this EK systems, it may explain the decrease in organic compounds degradation in the RP systems (comparing to CI and Sw). Besides bacteria distribution, it must be noted that low EOF produce low water mobility and a less efficient substance mixing effect, which could negatively affect the degrading process (Barba *et al.*, 2017). By combining with polarity reversals, the flow direction was changing each time the reversal was applied. Such conditions result in a lower contaminant dispersal through electroosmosis (Barba *et al.*, 2017; Mena *et al.*, 2016a,b), promoting biodegradation only in low distances (Wick *et al.,* 2007).

These may explain the similar degradations between Sw and RP systems. For instance, IBU attains a similar total degradation in experiment Sw-6h and RP-6h, 45% and 43%, respectively, see Table 4.5. Sw-6h shows contaminant concentration at the R compartment, suggesting an EOF movement towards the cathode that may be confirmed by a non-significant variation tendency of moisture content between the C compartment and R compartment, values around 12% (Cα) and 15% (Rα). Where RP-6h shows no evidence of EOF as no compound concentrations are found at the R compartment. Moisture content variations support this idea, with values higher at the central compartment than R compartment, values around 22% at Cα and 19% at the Rα (Table 4.4). Still, with the same total degradation percentages, it is believed that RP is promoting microorganisms to be in contact with bioavailable contaminants thus increasing biodegradation at small distances (central compartment), and in Sw system high electromobility of contaminants promoting bio- and electrochemical- degradation near the electrodes.

The laboratory experiments performed ensured that consistency was maintained in areas such as sample preparations (Section 3). In this case, the soil was sieved, and only the fine soil fraction was used in the experiments. The soil spiking and moisture maintenance were performed manually, it was accepted that there would be some variability in the results. As presented in Appendix 9, organic compounds mobilization in the duplicate microcosms presented a high variability with RSD reaching 109% (worst case).

In the field, it is expected that organic compounds dispersion and degradation reach higher RSDs values, as several factors affect the variability of the remediation efficiency, such as the porous medium micromorphology (porosity and tortuosity), sorption and pH changes (Wise, 2000). The pore space in a field soil matrix is an extremely heterogeneous environment. In lab scale this factor was diminished through sieving, also described in Section 3, but sill, the soil might have been more compacted in one section than the other, due to the microcosm manual preparation. Tortuosity refers to the diffusion path length of elements and/or molecules flowing through the soil due to the presence of other particles. It varies according to changes on moisture content and saturation of the soil, spread air and water flow paths in each experiment. The transport of contaminants through soil, especially in a clay soil, will not be in a straight-line motion across the field, it is more likely they travel

a tortuous path that benefit their mobilization (Harbottle, 2003), thus affecting contaminant distribution between the soil sections and increasing variability between microcosms.

Depending on the applied conditions, the degradation of the organic compounds through electro-degradation and/or biodegradation processes may promote the contaminants mineralization to CO_2 and H_2O (Amorim *et al*., 2013). In this study, new peaks were observed in the HPLC-DAD-FLD chromatograms that may correspond to new or related compounds (e.g. Figure 4.5). Further acknowledging Figure 4.5(a), PD4 observed in DAD-B and three peaks arising before IBU observed in both DAD-B and FLD-A (Figure 4.4(b) PD1, 2 and 3) could possibly be by-products. The identification of these compounds was attained using GC-MS and LC-MS, but, due to the low concentrations, the identification was not possible. It should be mentioned that the by-products can sometimes be more harmful than the parent compounds and their identification and definition of the degradation pathways should be considered in future studies. For example, Huang *et al*. (2015) indicated that IBU oxidation products generated a higher risk of acute toxicity than their parent chemical.

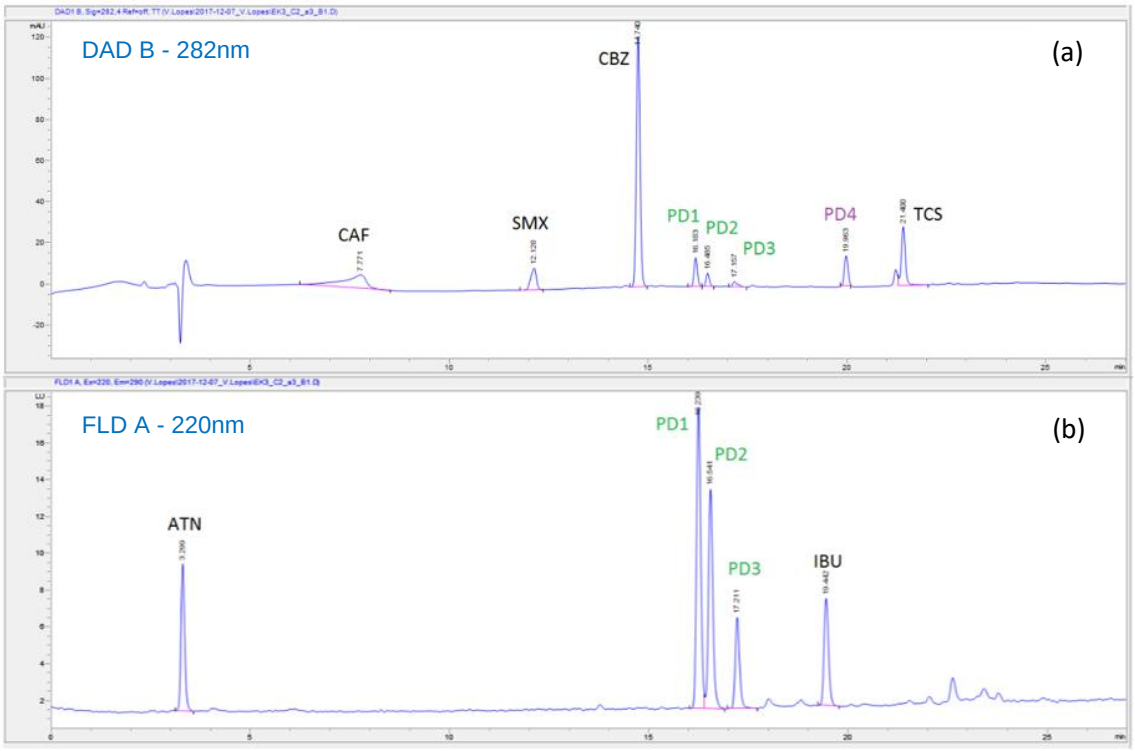


Figure 4.5. Sub-products at experiment CI-10, Cα3 (a) DAD B: Product degradation – PD1, 2, 3 and 4, (b) FLD A: Product degradation – PD1, 2 and 3

4.8. Technical viability and potential scaling up

The EK microcosm here studied was designed aiming an easy scaling up of the process, with easy applicability in the field, that has to consider many different environmental, technical and economic aspects.

Some organic compounds are difficult to remove with EK alone because of their low solubility. Therefore, to enhance the removal efficiency, the remediation should be conducted to maximize both the EK process and biodegradation and to minimize undesirable effects in the soil ecosystem. Having this in mind, the two best degrading experiments were CI-10 and Sw-12h and will be further discussed.

