Effect of salinity on the fate of pesticides in irrigated systems: a first overview

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Abstract

This review investigates the impact of salinity on the fate of the active compounds of pesticides in a cultivated environment. Due to the over-exploitation of water resources and intensification of agriculture, salinity outbreaks are being observed more often in cultivated fields under pesticide treatments. Nevertheless, there is a poor understanding of the incidence of varying water salt loads on the behavior of pesticides' active ingredients in soil and water bodies. The present review established that water salinity can affect the diffusion of pesticides' active ingredients through numerous processes. Firstly, by increasing the vapor pressure and decreasing the solubility of the compounds, which is known as the salting-out effect, salinity can change the colligative properties of water towards molecules and the modification of exchange capacity and sorption onto the chemicals. It has also been established that the osmotic stress induced by salinity could inhibit the biodegradation process by reducing the activity of sensitive microorganisms. Moreover, soil properties like dissolved organic matter, organic carbon, clay content, and soil texture control the fate and availability of chemicals in different processes of persistence in water and soil matrix. In the same line, salinity promotes the formation of different complexes, such as between humic acid and the studied active compounds. Furthermore, salinity can modify the water flux due to soil clogging because of the coagulation and dispersion of clay particle cycles, especially when the change in salinity ranges is severe.

Keywords salinity, pesticides, fate, sorption, degradation, solubility, volatilization.

Introduction

The intensification of agriculture has led to the use of huge amounts of pesticides to manage diseases and increase yields (Ahmad et al. 2019). This can trigger important environmental issues because of the possible fate of these molecules in water, soil, air, and biotas (Sharma et al. 2019), in addition to their possible accumulation in crops, which leads to their integration into the food chain (Sharma et al. 2017). As the use of these compounds is still increasing, and their impact on the environment is growing, their fate deserves more study (Freed et al. 1979), and a detailed understanding of different processes that affect pesticides' fate is very important (Kaufman 1974).

Soil salinity is a major problem in arid and semi-arid areas, it covers 20% and 33% of total cultivated and agricultural irrigated lands worldwide respectively (Shrivastava and Kumar 2015) affecting both agricultural soils and natural ecosystems (de Souza Silva and Francisconi 2012) as it is represented by the increase, in terms of concentration, of the readily soluble salts in the water that circulates in the soil (Navarro-Torre et al. 2023) Salt accumulation in the crop root zone results from insufficient annual drainage (Bresler et al. 1982) or the use of saline irrigation water (Bernstein 1975), which negatively impacts agricultural production (Abou-Hadid 2003) and may influence the fate of pesticides in the environment by modifying sorption capabilities(Bailey and White 1970; Delle Site 2000) and degradation (de Souza Silva and Francisconi 2012). Most cultivated plants are affected by salinity exposure. An electrical conductivity threshold of 4 dS/m for saturated soil paste is considered a pertinent classification key to distinguishing saline soils (Richards 1954). Moreover, salinity of irrigation water is known to affect yields at levels greater than 2 g/l for sensitive crops and 5 g/l for most other crops (Richards 1954).

Moreover, soil solution salinity over 10 g/l causes immediate death for most non-halophyte cultivated plants. Within this range of salinities, the fate of pesticide ingredients and their metabolites varies and can be affected by (i) the physical and chemical properties of soil, such as pH, cation exchange capacity (CEC), organic matter (OM), etc.; (ii) the soil water content; (iii) the properties of the active compounds; and (iv) the application procedures and the cropping practices. Most of these factors have been studied and are well documented (Wauchope et al. 2002; Müller et al. 2007; Iglesias et al. 2009; Kodešová et al. 2011; Carpio et al. 2021).

Except for the cited properties, only a few published studies have investigated the effect of salinity on the fate of active ingredients of pesticides in soil or water, and some studies suggested a possible interaction between these compounds and salts. Pesticide dissipates in various ways, which include leaching, sorption, chemical, and biological degradation, and volatilization (Oloye et al. 2021), as shown in Fig. 1. Salinity can interfere with these processes and modify the fate of these chemicals in the environment. Salinity is known to decrease the solubility of synthetic organic compounds, particularly in estuaries in contact with seawater. This effect is known as "the salting-out effect" and leads either to their precipitation and sorption by sediments and other possible materials or to their increased volatilization (Saranjampour et al. 2017).