It is important to note that a strong electric field like 50 mA presented the highest degradation percentages in 7 days, demonstrating that the electric density is an important factor to be considered when organic compounds are to be removed from a soil matrix. Research has shown that direct currents can lead to better contaminant removal than alternate or pulsing currents, possibly because alternate currents cause continuous changes in the soil polarization and consume a relatively high energy to discharge or recharge the double layer of soil particles (Röhrs *et al*., 2002). In this study, due to high pH variation in soil and graphite rod corrosion, CI-50 was rejected. Experiment CI-10 still promoted rod corrosion, as it was constantly applied for 24h, but in a much lower incidence than CI-50. In further studies 50 mA could be used using metal electrodes, these being most suitable for small-scale. Titanium and stainless steel are noted as effective electrode materials at the field-scale due to their reliability and low associated economic cost (Gill *et al.*, 2014). As the high pH changes are expected when using constant current, the Sw-12h and RP-12h should be further studied with the metal electrodes, as the 12h showed to be the best options for both Sw and RP systems.

Although experiment CI-10 in general improved contaminant degradations, soil properties were still considerably changed (e.g. pH, electrical conductivity, water content) and electromigration of highly soluble ionised inorganic species present in moist soil environments, including metal cations, chlorides, nitrates and phosphates is expected to occur (not evaluated in this dissertation). It could be suggested that, in order to apply these operating parameters (i.e., constant current at 10 mA for 24h) and maintain soil physico-chemical properties close to the original after the EK treatment, some amendments or physical treatments (e.g. soil excavation) should be performed to homogenise the soil.

Similar results of degrading efficiency comparing to CI-10 were achieved with experiment Sw-12h, that seems to be a good strategy to minimize EK effects on soil properties. The use of this technique provides an approach with minimum disturbance to the surface and decreasing energetic costs and increasing electrodes life expectancy.

According to literature (Kimura *et al*., 2007; Xuan *et al*. 2008; Robinson and Hellou 2009; Xu *et at.,* 2009b), biological degradation is the primary dissipation mechanism for most organic pollutants in the soil environment. Hence, this study also considered the significant exertion that microbes and natural reactions input in the degradation of organic compounds.

The behaviour of soil microflora and microfauna are strongly influenced by environmental parameters. Many bacteria operate in an optimum pH range, often around neutral. Therefore, the development of a pH gradient as seen in CI-10 (variation between 6.8 – 11.2) could be detrimental to their efforts. On the contrary, Sw-12h promoted soil mild conditions, like neutral soil pH (around

8), and that stimulates their activity. Theoretically Sw-12h may have benefit more from bioremediation than CI-10.

In terms of costs (further discussed in section 4.8.1), the high energy consumption (seen in CI-10) would be avoided by discontinuous periods of constant electric current (as Sw-12h). Lowering the overall cost of the remediation process which can be a major factor given the costs of other remediation technologies.

Experiments here presented were performed at laboratory scale, which implies that differences are expected if these conditions were to be replicated at field-scale (Figure 4.6). In this study, factors such as the homogeneity of soil and uniform distribution of contaminant and electric field distribution were controlled. On the contrary, at a typical contaminated site it must be taken in account the heterogeneity of soil structure (e.g. tortuosity factor), as well as the presence of unwanted electrically conductive objects such as metals (e.g. wires and pipes), moisture content and so on. This matter would have interference with the electrokinetic remediation, as the electric current usually travel along the easier path.

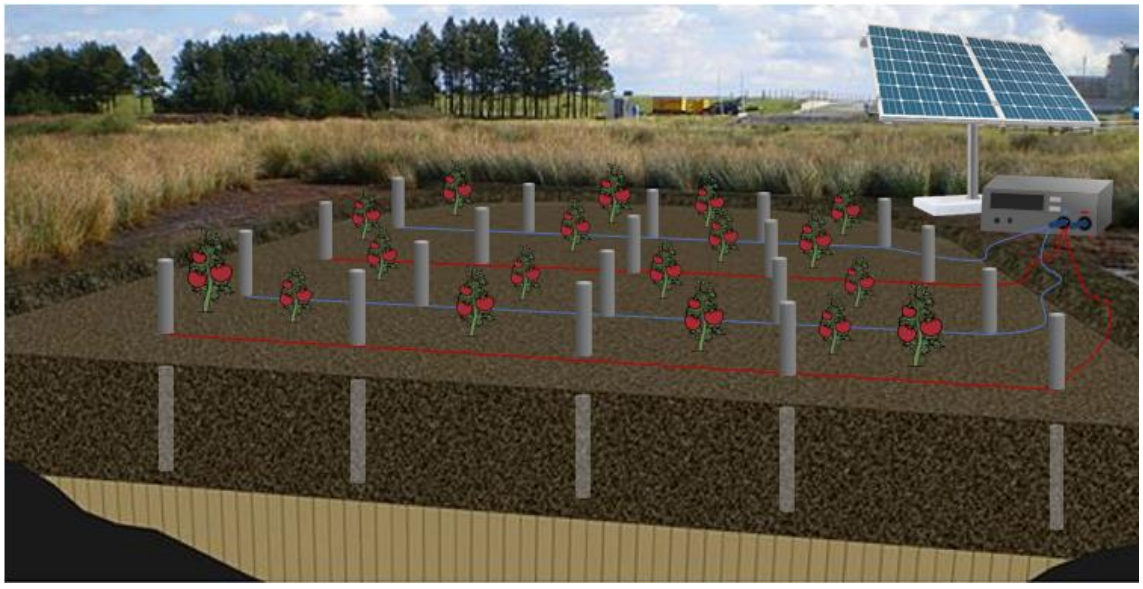


Figure 4.6. Up scaling electrokinetic remediation process in agricultural field (adapted from electrokinetic Limited, 2018)

Factors such as electrodes configuration (e.g. spacing) significantly affect results. The effectiveness of *in situ* remediation technologies depends on the contaminant chemistry and subsurface heterogeneities (including particle-scale heterogeneities such as fine-grained soils, soils with reactive minerals, and/or soils rich in organic matter, as well as macro-scale heterogeneities such as irregular soil layers). In this work, a uniform current density has been used but, in the field, this may be impracticable, as large sites would require large numbers of electrodes (Gill *et al.*, 2014).

4.8.1. Preliminary cost analysis

The main parameters and their importance in the overall process cost are (Virkutyte et al., 2002):

- Soil properties;
- Depth of contamination;
- Cost of accommodating electrodes and placing treatment zones (17% for materials and 40% for electrodes above the overall remediation costs);
- Clean-up time;
- Cost of labour (17% for labour; 16% for licenses and other fixed costs);
- Electrical power (10-15% for electricity).

The electricity consumption per unit volume of soil was calculated by the following equation (adapted from Yang and Liu, 2001):

$$E_u = \frac{1}{V_{soil}} \int_{t=0}^{t} V\ I\ dt \qquad (2.6)$$

where E_u is the electricity expenditure per unit volume of soil (kW h/m^3), V_{soil} the soil volume (m^3), V the electric potential difference across the electrodes (V), I the electric current (A), and t the treatment time (h).

The technique employed in experiment Sw-12h require a voltage drop across the soil of approximately 10 volts, at a current of 10 mA (0.01 A), this represents a power consumption of 0.1 W. The soil volume was around 5.07x10^{-4} m^3 (assuming a cube form cell of 130x130x30mm, no rounded corners), assuming that the soil remediation treatment would be carried for 7 days (84 hours in experiment Sw-12h), the consumption required under these conditions is 16.568 kW h/m^3. The electricity cost is €0,1408 per kilowatt-hour (PORDATA estimative price for industrial consumers, year 2017), then by multiplying E_u by the average electricity rate the remediation cost would be approximately 2.33 €/m^3.

Up scaling to a field of one hundred square metre site with a depth of one meter, soil remediation electric cost would fluctuate around 233 €. Depending on the type of energy used, this technology may become ecologically sustainable (through the use of solar/wind power).

In addition to the electricity cost, the cost of material involved, such as graphite rods, must be considered in the estimation of operating cost. As well as the water (irrigation) to maintain soil conditions that provide the compound degradation as seen in Sw-12.

Since all electrodes in soil remediation applications undergo corrosion, fouling and passivation, the use of low cost materials, as stainless steel or graphite, is commonly preferred for real scale applications.

Hypothetically, Sw-12h would be an ecological friendly and cost-effective processing solution.

5. CONCLUSIONS

In this dissertation, EK parameters were tested in a lab scale microcosm. The main objective was to promote the degradation of different CECs while avoiding drastic changes in soil physico-chemical parameters.

Among the studied compounds, CAF was less susceptible to biodegradation whereas SMX was more biodegraded. In all EK experiments the degradation trend was similar to the C-t7, SMX > ATN ≥ IBU > TCS > CAF. Organic contaminants removal was higher under constant current intensity, but extreme pH fronts throughout the soil and depletion of ions from the central compartment was observed. Using constant current, soil mild conditions were not stable and, by switching the polarity of the electric field, the objective of maintaining soil pH close to original was achieved. However, electro-polarization reversal was not favourable to the removal of organic contaminants. The periodic current application (Sw system), specifically ON/OFF for 12h, presented to be the best option. This means that the use of Sw promotes an approach with minimum disturbance to the surface while efficiently removing organic contaminants from soils irrigated with effluent containing these five PPCPs, with SMX and IBU degrading more 8% than in natural attenuation at a 7 day period, ATN more 18%, TCS more 24% and CAF more 30%.

This study suggests that the addition of enhancement agents in order to keep the pH within a suitable range, may not be necessary. With ON/OFF for 12h and an applied current of 10 mA, extreme pH fronts were avoided, thus maintaining soil at mild conditions with pH around neutral (7.03±0.2). Still, it allowed to maintain the necessary pH gradient that EK depends on, ranging between a minimum pH of 7.42 to a maximum of 9.06; soil moisture allowed to keep a conductive adequate for electromigration without the soil being saturated, which avoided possible competing effects of tortuosity.

It is suggested that the degradation process of the organic contaminants during EK process occurs by (i) electrochemical reactions and (ii) EK enhanced biodegradation. The results allowed to hypothesise that degradation of the organic contaminants in this particular type of soil, depending on the applied conditions, may occur in two distinct ways: compounds mobilize towards lateral compartments were degradation takes place; or compounds show low mobilization and degrade at the central compartment.

In this study EK showed to be a promising *in situ* technology for CECs removal from soil, thus decreasing environmental and human associated risks.

6. FUTURE DEVELOPMENTS

At the end of this study, as it may be considered that mobilization of compounds is affected by the physico-chemical properties of each organic compounds and the environment that they are exposed to, including soil type and characteristics, rainfalls, temperature and sunlight. To better evaluate the fate of PPCPs in soils, long term field studies at real environmental conditions are thus needed. For that, analytical procedures that require sampling of the effluent used for irrigation and soil (pre- and post-application and at various depths), to create a profile of contaminant mobilization and concentration in each soil section, need to be developed. In addition, the collection of samples of the surrounding surface waters and soils to monitor the immediate and the study of the uptake by plants may be of great support on the evaluation of EK remediation efficiency over time.

Biodegradation showed to be an important degradation pathway, as pointed by the results here obtained. A quantitative and qualitative evaluation of the biological activity during the remediation timeframe would provide a better understanding of the mechanisms involved and confirm the hypothesis raised in this dissertation.

One factor that influences the remediation is the type of electrodes, their configuration and current intensity. The application of graphite, platinum, gold and silver are the most suitable electrodes used for research purposes. Because of larger dimensions of pilot studies and high corrosion susceptibility of some of the electrodes (e.g. graphite as studied in the present dissertation), further studies can take-off with electrodes less susceptible to corrosion (e.g. titanium and stainless steel) this may represent a cost-efficient option. Therefore, subsequent research would be the application of high currents with electrodes less susceptible to corrosion. This is because of the higher degradations attained with a higher current intensity (Experiment CI-50 at 50 mA), simulating the direct electrode placement in the moist contaminated matrix. Also, the combination of other electrode' configurations, geometrical distributions, the number of electrodes in the system and electrode spacing, not studied in the present dissertation, with operational modes such as the ones studied in the present dissertation, may provide answers to the proposition of moving the electrode location closer to the target, reducing traveling distances and size of ineffective areas of effects induced by the DC electric field applied into the substances, thus improving the degradation rates.

Still, given the observations in the present work, previous research at laboratory scale would help to understand the soil changes and behaviours, such as the one observed in section 4 where the formation of a circle of a reddish-brown was observed around the electrodes (anodes), to confirm the hypothesis given, a soil analysis should be performed for the quantification of metal species in all soil sections, e.g. quantification through Atomic Absorption Spectrometry.

Because of the number of the additional peaks observed in all the experiments it is important to further investigate the degradation products of the parent compounds of interest in agricultural soil, once these by-products may be more dangerous to human health and the enviromnent than the parent compounds.

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ANNEXES

Annex 1. Tukey's multiple comparisons test list for soil pH between same sections for all experiments