The purpose of the present review is to explore the potential effect of salinity on the environmental fate of some pesticides in cultivated areas considering a range of salinity in accordance with the survival of the plants. We collected published research papers investigating the effects of salinity on synthetic substances from laboratory and field experiments, which were mostly in the scope of oceanographic studies and agronomy. We focused on salinity's chemical impacts on sorption, solubility, degradation, and volatilization of pesticides and changes in hydrodynamic soil characteristics, which are the main processes affecting the fate of pesticides in cultivated soils (Wagenet 1983). Understanding the possible effects of salinity on pesticides' fates will allow us to distinguish situations with enhanced risk of contamination by pesticides due to salinity change and to provide recommendations to farmers and environmental agencies. Therefore, we discuss the effect of salinity on each process by considering the direct and indirect effects on the fate of some molecules in the environment under different conditions.
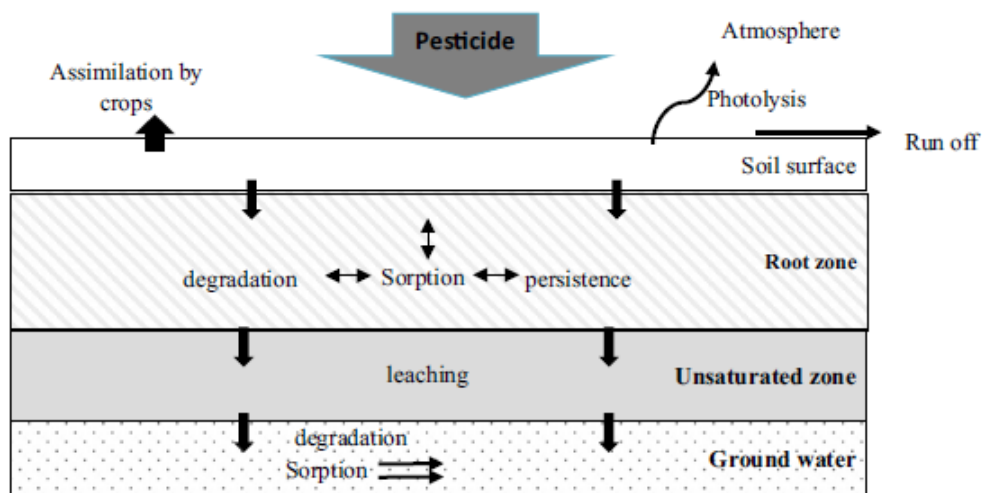

Fig. 1 Possible pathway of pesticides' fates in the environment (adapted from (Müller et. al. 2007))

Methods

We examined peer-reviewed articles discussing the influence of changing salinity on the fate of pesticides in the environment in several scientific publication databases (Google Scholar, Scopus, Science Direct, and Springer). To obtain the right information and to be able to include articles in the review, we added salinity, pesticides, the name of the active substances of pesticides, and some of the other possible keywords related to the environment, agriculture, adsorption, desorption, degradation, solubility, volatilization, and ionic strength. These different combinations led to multiple articles, which were filtered to exclude the irrelevant ones and duplicates. Finally, our review comprised 100 peer-reviewed scientific publications that were published between 1889 and 2021.

After analyzing these articles, we divided our review into seven sections. "Effect of salinity on soil hydrodynamics" describes the interaction of different electrolytes applied to soil and thr variation of the ionic force. This variation of soil or water salinity is explained in the second section, "Variations of salinity due to irrigation and scheduling of treatments." Different reactions of pesticides to salinity depending on each possible fate in the environment are detailed in the following sections: "The effect of salinity on the solubility of pesticides," "Effect of salinity on the sorption of pesticides," "Effect of salinity on pesticide degradation," and "Effect of salinity on pesticide volatilization." Finally, we synthesized the essential results and recommendations in the section, "Synthesis" and "Conclusions" which are presented in the last section of the paper.

We established the tables showing the effect of salinity on the solubility of pesticides and the groundwater ubiquity score (GUS). We collected all the information available in the chosen articles, and the lacking data on some

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pesticides were purchased from the "Pesticide Properties Database" website. For the solubility, the Setschenow constant (K_{salt}) was unavailable for the chosen pesticides under different salinity levels, so we used combinations of equations from Ni et al. (2000) and Ni and Yalkowsky (2003). For figures that show the effect of salinity on the adsorption and degradation of pesticides, a critical skimming of the available parameters in our database was performed to homogenize all data, which were grouped in an Excel sheet. All figures were designed using Excel.

Effect of salinity on soil hydrodynamics

Pesticides may be displaced in and above the soil by convection and diffusion in solution or adsorbed by suspended matter. Therefore, the fate of pesticides is controlled by water fluxes that depend on hydrodynamic soil characteristics. Soil scientists demonstrated the capacity of salinity to change the hydrodynamic characteristics of the soil (Yaron and Thomas 1968; Shainberg and Letey 1984; Quirk 1986; Rengasamy 2016). Solutions with high ionic strength percolating through and upon soil layers favor clay coagulation, particularly when bivalent ions (Ca^{2+}, Mg^{2+}, and Fe^{2+}) are present in the soil, depending on the CEC. However, solutions with low ionic concentrations may favor clay dispersion, particularly when monovalent ions (Na^+, K^+, and H^+) are present in the soil.