Code	Tukey's multiple comparisons test		Mean Diff.	95,00% CI of diff	Significant?	Summary	Adjusted P value
§	C-t0	CI-50_a5	-4.228	-6,269 to -2,188	Yes	****	<0,0001
		CI-50_a6	-4.848	-6,889 to -2,808	Yes	****	<0,0001
		CI-50_b1	2.077	0,03643 to 4,117	Yes	*	0.0383
		CI-50_b5	-3.078	-5,119 to -1,038	Yes	****	<0,0001
		CI-50_b6	-4.273	-6,314 to -2,233	Yes	****	<0,0001
		CI-10_a5	-3.963	-6,004 to -1,923	Yes	****	<0,0001
		CI-10_a6	-3.758	-5,799 to -1,718	Yes	****	<0,0001
A	CI-50_a1	CI-50_a4	-3.235	-5,906 to -0,5637	Yes	**	0.0014
		CI-50_b4	-2.775	-5,446 to -0,1037	Yes	*	0.0278
		Sw-6h_a1	-3.12	-5,791 to -0,4487	Yes	**	0.0031
		Sw-24h_a1	-3.065	-5,736 to -0,3937	Yes	**	0.0045
		RP-12h_a1	-3.02	-5,691 to -0,3487	Yes	**	0.006
		RP-24h_a1	-2.705	-5,376 to -0,03371	Yes	*	0.0415
B	CI-50_a2	CI-50_a4	-2.715	-5,386 to -0,04371	Yes	*	0.0392
		RP-12h_a2	-2.86	-5,531 to -0,1887	Yes	*	0.0167
C	CI-50_a5	Ct7 a5	-3.75	-6,421 to -1,079	Yes	****	<0,0001
		CI-50_a1	-6.175	-8,846 to -3,504	Yes	****	<0,0001
		CI-50_a2	-5.655	-8,326 to -2,984	Yes	****	<0,0001
		CI-50_a3	-4.495	-7,166 to -1,824	Yes	****	<0,0001
		CI-50_a4	-2.94	-5,611 to -0,2687	Yes	*	0.0101
		Sw-24h_a5	3.085	0,4137 to 5,756	Yes	**	0.0039
		RP-6h_a5	4	1,329 to 6,671	Yes	****	<0,0001
		RP-12h_a5	3.63	0,9587 to 6,301	Yes	****	<0,0001
		RP-24h_a5	3.12	0,4487 to 5,791	Yes	**	0.0031
D	CI-50_a6	Ct7 a6	-4.865	-7,536 to -2,194	Yes	****	<0,0001
		CI-50_a1	-6.795	-9,466 to -4,124	Yes	****	<0,0001
		CI-50_a2	-6.275	-8,946 to -3,604	Yes	****	<0,0001
		CI-50_a3	-5.115	-7,786 to -2,444	Yes	****	<0,0001
		CI-50_a4	-3.56	-6,231 to -0,8887	Yes	***	0.0001
		CI-50_b1	6.305	3,634 to 8,976	Yes	****	<0,0001
		CI-50_b2	5.145	2,474 to 7,816	Yes	****	<0,0001
		CI-50_b3	4.45	1,779 to 7,121	Yes	****	<0,0001
		CI-50_b4	3.4	0,7287 to 6,071	Yes	***	0.0004
		Sw-6h_a6	4.04	1,369 to 6,711	Yes	****	<0,0001
		Sw-12h_a6	3.095	0,4237 to 5,766	Yes	**	0.0037
		Sw-24h_a6	4.015	1,344 to 6,686	Yes	****	<0,0001

Code	Tukey's multiple comparisons test		Mean Diff.	95,00% CI of diff	Significant?	Summary	Adjusted P value
		RP-6h_a6	3.99	1,319 to 6,661	Yes	****	<0,0001
		RP-12h_a6	4.11	1,439 to 6,781	Yes	****	<0,0001
		RP-24h_a6	3.025	0,3537 to 5,696	Yes	**	0.0059
E	CI-50_b1	CI-50_a4	3.365	0,6937 to 6,036	Yes	***	0.0005
		CI-50_b4	-2.905	-5,576 to -0,2337	Yes	*	0.0126
		Sw-6h_b1	-2.845	-5,516 to -0,1737	Yes	*	0.0183
		Sw-24h_b1	-3.215	-5,886 to -0,5437	Yes	**	0.0016
		RP-6h_b1	-2.9	-5,571 to -0,2287	Yes	*	0.013
		RP-12h_b1	-2.87	-5,541 to -0,1987	Yes	*	0.0157
		RP-24h_b1	-3.185	-5,856 to -0,5137	Yes	**	0.002
F	CI-50_b5	CI-50_a1	-5.025	-7,696 to -2,354	Yes	****	<0,0001
		CI-50_a2	-4.505	-7,176 to -1,834	Yes	****	<0,0001
		CI-50_a3	-3.345	-6,016 to -0,6737	Yes	***	0.0006
		CI-50_b1	-5.155	-7,826 to -2,484	Yes	****	<0,0001
		CI-50_b2	-3.995	-6,666 to -1,324	Yes	****	<0,0001
		CI-50_b3	-3.3	-5,971 to -0,6287	Yes	***	0.0009
G	CI-50_b6	Ct7 b6	-3.77	-6,441 to -1,099	Yes	****	<0,0001
		CI-50_a2	-5.7	-8,371 to -3,029	Yes	****	<0,0001
		CI-50_a1	-6.22	-8,891 to -3,549	Yes	****	<0,0001
		CI-50_a3	-4.54	-7,211 to -1,869	Yes	****	<0,0001
		CI-50_a4	-2.985	-5,656 to -0,3137	Yes	**	0.0076
		CI-50_b1	-6.35	-9,021 to -3,679	Yes	****	<0,0001
		CI-50_b2	-5.19	-7,861 to -2,519	Yes	****	<0,0001
		CI-50_b4	-3.445	-6,116 to -0,7737	Yes	***	0.0003
		Sw-12h_b6	3.02	0,3487 to 5,691	Yes	**	0.006
		Sw-24h_b6	3.6	0,9287 to 6,271	Yes	****	<0,0001
		RP-6h_b6	3.73	1,059 to 6,401	Yes	****	<0,0001
		RP-12h_b6	3.62	0,9487 to 6,291	Yes	****	<0,0001
		RP-24h_b6	2.81	0,1387 to 5,481	Yes	*	0.0226
H	CI-10_a5	Ct7 a5	-3.485	-6,156 to -0,8137	Yes	***	0.0002
		CI-10_a1	-4.455	-7,126 to -1,784	Yes	****	<0,0001
		CI-10_a2	-4.16	-6,831 to -1,489	Yes	****	<0,0001
		CI-10_a3	-2.96	-5,631 to -0,2887	Yes	**	0.0089
		CI-10_b1	4.335	1,664 to 7,006	Yes	****	<0,0001
		CI-10_b2	4.185	1,514 to 6,856	Yes	****	<0,0001
		CI-10_b3	2.9	0,2287 to 5,571	Yes	*	0.013
		CI-10_b4	3.155	0,4837 to 5,826	Yes	**	0.0024

Code	Tukey's multiple comparisons test		Mean Diff.	95,00% CI of diff	Significant?	Summary	Adjusted P value
		Sw-24h_a5	2.82	0,1487 to 5,491	Yes	*	0.0213
		RP-6h_a5	3.735	1,064 to 6,406	Yes	****	<0,0001
		RP-12h_a5	3.365	0,6937 to 6,036	Yes	***	0.0005
		RP-24h_a5	2.855	0,1837 to 5,526	Yes	*	0.0172
I	CI-10_a6	Ct7 a6	-3.775	-6,446 to -1,104	Yes	****	<0,0001
		CI-10_a1	-4.25	-6,921 to -1,579	Yes	****	<0,0001
		CI-10_a2	-3.955	-6,626 to -1,284	Yes	****	<0,0001
		CI-10_a3	-2.755	-5,426 to -0,08371	Yes	*	0.0312
		CI-10_b1	4.13	1,459 to 6,801	Yes	****	<0,0001
		CI-10_b2	3.98	1,309 to 6,651	Yes	****	<0,0001
		CI-10_b3	2.695	0,02371 to 5,366	Yes	*	0.0439
		CI-10_b4	2.95	0,2787 to 5,621	Yes	**	0.0095
		Sw-6h_a6	2.95	0,2787 to 5,621	Yes	**	0.0095
		Sw-24h_a6	2.925	0,2537 to 5,596	Yes	*	0.0111
		RP-6h_a6	2.9	0,2287 to 5,571	Yes	*	0.013
		RP-12h_a6	3.02	0,3487 to 5,691	Yes	**	0.006

Annex 2. Tukey's multiple comparisons test list for soil EC between same sections for all experiments