Soils with Na/CEC ratios (exchangeable sodium percentage (ESP)) over a threshold of 15% are considered "sodic soils" (Shainberg and Letey 1984). These soils may suffer from a dispersion phenomenon if exposed to fresh water. Soil dispersion comes with the destruction of the soil aggregates and the clogging of soil pores, resulting in a strong decrease in saturated hydraulic conductivity. These changes in soil structure hinder the remediation of the soil salinity as water cannot easily percolate through the dispersed layer. Soils that are exposed to the increase of sodium are characterized by a poor structure dominated by microporosity and low hydraulic conductivity and aeration (Rengasamy 2016) Irrigation with water presenting a high concentration of sodium is associated with significant evapotranspiration and poor drainage, as often encountered in semi-arid conditions. When this happens, salts concentrate in the root zone, permeability is increased because of clay coagulation, and sodium accumulates in the exchange complex of the soil. When rainfall or fresh water is applied to the soil, in the absence of a source of bivalent anions, the soil solution will be diluted, and with a high Na content, the soil may disperse (Eloubaidy et al. 1993). Using gypsum (or calcite) as a supplier of Ca^{2+} to the soil solution may prevent dispersion in certain conditions and maintain permeability (Ilyas et al. 1993; Rengasamy 2016; Navarro-Torre et al. 2023).

Variations of salinity due to irrigation and scheduling of treatments

When supplied with groundwater, irrigated soils in arid climates and coastal environments may also be affected by salinity. The upper limit for irrigation water in the case of salt-tolerant plants and permeable soil is known to be around 5 g/L (Zaman et al. 2018). Under the influence of evapotranspiration and deficient drainage, such salt supplies may trigger high salt concentrations in soil solutions, particularly near the surface, where higher capillarity driven by evaporation may form salt crusts (Grünberger et al. 2008). In contrast, when irrigation with groundwater alternates with supplies of fresh water from rainfall or from other sources of irrigation, like surface water from reservoirs or rivers, previously salt-enriched soils may suffer from dilution and dispersion at the first soil layer near the surface.

The effect of salinity on the solubility of pesticides

The mobility of phytosanitary chemical components is directly affected by their aqueous solubility (Schwarzenbach et al. 2003), which is strongly influenced by the presence of other electrolytes like soluble salts. Applied chemicals are transferred by water or soil solution to different environmental areas (Gunther et al. 1968). These chemicals' properties are very diverse and demonstrate variability in their solubility. For example, in distilled water, solubility varies from several grams to fractional pictograms per 0.1 liters, whereas with tap water containing moderate amounts of ions like calcium and magnesium ions, the solubility of some categories of compounds is increased. Thus, the solubility of chemicals in distilled water is not the same as in other types of water (Gunther et al. 1968).

The presence of salts in aqueous solutions influences solubility and can modify the properties of organic compounds in water (Xie et al. 1997). This behavior generally depends on the polarity of the salt and the solute (Ni et al. 2000). Moreover, chemical equilibrium reactions between solid and aqueous phases depend on the activity coefficients of the solutes and water as a solvent. Water's activity is decreased when the concentration of the solutes

144 increases (Jeon et al. 2011). Therefore, water molecules will be less available to dissolve ionic components, and the
145 solubility of some phytosanitary chemicals will be reduced.
146   Salting-out (decreasing of solubility in the presence of solutes) and salting-in (increasing of solubility in the
147 presence of solutes) describe the behavior of chemicals with salinity variation in aqueous solutions (Masterton and
148 Lee 1972). The salting-out effect is described by the Setschenow constant (Eq. 1) (Setschenow 1889):

149
$$log_{10}\left(\frac{S_{salt}}{S_0}\right) = -K_{salt}C_{salt} \qquad (1)$$

150

151 where S_{salt} is the solubility of the chemical in an aqueous saline solution, S_0 is the solubility of the chemical in pure
152 water, K_{salt} is the Setschenow constant (l.mol^{-1}), and C_{salt} is the molar concentration of the electrolyte (mol. l^{-1}). The
153 effect of salinity on the solubility of organic compounds has been studied by several scientists, and some of them
154 established equations that combine different constants and parameters such as the octanol-water partition coefficient
155 (K_{ow}) and LeBas volume (V_{LeBas}) to predict the constant K_{salt} for non-electrolytes in a solution of NaCl (Ni et al.
156 2000; Ni and Yalkowsky 2003):

157

$$K_{salt} = 0.039log_{10}(K_{ow}) + 0.017 \qquad (2)$$

$$log\left(\frac{S}{S0}\right) = -(0.039log_{10}(K_{ow}) + 0.017)C_{salt} \qquad (3)$$

158

159 where K_{salt} is the empirical Setschenow constant, C_{salt} is the molar concentration of the electrolyte, S_0 , and S are the
160 solubilities of the solute in water and saline solution, respectively, and K_{ow} is the octanol-water constant.
161   These equations establish a relationship between K_{salt} and the liposolubility of the substances. A liposoluble
162 ingredient with $log_{10}(K_{ow}) > 3$ will have $K_{salt} > 0.134$ (L.mol^{-1}). Consequently, its solubility will be decreased by
163 more than 17% by a molar concentration of NaCl of 58.4 g/L. Two other relationships related to the LeBas volume
164 (V_{LeBas}) and the molar volume (cm^3 mol^{-1}) have also been established:

165

166
$$K_{salt} = -0.027log_{10}S_0 + 0.135 \qquad (4)$$
167
$$K_{salt} = 0.0018V_{LeBas} \qquad (5)$$

168

169   Previously, solubility and K_{salt} were related as shown by Xie et al. (1997), but K_{salt} had a better correlation to
170 the octanol-water partition constant than the LeBas volume and logS$_0$. Because of the lack of information on the
171 effect of salinity on the solubility of pesticides, these previously cited equations have been used to have a better
172 view of the possible effects of the increase in salt concentration on the fate of some pesticides. Knowing the solubility
173 in freshwater or V_{LeBas} of cited pesticides makes it easy to determine their solubilities under several salinities, as
174 shown in Table 1. The choice of salinity range is based on the tolerance to salinity for different crops by assuming
175 that a salinity of 2 g/l is tolerable by sensitive crops and that only tolerant crops can survive to a salinity of 5 g/l
176 (Richards 1954).
177   Solubility plays a big role in conditioning the fate of pesticides in the environment and it can be considered as
178 the most important factor that can be used to evaluate their behavior (Schwarzenbach et al. 2003). This factor
179 regulates the adsorption of chemicals by sediments and soil, as reported by Babu et al. (2011), who showed that
180 malathion adsorption on sediments was very low in saline conditions due to its high solubility in water (145 mg/l at
181 25°C). In contrast, the adsorption of chlorpyrifos was found to have the highest levels in sediments because of its
182 low solubility in water and short half-life.
183   Even if sodium chloride is overwhelmingly dominant in concerns about salinity in cultivated soils, other
184 dissolved salts may be present (Cheverry and Fontes 1979; Eugster and Maglione 1979). Their potential to decrease
185 or increase the solubility of lindane has been studied by Masterton and Lee (1972), and the pesticide showed a
186 different behavior with different types of dissolved salts at high concentrations. Most of the tested salts decreased
187 the solubility of lindane, especially with alkali fluorides (KF and NaF). The salts that increased the solubility of
188 lindane in the water contained large cations like $(CH_3)_4^+$ and $(C_2H_5)_4N^+$ or large halide ions like I$^+$. Those that
189 decreased the solubility of lindane can be divided into three groups depending on the size of the anions: i) salts
190 including fluoride electrolytes (ionic size equal to 147 pm), ii) salts with chloride ions (ionic size equal to 175 pm),
191 and iii) salts containing bromide ions (ionic size equal to 186 pm).
192   When in contact, cations and organic functional groups may react and establish bridges that lead to the
193 construction of a complex called a "salt linkage." Cations are then surrounded by water molecules that favor organic
194 functional groups to substitute for water or to generate an inner-sphere complex. The incapability of the organic
195 molecules of displacing the water molecules leads to the water-bridging phenomenon (Koskinen and Harper 1990).

196 Furthermore, the capability of organic molecules to replace a water molecule is dependent on the ionic size and the
197 heat of hydration of the salt cation. As a result, the smaller the size of the cation involved, the less bridging occurs.
198
199

Table 1 Effect of salinity on the solubility of some pesticides

	Chemical family	Common name	Log (K_{ow}) [a]	K_{salt} [c]	(S_0) [b] (g/l)	(S) [d] 2 g/l	(S) [d] 5 g/l
Insecticides	Organochlorines	Lindane	3.5	0.1535	0.00852	0.00146	0.00025
		Endosulfan	4.74	0.2019	0.00032	0.00013	0.00003
		Chlordecone	4.5	0.1925	0.003	0.00124	0.00033
	Organophosphorus	Chlorpyrifos	4.7	0.2003	0.001	0.00042	0.00010
		Propetamphos	3.82	0.166	0.11	0.05122	0.01627
Herbicides	Substituted ureas	Linuron	3	0.134	0.064	0.03442	0.01364
		Diuron	2.87	0.129	0.036	0.01966	0.00807
		Isoproturon	2.5	0.115	0.07	0.04143	0.01879
	Chloroacetamide	Alachlor	3.09	0.137	0.24	0.12741	0.04928
	Triazines	Atrazine	2.7	0.122	0.035	0.01993	0.00856
	Nitriles	Dichlobenil	2.7	0.122	0.0212	0.012207	0.00519
	Uracils	Bromacil	1.88	0.090	0.815	0.538	0.288
	Triazines	Simazine	2.3	0.107	0.005	0.003	0.001
	Triazines	Terbuthylazine	3.4	0.150	0.007	0.003	0.001
	Triazines	Hexazinone	1.17	0.063	33	24.732	16.046
	Pyridazinones	Norflurazon	2.45	0.113	0.034	0.020	0.009
	Neonicotinoids	Imidacloprid	0.57	0.039	0.610	0.509	0.388