Code	Tukey's multiple comparisons test		Mean Diff.	95,00% CI of diff	Significant?	Summary	Adjusted P value
§	C-t0	CI-50_a6	-1.95	-3,251 to -0,6487	Yes	****	<0,0001
A	CI-50_a6	Ct7 a6	-1.93	-3,634 to -0,2262	Yes	**	0.0058
		CI-50_a3	-2.412	-4,116 to -0,7082	Yes	****	<0,0001
		CI-50_a4	-2.375	-4,079 to -0,6712	Yes	****	<0,0001
		CI-50_a5	-1.78	-3,484 to -0,07619	Yes	*	0.0253
		CI-50_b1	1.78	0,07619 to 3,484	Yes	*	0.0253
		CI-50_b2	1.81	0,1062 to 3,514	Yes	*	0.0191
		CI-50_b3	2.469	0,7647 to 4,172	Yes	****	<0,0001
		CI-50_b4	2.484	0,7797 to 4,187	Yes	****	<0,0001
		CI-50_b5	2.215	0,5112 to 3,919	Yes	***	0.0002
		CI-10_a6	2	0,2962 to 3,704	Yes	**	0.0028
		Sw-6h_a6	1.725	0,02119 to 3,429	Yes	*	0.0416
		Sw-12h_a6	2.315	0,6112 to 4,019	Yes	****	<0,0001
		Sw-24h_a6	1.77	0,06619 to 3,474	Yes	*	0.0278
		RP-6h_a6	2	0,2962 to 3,704	Yes	**	0.0028
		RP-12h_a6	1.955	0,2512 to 3,659	Yes	**	0.0045
		RP-24h_a6	2.17	0,4662 to 3,874	Yes	***	0.0004

Annex 3. Tukey's multiple comparisons test list for soil moisture content between same sections for all experiments

Code	Tukey's multiple comparisons test		Mean Diff.	95,00% CI of diff	Significant?	Summary	Adjusted P value
A	Ct7 b1	Ct7 a5	-9.13	-18,01 to -0,2506	Yes	*	0.0336
		Ct7 a6	-8.925	-17,8 to -0,046	Yes	*	0.0465
		Ct7 b2	9.528	0,6492 to 18,41	Yes	*	0.0172
		Ct7 b3	9.299	0,4196 to 18,18	Yes	*	0.0254
		Ct7 b4	10.01	1,131 to 18,89	Yes	**	0.0073
		Ct7 b5	9.678	0,799 to 18,56	Yes	*	0.0133
		Ct7 b6	9.993	1,114 to 18,87	Yes	**	0.0076
		CI-50_b1	9.795	0,9164 to 18,67	Yes	*	0.0108
		CI-10_b1	11.31	2,431 to 20,19	Yes	***	0.0006
		Sw-6h_b1	10.39	1,513 to 19,27	Yes	**	0.0036
		Sw-12h_b1	10.6	1,716 to 19,47	Yes	**	0.0024
		RP-12h_b1	10.55	1,668 to 19,43	Yes	**	0.0027
		RP-24h_b1	10.32	1,44 to 19,2	Yes	**	0.0041
B	Sw-6h_a3	RP-6h_a3	-9.513	-18,39 to -0,6335	Yes	*	0.0177
		RP-12h_a3	-9.057	-17,94 to -0,1783	Yes	*	0.0377
C	Sw-6h_a5	Sw-24h_a5	-9.284	-18,16 to -0,4052	Yes	*	0.026
D	RP-24h_a4	RP-6h_a4	9.624	0,7449 to 18,5	Yes	*	0.0146
		RP-12h_a4	8.951	0,07211 to 17,83	Yes	*	0.0447

Annex 4. pH standard deviation for each experiment in a given soil section

Soil compartment	Soil section	SD								
		CT7	CI-50	CI-10	Sw-6h	Sw-12h	Sw-24h	RP-6h	RP-12h	RP-24h
Lα	**α1**	0.1	0.8	0.0	1.7	0.2	1.6	0.1	0.2	0.4
	α2	0.5	0.1	0.5	0.6	0.1	1.4	0.2	0.1	0.6
Cα	**α3**	0.1	0.1	0.1	0.2	0.5	0.3	0.3	0.1	0.1
	α4	0.2	0.4	0.2	0.1	0.3	0.5	0.0	0.8	0.0
Rα	**α5**	0.2	0.1	0.9	0.2	0.1	1.9	0.1	0.7	0.1
	α6	0.1	0.9	0.0	2.0	0.1	1.5	0.6	0.0	0.5
Lβ	**β1**	0.6	0.2	0.4	1.7	0.1	1.3	0.1	0.0	0.8
	β2	0.5	0.2	0.3	0.8	0.0	1.2	0.1	0.3	0.7
Cβ	**β3**	0.1	0.5	0.3	0.0	0.4	0.2	0.1	0.0	0.1
	β4	0.0	0.8	0.5	0.3	0.6	0.1	0.1	0.6	0.0
Rβ	**β5**	0.3	0.7	0.2	0.9	0.5	1.2	0.2	0.4	0.2
	β6	0.4	1.1	0.6	0.3	0.0	1.3	0.3	0.4	0.0

Annex 5. Electrical conductivity standard deviation for each experiment in a given soil section

Soil compartment	Soil section	SD								
		CT7	CI-50	CI-10	Sw-6h	Sw-12h	Sw-24h	RP-6h	RP-12h	RP-24h
Lα	**α1**	0.1	0.3	0.0	0.9	0.0	0.6	0.1	0.1	0.5
	α2	0.1	0.0	0.1	0.1	0.3	1.2	0.0	0.1	0.7
Cα	**α3**	0.1	0.0	0.0	0.1	0.0	0.0	0.2	0.0	0.0
	α4	0.1	0.1	0.0	0.2	0.0	0.0	0.0	0.2	0.0
Rα	**α5**	0.1	0.1	0.2	0.1	0.0	0.8	0.1	0.1	0.0
	α6	0.1	2.7	0.0	0.8	0.0	0.8	0.1	0.1	0.0
Lβ	**β1**	0.0	0.1	0.1	0.4	0.0	0.4	0.1	0.0	0.4
	β2	0.1	0.1	0.0	0.0	0.1	0.6	0.0	0.0	0.7
Cβ	**β3**	0.1	0.0	1.0	0.0	0.0	0.0	0.0	0.1	0.1
	β4	0.1	0.0	0.0	0.1	0.0	0.0	0.0	0.0	0.1
Rβ	**β5**	0.1	0.2	0.0	0.4	0.0	0.7	0.2	0.1	0.0
	β6	0.1	0.8	0.0	0.0	0.0	0.2	0.1	0.1	0.0

Annex 6. Moisture content standard deviation for each experiment in a given soil section

Soil compartment	Soil section	SD								
		CT7	**CI-50**	**CI-10**	**Sw-6h**	**Sw-12h**	**Sw-24h**	**RP-6h**	**RP-12h**	**RP-24h**
Lα	**α1**	3.00	4.78	2.19	1.84	1.27	0.68	0.78	0.05	2.32
	α2	2.30	3.67	0.21	1.79	1.66	1.15	3.30	0.80	1.97
Cα	**α3**	3.25	0.83	0.44	0.81	1.48	2.19	0.24	0.25	0.05
	α4	2.05	0.36	0.72	0.33	1.51	0.58	0.81	0.05	2.11
Rα	**α5**	3.19	0.04	0.62	0.72	0.02	6.22	2.06	0.43	0.36
	α6	0.89	0.48	0.07	0.22	0.01	0.37	0.76	1.30	1.77
Lβ	**β1**	10.99	2.15	1.12	1.45	1.32	2.08	2.27	0.16	0.67
	β2	1.44	1.29	0.04	0.27	0.05	0.70	1.98	1.63	1.86
Cβ	**β3**	1.39	0.38	0.30	0.60	2.09	1.68	2.53	0.82	0.77
	β4	0.62	1.19	1.35	0.05	0.86	0.44	1.43	1.97	1.16
Rβ	**β5**	2.19	3.39	0.17	1.38	0.22	0.39	3.88	0.81	0.70
	β6	1.93	3.67	1.15	1.51	2.51	2.94	1.72	1.04	0.42

Annex 7. Resume of statistical significant differences observed between the compounds within the same experiment.