[a] Log (K_{ow}) at pH=7 and Temperature= 20°C available at PPDB (pesticides properties database)
[b] Solubility in water at 20°C available at PPDB (pesticides properties database)
[c] Setschenow constant predicted from (equation 2)
[d] Solubility in saline water predicted from (equation 4)

200

Effect of salinity on the sorption of pesticides

Effect of salinity on the adsorption process

203 Sorption reactions are considered to be one of the key processes that regulate and control the interaction between
204 pesticides, water, and different soil phases (McCarthy and Zachara 1989). Thus, sorption and desorption are often
205 steps that limit the rate of global dissipation in soils (Oloye et al. 2021). They have a large effect on the rate of
206 volatilization, solubility, and degradation of chemicals as they influence the concentration of pesticides remaining
207 in the soil matrix (Müller et al. 2007). They also influence transport and both chemical and biological
208 transformations (Koskinen and Harper 1990). Sorption depends on both the properties of the sorbent and the
209 chemical (Oloye et al. 2021) and it can be increased, decreased, or even kept constant with changes in the sorbent
210 properties (Mamy and Barriuso 2007).
211 The literature is replete with papers that investigate the sorption of various pesticides' active compounds under
212 different laboratory and field conditions, such as pH (Gao et al. 1998; Tsai et al. 2003; Sheng et al. 2005; Kodešová
213 et al. 2011). However, there are few experimental data and studies that define the relationship between salinity and
214 the sorption process (Oloye et al. 2021). Sorption is distinguished by the partitioning coefficient K_d, which indicates
215 the distribution of solutes between soil and water (Wauchope et al. 2002):

$$Kd = \frac{Cs}{Ce} \quad (6)$$

217 where C_s is the concentration of solute retained on particles ($\mu g.g^{-1}$), and C_e is the concentration of solute at
218 equilibrium in the solution ($\mu g.ml^{-1}$). K_d has the units of a ratio between volume and weight ($ml.g^{-1}$ or $L.kg^{1}$). In
219 some cases, the carbon normalized sorption coefficient K_{oc} (Eq. 7) is used to quantify the attraction of synthetic
220 compounds to the soil organic carbon fraction because the sorption process also occurs with organic soil fraction,
221 not only the mineral fraction (Wauchope et al. 2002; Gagné et al. 2011):

$$K_{oc} = \frac{K_{ds}}{f^{oc}} \quad (7)$$

223 where f^{oc} is the organic carbon content (%), K_{ds} is the sorption distribution coefficient of organic matter, and K_{oc} is
224 the carbon normalized sorption coefficient.
225 K_{ds} is highly influenced by pesticide characteristics like molecular size, molecular charge, anionic exchange,
226 etc. (Gao et al. 1998), and salinity. Salinity has a large effect on the partitioning of solutes between the solid phase
227 and the aqueous phase as it can intervene in different ways in the modification of some structural factors governing
228 the sorption. The activity of water can decline with the accretion of salt ions by capturing water molecules (Jeon et

229 al. 2011). This leads to a decrease in solubility (Leberman and Soper 1995; Turner and Rawling 2001) and modifies
230 the charge state of the sorbent (Dontsova and Bigham 2005; Higgins and Luthy 2006). This portioning coefficient,
231 K_{ds}, is then used to describe and evaluate the sorption process by establishing kinetics and isotherm models, like the
232 Langmuir, Elovich, Freundlich, Temkin, Fowler-Guggenheim, Hill De Boer, Kiselev, and other models (Yu and
233 Larionov 1961; Ferrandon et al. 1989; Largitte and Pasquier 2016)).

234   The simplest and most used equation to define the portioning coefficient relationship between the matrix and
235 water concentration is a linear equation. It is suitable for a determinate range of ingredient concentrations, assuming
236 that sorption sites are not all occupied. Freundlich isotherms (Eq. 8) and the Langmuir equation (equation 9) are
237 used when the concentration of adsorbed pesticide influences the number and quality of the available sorption sites
238 (Gagné et al. 2011):

$$C_s = K_f (C_e)^n \qquad (8)$$

240 where K_f is the Freundlich sorption coefficient, n is a linearity parameter, and C_e and C_s are previously described in
241 (Eq. 6). When n = 1, the equation is a simple proportion, and K_f is equal to K_d:

$$C_s = \frac{C_{s,max} K_L C_e}{1 + K_L C_e} \qquad (9)$$

243 where $C_{s,max}$ is the maximal sorption capacity, and K_L is the Langmuir sorption coefficient related to the energy of
244 sorption.

245   The effect of salinity on the sorption of pesticides depends on factors such as the characteristics of chemicals
246 themselves as they are responsible for their sorption in soil (Bailey and White 1970), as well as the type and
247 concentration of salt, and the type of sorbent (Tramonti et al. 1986; Laird et al. 1992; Gonzalez-Davila et al. 1992;
248 Lee et al. 2003; Ureña-Amate et al. 2005; Li et al. 2006; García-Ortega et al. 2011). It can lead to a decrease or
249 increase in pesticide sorption. For instance, Noicharoen et al. (2012) studied the effect of marine high marine salinity
250 on paraquat's adsorption onto river sediments. Paraquat is an herbicide characterized by high adsorption on organic
251 materials in soils. They also studied its immobility, resistance to bio- and photodegradation, and its high half-life in
252 the environment.

253   Salinity from 10 to 20 g/l contributes to the decrease of sorption compared to very low salinities of freshwater
254 (0 g/l). The Freundlich constant (K_F) decreased from freshwater to saline water at a salinity of 10 g/l by 69.1% and
255 by 75.4% at a salinity of 20 g/l. This decrease is due to the saline waters' high concentrations of cations, such as
256 sodium, calcium, and magnesium, which affect the adsorption of paraquat due to the competition for available
257 exchange sites. When Na^+, Ca^{2+}, and Mg^{2+} are on exterior or open sites, paraquat displaces them, but it is more
258 difficult for the chemical to compete for adsorption sites with divalent inorganic cations when CEC rises. This
259 phenomenon is particular to substances with ionic structures, and paraquat is frequently present as a dichloride
260 (Noicharoen et al. 2012).

261   Linuron is an herbicide characterized by low solubility in water and low vapor pressure. At the same
262 concentration of 20 g/l of NaCl, the adsorption of linuron on modified bentonites was decreased by 50% compared
263 to 0 g/l of NaCl (El-Nahhal and Lagaly 2005). This was the result of the role that salts play in the structure of water.
264 When the concentration of salt increases, it penetrates the space between the sorbent's layers, which leads to a
265 decrease in the adsorption of a second component (Leontidis 2002; El-Nahhal and Lagaly 2005).

266   Evaluations of the sorption potential of chemicals under specific conditions are mainly conducted in the
267 laboratory. Batch equilibrium experiments are the protocols most used to measure coefficients of adsorption and
268 desorption. Protocols usually use salts (mainly $CaCl_2$ and KCl) to improve the centrifugation step by coagulation
269 and minimize cation exchange. Nevertheless, the addition of salt was found to affect sorption values. For instance,
270 Li et al. (2006) found that when the concentration of KCl increased from 0.01 M to 0.3 M, the adsorption of alachlor
271 increased by more than 5 times, and for atrazine, dichlorobenil, and diuron, it increased by almost 3.5 times. Along
272 the same lines, Alva and Singh (1991) reported that for a concentration between 1 and 2 M, the adsorption of
273 bromacil, simazine, norflurazon, and diuron increased by 25%, 27%, 21%, and 20%, respectively. These results do
274 not prevent KCl from decreasing the adsorption in other cases. For example, Tramonti et al. (1986) reported that at
275 a KCl concentration of 0.1 M, the adsorption of lindane on fulvic acid decreased by almost 60%.

276   An increase in $CaCl_2$ concentration from 0.001 M to 1 M increased the adsorption of alachlor and atrazine on
277 smectite by 2.17 times and 1.13 times, respectively (Li et al. 2006). It also increased those of bromacil, simazine,
278 norflurazon, and diuron on fine sand by 33%, 32%, 14%, and 17%, respectively (Alva and Singh 1991). It was also
279 increased for atrazine by 1.04 times on humic acid and by 1.44 times on silica gel. Rodríguez-Liébana et al. (2011)
280 showed decreases by 5 times and 2 times for a-cypermethrin and deltamethrin, respectively. In other cases, $CaCl_2$
281 decreased the adsorption of dichlobenil on smectite by 0.78 times and that of diuron by 0.93 times (Li et al. 2006).

282   These results demonstrate the various ways in which pesticides can be maintained or not in the matrix. The
283 increase of the ionic strength due to the presence of KCl promotes the formation of ordered clay quasicrystals and
284 the narrowing of the distance between clay layers, which leads to the easy incorporation of pesticides and enhances
285 the sorption (Li et al. 2006). However, the ionic strength does not play a big role in enhancing the sorption of
286 dichlobenil and diuron when using $CaCl_2$. This is due to the hydration enthalpy of Ca^{2+}, which is greater than that