Experiment	Tukey's multiple comparisons test	Comparing to	Mean Diff,	95,00% CI of diff,	Summary	Adjusted P Value
C-t7	TCS	SMX	44	23,91 to 64,09	****	<0,0001
		IBU	29	8,906 to 49,09	****	<0,0001
		ATN	-27	-47,09 to -6,906	***	0,0002
	CAF	SMX	58	37,91 to 78,09	****	<0,0001
		IBU	43	22,91 to 63,09	****	<0,0001
		ATN	-41	-61,09 to -20,91	****	<0,0001
CI-50	SMX	IBU	36	15,91 to 56,09	****	<0,0001
		TCS	63	42,91 to 83,09	****	<0,0001
	IBU	TCS	27	6,906 to 47,09	***	0,0002
CI-10	SMX	IBU	38	17,91 to 58,09	****	<0,0001
		TCS	29	8,906 to 49,09	****	<0,0001
	IBU	ATN	-22	-42,09 to -1,906	*	0,013
	CAF	ATN	-56	-76,09 to -35,91	****	<0,0001
		IBU	34	13,91 to 54,09	****	<0,0001
		CAF	72	51,91 to 92,09	****	<0,0001
		TCS	43	22,91 to 63,09	****	<0,0001
Sw-6h	SMX	TCS	22	1,906 to 42,09	*	0,013
	CAF	ATN	-48	-68,09 to -27,91	****	<0,0001
		IBU	38	17,91 to 58,09	****	<0,0001
		CAF	56	35,91 to 76,09	****	<0,0001
		CAF	34	13,91 to 54,09	****	<0,0001
Sw-12h	TCS	SMX	28	7,906 to 48,09	****	<0,0001
		ATN	-21	-41,09 to -0,9057	*	0,027
	CAF	ATN	-29	-49,09 to -8,906	****	<0,0001
		IBU	21	0,9057 to 41,09	*	0,027
		SMX	36	15,91 to 56,09	****	<0,0001
Sw-24h	SMX	TCS	43	8,196 to 77,8	**	0,0013
	CAF	ATN	-53	-87,8 to -18,2	****	<0,0001
		IBU	48	13,2 to 82,8	****	<0,0001
		SMX	67	32,2 to 101,8	****	<0,0001
RP-6h	SMX	IBU	21	0,9057 to 41,09	*	0,027

Experiment	Tukey's multiple comparisons test	Comparing to	Mean Diff,	95,00% CI of diff,	Summary	Adjusted P Value
		TCS	43	22,91 to 63,09	****	<0,0001
		ATN	25	4,906 to 45,09	**	0,0011
		CAF	69	48,91 to 89,09	****	<0,0001
	IBU	TCS	22	1,906 to 42,09	*	0,013
	CAF	ATN	-44	-64,09 to -23,91	****	<0,0001
		TCS	26	5,906 to 46,09	***	0,0005
		IBU	48	27,91 to 68,09	****	<0,0001
RP-12h	TCS	IBU	56	35,91 to 76,09	****	<0,0001
		SMX	73	52,91 to 93,09	****	<0,0001
		ATN	-54	-74,09 to -33,91	****	<0,0001
	CAF	ATN	-50	-70,09 to -29,91	****	<0,0001
		IBU	52	31,91 to 72,09	****	<0,0001
		SMX	69	48,91 to 89,09	****	<0,0001
RP-24h	SMX	ATN	26	5,906 to 46,09	***	0,0005
		CAF	66	45,91 to 86,09	****	<0,0001
		IBU	23	2,906 to 43,09	**	0,006
		TCS	69	48,91 to 89,09	****	<0,0001
	TCS	IBU	46	25,91 to 66,09	****	<0,0001
		ATN	-43	-63,09 to -22,91	****	<0,0001
	CAF	ATN	-40	-60,09 to -19,91	****	<0,0001
		IBU	43	22,91 to 63,09	****	<0,0001

Annex 8. Resume of statistical significant differences observed for the same compound between the different experiments.

Compound	Tukey's multiple comparisons test	Comparing to	Mean Diff,	95,00% CI of diff,	Adjusted P Value	Adjusted P Value
SMX	CI-50	C-t7	-33	-53,09 to -12,91	****	<0,0001
		RP-12h	29	8,906 to 49,09	****	<0,0001
		RP-24h	27	6,906 to 47,09	***	0,0002
		RP-6h	33	12,91 to 53,09	****	<0,0001
		Sw-12h	25	4,906 to 45,09	**	0,0011
		Sw-6h	34	13,91 to 54,09	****	<0,0001
	CI-10	C-t7	-21	-41,09 to -0,9057	*	0,027
		RP-6h	21	0,9057 to 41,09	*	0,027
		Sw-6h	22	1,906 to 42,09	*	0,013
TCS	CI-10	C-t7	-36	-56,09 to -15,91	****	<0,0001
		RP-6h	35	14,91 to 55,09	****	<0,0001
		CI-50	-22	-42,09 to -1,906	*	0,013
	Sw-12h	C-t7	-24	-44,09 to -3,906	**	0,0026
		RP-6h	23	2,906 to 43,09	**	0,006
	Sw-6h	C-t7	-21	-41,09 to -0,9057	*	0,027
		Sw-6h	40	19,91 to 60,09	****	<0,0001
	RP-12h	C-t7	25	4,906 to 45,09	**	0,0011
		CI-10	61	40,91 to 81,09	****	<0,0001
		CI-50	39	18,91 to 59,09	****	<0,0001
		RP-6h	26	5,906 to 46,09	***	0,0005
		Sw-12h	49	28,91 to 69,09	****	<0,0001
		Sw-24h	36	7,582 to 64,42	***	0,0007
		Sw-6h	46	25,91 to 66,09	****	<0,0001
	RP-24h	CI-10	55	34,91 to 75,09	****	<0,0001
		CI-50	33	12,91 to 53,09	****	<0,0001
		Sw-12h	43	22,91 to 63,09	****	<0,0001
		Sw-24h	30	1,582 to 58,42	*	0,0232
CAF	Sw-12h	C-t7	-30	-50,09 to -9,906	****	<0,0001
		CI-10	-23	-43,09 to -2,906	**	0,006
		RP-12h	37	16,91 to 57,09	****	<0,0001
		RP-24h	32	11,91 to 52,09	****	<0,0001
		RP-6h	41	20,91 to 61,09	****	<0,0001