287 of K$^+$ and promotes more clay coagulation. This leads to the establishment of interaction between functional groups
288 of pesticides (Li et al. 2006).
289   Ionic strength has a role in dispersing soil aggregates and increasing the charge sites available for minerals,
290 which promotes the adsorption of pesticides. The increase in available sites increases the adsorption of ionic
291 pesticides, but not non-ionic ones, which are mainly adsorbed by cation-pesticide bonding (Gillman and Bell 1976;
292 Berkheiser et al. 1980; Gillman et al. 1981; Bolan et al. 1986; Alva and Singh 1991). This demonstrates the big role
293 that ionic strength has in the stimulation of adsorption, which shows the importance of electrostatic interactions in
294 the adsorption process (Kovaios et al. 2011). Furthermore, Ca^{2+} cations can interact with pesticides' functional
295 groups and enhance adsorption more than Na$^+$ cations, as demonstrated by Pereira et al. (2020). They studied the
296 effect of NaCl and CaCl$_2$ on the adsorption of glyphosate on montmorillonite and found that an increase in NaCl
297 concentration from 0.1 M to 0.5 M decreased the glyphosate adsorption compared to the increase in CaCl$_2$
298 concentration. This is in line with the results from the work of Spark and Swift (2002) which showed the increase
299 of 2,4-D adsorption at high Ca^{2+} suggesting that a salt bridge might be involved in some of the absorption, with the
300 Ca^{2+} cation functioning as a bridge between the pesticide and the negatively charged organic matter or negatively
301 charged clay particles.
302   The characteristics of the active compound also affect sorption. For instance, industrial propetamphos (PPT-
303 Ind) and propetamphos-Analar (PPT-A) behave differently upon changes in salinity from 0 to 40 g/kg. After 24 h,
304 the increase of salinity led to increased adsorption of PPT-A by 1.45 times in high estuary sediment and by 1.31
305 times in low estuary sediment. For the PPT-Ind, the increase of salinity increased its adsorption by 1.28 times in
306 high estuary sediments (García-Ortega et al. 2011).
307   K$_f$ of atrazine adsorption on two soil samples increased from 1.14 at a soil salinity of 1 mM to 1.41 and 1.84 at
308 salinities of 8.64 and 9 mM, respectively. In contrast, when the salinities reached 40 mM of sodium and 60 mM of
309 calcium, the desorption process was enhanced, and sorption was decreased (Gonzalez-Davila et al. 1992). High
310 sodium concentrations may alter the configuration of the diffuse layer in soil particles, which favors the interaction
311 of atrazine with the adsorbed surfaces. Therefore, after passing a certain salinity threshold, the sorption capability
312 of atrazine decreased (Gonzalez-Davila et al. 1992).
313   Kodešová et al. (2011) investigated the adsorption of some pesticides on different soils with different properties
314 under different environmental conditions. The results showed that when combined with other parameters, salinity
315 affects the sorption of the studied compound. The coefficient K$_f$ of terbuthylazine and hexazinone, two pesticides
316 with moderate solubility and adsorption ability, depends on the organic matter content, sorption capacity saturation,
317 and salinity. For hexazinone, K$_f$ had a better correlation with the combined effect of clay content, pH$_{Kcl}$, and salinity
318 than with each parameter separately. For chlormequat chloride, a better correlation was obtained when combining
319 sand content, pH$_{Kcl}$, and salinity.
320   Some research works have found that salinity decreases the adsorption process, which can occur for many
321 different reasons. (Mézin and Hale 2004) investigated the effect of salinity on the adsorption of DDT and
322 chlorpyrifos (CPF) on humic acid by solid-phase microextraction uptake. The results showed that the sorption of
323 DDT on humic acid was greater than that of CPF and was affected by the increase in salinity. For both pesticides,
324 the impact was more significant at low salinity levels between 1 and 5‰, which means that increasing salinity levels
325 (20‰) decreases the adsorption of these two pesticides on humic acid. The authors concluded that riverine transport
326 of DDT and the lesser range of CPF could be initially controlled by their association with dissolved organic carbon
327 (DOC). Upon encountering an increasing salinity regime, the pesticides may be released from the DOC back into
328 the freely dissolved pool and hence become bioavailable again.
329   Similarly, Gonzalez-Davila et al. (1992) studied the sorption of lindane on chitin in seawater, showing that the
330 decrease in salinity leads to a decrease in the adsorption-desorption process. This decrease is due to the impact that
331 salinity has on the charge of the surface and the layer properties of the humidified particles. It can also be affected
332 by the ionic strength of solutes, which leads to the diffusion of solutes into the pores.
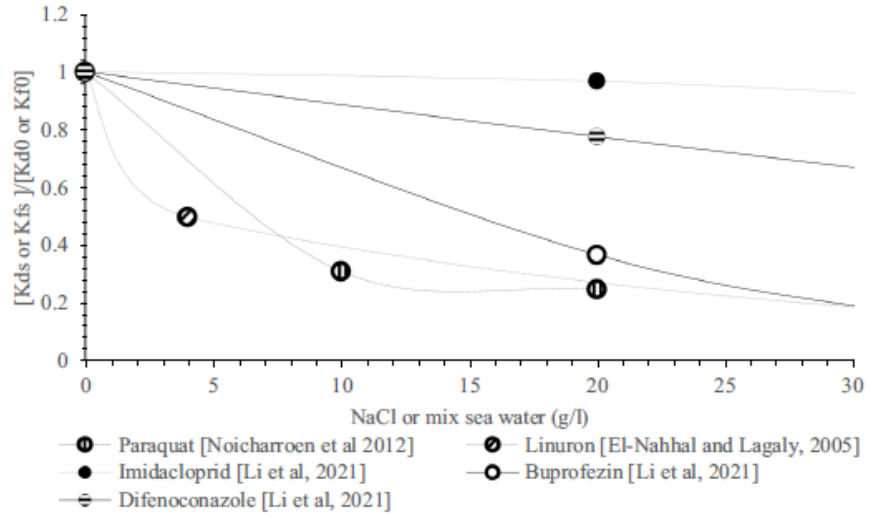333   In some cases, the high mobility of the chemical to the aqueous phase and its retention by sediments are
334 explained by persistent chemicals being adsorbed by a biological matrix, which was studied by Soubaneh et al.
335 (2015). The experiment consisted of testing the persistence of two toxaphene congeners, B8-1413 and B9-1679, on
336 marine sediments at high salinity (30 psu). The results showed that these two chemicals were distributed between
337 sediments and a biological matrix with high sorption values, but on average, they were 2.5 times less entrapped in
338 sediments compared to B7-1450 (Soubaneh et al. 2014), which is known to accumulate predominantly in sediments.
339   All these results demonstrate that chemicals' fates are subject to competition between different processes that
340 lead to the variability of the movement of pesticides in the environment. Depending on the type of sorbent, chemicals
341 behave differently with different salinity ranges. Many studies have used different types of sorbents, ranging from
342 soil and water to other types, such as organic ones like chitin, and even plastic, which acts as a carrier for pesticides
343 in water.
344   Li et al. (2021) studied the adsorptive capacity of polyethylene microplastic for three pesticides (imidacloprid,
345 buprofezin, and difenoconazole) under saline conditions. They established that increasing NaCl levels (0%, 2%, and