Compound	Tukey's multiple comparisons test	Comparing to	Mean Diff,	95,00% CI of diff,	Adjusted P Value	Adjusted P Value
		Sw-24h	29	0,5824 to 57,42	*	0,038
ATN	CI-10	C-t7	-22	-42,09 to -1,906	*	0,013
		RP-24h	25	4,906 to 45,09	**	0,0011
		RP-6h	30	9,906 to 50,09	****	<0,0001
	Sw-12h	RP-24h	21	0,9057 to 41,09	*	0,027
		RP-6h	26	5,906 to 46,09	***	0,0005

Annex 9. Associated RSD of the organic compounds distribution per section within soil section for all experiments

Soil Sections	Average (mg/kg d.w.)									RSD (%)								
	C-t7	CI-50	CI-10	Sw-6h	Sw-12h	Sw-24h	RP-6h	RP-12h	RP-24h	C-t7	CI-50	CI-10	Sw-6h	Sw-12h	Sw-24h	RP-6h	RP-12h	RP-24h
	SMX																	
Lα	0.15	0.05	0.33	0.88	0.24	0.13	0.17	0.09	0.14	5%	8%	3%	36%	10%	*	19%	*	17%
Cα	2.27	n.d.	0.55	1.91	1.46	1.13	1.76	1.46	1.48	0%	n.d.	24%	35%	9%	9%	17%	0%	18%
Rα	0.20	n.d.	0.10	0.55	n.d.	0.12	0.05	0.19	n.d.	7%	n.d.	*	52%	n.d.	8%	10%	16%	n.d.
Lβ	0.09	0.07	0.18	0.30	0.15	0.10	0.20	0.04	0.09	1%	1%	56%	5%	44%	35%	0%	1%	1%
Cβ	0.83	0.03	0.44	0.51	0.87	0.58	1.02	0.81	0.62	8%	8%	8%	15%	13%	20%	1%	21%	10%
Rβ	0.13	0.04	0.00	0.30	0.09	0.19	0.05	0.20	n.d.	8%	11%	0%	*	*	14%	3%	28%	n.d.
	IBU																	
Lα	0.70	1.73	2.33	1.84	0.66	0.63	0.42	n.d.	0.49	0%	2%	19%	42%	27%	44%	15%	n.d.	25%
Cα	3.96	n.d.	2.75	3.70	3.24	2.67	4.26	3.06	3.42	3%	n.d.	4%	64%	8%	13%	13%	6%	8%
Rα	0.60	n.d.	0.39	1.45	0.24	0.68	n.d.	0.28	n.d.	1%	n.d.	3%	107%	12%	*	n.d.	*	n.d.
Lβ	0.08	1.18	0.44	0.35	0.30	0.36	0.18	0.19	0.44	*	1%	30%	45%	19%	*	7%	*	22%
Cβ	1.19	0.14	1.12	0.68	0.82	0.57	1.41	1.81	0.93	3%	*	22%	55%	2%	27%	12%	11%	2%
Rβ	0.16	0.10	n.d.	0.63	0.31	0.37	n.d.	0.25	n.d.	0%	*	n.d.	*	*	29%	n.d.	8%	n.d.
	TCS																	
Lα	0.70	1.22	0.88	1.80	0.56	0.78	0.53	0.35	0.71	0%	3%	17%	83%	5%	3%	3%	12%	5%
Cα	7.12	1.07	4.34	4.70	5.18	4.38	7.97	7.72	7.46	2%	55%	20%	65%	21%	15%	28%	5%	11%
Rα	0.70	1.07	0.32	2.27	0.61	0.67	0.55	1.38	0.53	3%	21%	43%	95%	28%	13%	26%	25%	23%
Lβ	0.45	0.79	0.29	n.d.	0.50	0.88	0.53	0.47	0.49	3%	60%	*	n.d.	36%	17%	9%	18%	*
Cβ	1.71	0.43	0.76	1.10	0.50	0.89	0.72	1.43	0.83	5%	43%	37%	69%	24%	16%	21%	8%	11%
Rβ	0.63	0.75	0.45	0.84	0.47	0.51	0.43	0.86	1.22	5%	19%	25%	93%	18%	9%	10%	5%	9%
	CAF																	
Lα	n.d.	0.00	n.d.	1.08	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-	n.d.	8%	n.d.	n.d.	n.d.	n.d.	n.d.
Cα	4.15	0.00	3.53	2.03	2.68	2.93	3.70	3.55	3.03	5%	-	25%	29%	32%	5%	9%	2%	2%

Soil Sections	Average (mg/kg d.w.)									RSD (%)								
	C-t7	Cl-50	Cl-10	Sw-6h	Sw-12h	Sw-24h	RP-6h	RP-12h	RP-24h	C-t7	Cl-50	Cl-10	Sw-6h	Sw-12h	Sw-24h	RP-6h	RP-12h	RP-24h
Rα	n.d.	0.00	n.d.	0.89	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-	n.d.	3%	n.d.	n.d.	n.d.	n.d.	n.d.
Lβ	n.d.	0.00	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Cβ	n.d.	0.00	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
Rβ	n.d.	0.00	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	-	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
	ATN																	
Lα	0.62	0.00	0.52	1.90	0.23	0.75	0.40	0.24	0.30	3%	-	45%	109%	28%	38%	53%	*	10%
Cα	6.48	0.00	4.96	5.12	4.28	3.22	6.37	5.08	5.37	6%	-	23%	70%	24%	15%	13%	3%	12%
Rα	0.32	0.00	0.69	2.55	0.29	0.28	0.29	0.26	0.30	2%	-	62%	101%	17%	34%	7%	17%	29%
Lβ	0.21	0.00	0.12	0.18	0.21	0.27	0.30	0.29	0.24	1%	-	5%	21%	2%	26%	42%	19%	*
Cβ	0.69	0.00	0.40	0.68	0.28	0.41	0.54	0.60	0.37	7%	-	45%	71%	13%	9%	52%	9%	11%
Rβ	0.23	0.00	0.19	0.47	0.18	0.17	0.22	0.36	0.39	6%	-	6%	69%	6%	25%	13%	13%	5%

* *No stadard deviatios as one of the microcosm replicates presented values below MLD*

- Compound not tested

n.d. Not detected, below MLD

ANNEX 10

EREM 2018: "The 16th International Symposium on Electrokinetic Remediation"
Oral communication.

Electrokinetic remediation of PPCPs in soil: Effect of operating parameters.

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Water resources are under increasing pressure from rapidly growing demands across the globe. Thus, effluent reuse becomes increasingly important as an indispensable component of the integral water resource management, and is widely regarded as a sustainable approach in agricultural irrigation. However, it has been reported that pharmaceuticals and personal care products (PPCPs) are not completely removed from effluents in wastewater treatment plants (WWTPs), potentially exposing crops irrigated with these waters - reclaimed wastewater (RWW) - to these chemicals.

The electrokinetic (EK) process was applied to soil to assess the technology potential for PPCPs remediation. The initial technology optimization parameters were designed aiming a future *in situ* application. Basically, rectangular boxes (15x15x5 cm) were filled with 0.6 kg of non-sterilized soil. The microcosms were divided into three compartments (cathode:central:anode). Four graphite rods were used as electrodes as they are low cost and inert. The soil in the central compartment was spiked with the contaminants. For the evaluation of the system, a total of 8 EK experiments where conducted plus 2 controls (without current), all in duplicate. PPCPs were determined in distinct soil sections across the microcosm to assess the contaminants mobility under the influence of an electric field. Soil physicochemical parameters (including phosphorus availability) were also characterized. Results so far attained made evident that EK effect on PPCPs degradation depends on the conditions applied, in particular they apparently alter the diversity of degradation products being formed HPLC-DAD-FLD (data under validation).

Collectively, our results highlight the potential of EK as a promising technology for PPCPs removal from soil through enhancement of their degradation.

Keywords: Contaminants of emerging concern; soil remediation; electrochemistry; degradation; mobilization

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ANNEX 11

NAXOS 2018: "6th International Conference on Sustainable Solid Waste Management"

Poster communication.

Influence of the spiking procedure on organic contaminants recovery from soil

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As world demands for water grow, effluent reuse becomes increasingly important as an indispensable component of the integral water resource management, and is widely regarded as a sustainable approach in agricultural irrigation. Effluent reuse in agriculture also contributes to nutrients recycling, as phosphorus, alleviating pressure on over-exploited resources (e.g. phosphate rock, included in the EU list of 20 Critical Raw Materials). However, it has been reported that pharmaceuticals and personal care products (PPCPs) are not completely removed from effluent in wastewater treatment plants (WWTPs). Thus, the use of reclaimed wastewater (RWW) for the irrigation of crops may result in the continuous exposure of the agricultural environment to pharmaceutical and personal care products (PPCPs). In recent years, certain evidence indicates that these organic contaminants may become disseminated in agricultural soils as a result of irrigation with RWW but also due to the amendment with manure and biosolids. The PPCPs, and other related compounds, may undergo sorption/desorption and transformation processes (both biotic and abiotic), and have the potential to affect the soil microbiota. PPCPs found in the soil pore water (bioavailable fraction) as a result of RWW irrigation may be taken up by crop plants, bioaccumulate within plant tissues and subsequently enter the food webs, representing an important alternative pathway for the exposure of humans to PPCPs, with potential health implications.

While investigating the fate and remediation strategies for organic contaminants in the environment, unavoidably, a number of chemical analyses must be performed regarding the amount or the concentration of the parent compounds and/or their transformation products and/or their metabolites in samples taken from the relevant environmental receptors.

One important aspect when conducting laboratory scale studies, with non-contaminated samples, is the way with which the spiking procedure is generally performed to determine the recovery of the analytical method and prior the beginning o. Spiking environmental samples, in particular solid samples, with standard solution followed by immediate extraction, can lead to an overestimation of the recovery. This is so, because no time is given to the system to establish possible equilibria between the solid matter inorganic and/or organic—and the contaminant. Therefore, the spiking procedure needs to be reconsidered by including a study of the extractable amount of the contaminant versus the time elapsed between spiking and the extraction of the sample, as well as the conditions to which the samples were exposed to (e.g. light/no light).

In this work, the spiking procedure was investigated using 3 PPCPs as target analytes, a nonsteroidal anti-inflammatory, an antibiotic and an antibacterial and antifungal agent: Ibuprofen (IBU), sulfamethoxazole (SMX) and triclosan (TCS). The soil used was collected from an agricultural field used for organic tomato growth located in Santarém (39°12'42.6"N 8°42'41.5"W), Portugal.

Initially, an analytical methodology was developed enabling the determination of 3 PPCPs in soil samples. The target analytes are a nonsteroidal anti-inflammatory, an antibiotic and an antibacterial and antifungal agent: Ibuprofen (IBU), sulfamethoxazole (SMX) and triclosan (TCS). The sample preparation procedure is based on the quick, easy, cheap, effective, rugged and safe (QuEChERS) principle based on a salting-out extraction with a solvent (acetonitrile) followed by filtration using PTFE syringe filters (Table 1). Analysis was performed by high-performance liquid chromatography (HPLC) with diode array (DAD) and fluorescence (FLD) detectors (Table 2).

Table 1. QuEChERS extraction recoveries and validation parameters.

Compound	Recovery SE (%)[a]	Matrix effect (%)	Recovery (%)[b]	Repeatability (CV %)	Intermediate Precision (CV %)	MDL (mg/kg d.w.)	MQL (mg/kg d.w.)
SMX	91	+ 19	72	8.5	5.5	0.4	1.1
TCS	95	+ 23	91	19	6.1	1.2	3.6
IBU	102	+ 24	112	5.1	7.3	0.3	0.9

Legend: [a] Recovery for the spiked extracts; [b] Recovery for the spiked matrix;

Table 2. HPLC-DAD-FL method validation parameters

Compound	LOD[a] (mg/L)	LOQ[b] (mg/L)	Working range (mg/L)	r^2
IBU	0.18	0.55	0.5-15.0	1.000
SMX	0.58	1.75	0.5-15.0	0.999
TCS	0.14	0.45	0.5-15.0	1.000

For the spiking experiments the following variables were studied:

i. spiking volume;
ii. mechanical shaking, enhance compounds contact with soil and homogenization;
iii. sample drying, to allow water and solvent evaporation;
iv. storage at 4ºC, to simulate contamination aging while decreasing biological activity.

All tests were carried out in duplicate.

The results showed that the drying process had the highest impact on PPCPs recovery. The obtained results also indicate that by using a spiking volume of 1:1 (w:v), allowed to obtain higher recoveries with lower standard deviations. As the water was not evaporated, most of the PPCPs were in a bioavailable form, being more easily extracted. The best recoveries and the lowest relative standard deviations (RSD) were achieved when the soil was spiked using volume of 1:1 (w:v), followed by 2h of mechanical shaking and 3 days at 4ºC (91±2%, 72±1%, 112±6% for IBU, SMX and TCS, respectively).

The results here obtained are of valuable knowledge for the study of PPCPs in soil samples were a spiking procedure is required as it allows the development of reliable spiking procedures prior conducting remediation or environmental fate studies.

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ANNEX 12

10ENC: "10º Encontro Nacional de Cromatografia"
Poster communication.

A QuEChERS method followed by liquid chromatography for the quantification of three organic contaminants in soil samples

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Soil fertility is a condition regarded by the European Environment Agency as a natural capital. Sewage sludge is the residue originated from the wastewater treatment. The EU encourages treated sewage sludge (biosolids) use in agriculture (Directive86/278/EEC) as they are rich in organic matter also containing essential elements (e.g. nutrients). Although biosolids can improve soil fertility, there is an environmental and human risk due to the presence of organic contaminants (OCs), namely pharmaceutical and personal care products (PPCPs).

PPCPs are emerging OCs being frequently detected in biosolids worldwide. Once in the amended soils, PPCPs can be mobilized contaminating groundwater or be accumulated by living organisms, representing both an environmental and a health risk.

In this work, an analytical methodology is presented enabling the determination of three PPCPs in soil samples. The target analytes are a nonsteroidal anti-inflammatory, an antibiotic and an antibacterial and antifungal agent: Ibuprofen, sulfamethoxazole and triclosan.

The sample preparation procedure is based on the quick, easy, cheap, effective, rugged and safe (QuEChERS) principle based on a salting-out extraction with a solvent (acetonitrile) followed by a dispersive solid phase extraction (d-SPE). Analysis is performed by high-performance liquid chromatography (HPLC) with diode array (DAD) and fluorescence (FLD) detectors.

The method for the extraction, separation, detection and identification of these organic contaminants in the soil will provide a powerful tool to trace them in the environment and monitor the development of remediation technologies.

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