346 3.5%) decrease the adsorption of these pesticides onto microplastics. Fig. 2 shows the behavior of some pesticides
347 in the literature, which are described by the ratio between the adsorption constant in saline and non-saline conditions
348 when NaCl salt is prevalent.
349

Fig. 2 Effect of increasing salinity on some pesticides' adsorption

Paraquat [Noicharroen et al 2012]   Linuron [El-Nahhal and Lagaly, 2005]
Imidacloprid [Li et al, 2021]   Buprofezin [Li et al, 2021]
Difenoconazole [Li et al, 2021]

350

351 **Effect of salinity on the desorption process**

352 The desorption process is the inverse of adsorption and corresponds to the release of the adsorbed molecules in an
353 aqueous phase from the solid phase. Understanding this mechanism is very important as it shows whether a chemical
354 is reversibly or irreversibly adsorbed on a sorbent. It can be time-dependent and require energy to be activated
355 (Pignatello and Xing 1996; Beulke et al. 2004). It can also affect the extent of release of pesticides from sediment
356 (Gao et al. 1998). It can be sometimes much less effective and incomplete, even after a long equilibration time (Gao
357 et al. 1998). But in some cases, it can occur and complete in minutes after the adsorption process, and more time is
358 not required to produce more desorption (Gonzalez-Davila et al. 1992).
359   When the adsorption is reversible, the same amounts of a chemical can be adsorbed and desorbed on solid
360 phases. However, when adsorption is irreversible, a hysteresis process can occur, which is explained by the adhesion
361 of the pesticide molecule to soil aggregates, diffusion inside the nanopores, and adsorption and loss due to
362 degradation (Pignatello and Xing 1996; Beulke et al. 2004). Desorption is also described by isotherms with
363 Freundlich models established by Barriuso et al. (1992) to consider the adsorbed amounts of chemicals before the
364 desorption process occurs. For this, the Freundlich equation becomes (Eq.10):
365

366 $$(Q_{ads0} - Q_{ads}) = K_{fd} * (C_{e0} - C_e)^{n_{fd}} \qquad (10)$$

367

368 where Q_{ads} is the amount adsorbed at a time t (µg/Kg), Q_{ads0} is the amount initially adsorbed (µg/Kg), K_{fd} is the
369 desorption capacity constant (l/g), n_{fd} is the desorption intensity, C_{e0} is the concentration at equilibrium before the
370 desorption is conducted (µg/l), and C_e is the final concentration (µg/l).
371   Commonly, research papers on the sorption process investigate adsorption and desorption at the same time.
372 Nevertheless, depending on the goal and the problems, it can sometimes not be a priority for researchers to study
373 the desorption process. Some cited research has studied this inverse process for further explanation of the effect that
374 salinity has on sorption and to explain the behavior of chemicals in the environment under different laboratory and
375 field conditions.
376   Desorption processes can be very competitive with sorption, with desorption taking place very rapidly after
377 sorption starts. This does not mean that this competitive behavior can be observed for similar chemicals. To explain
378 this, Soubaneh et al. (2014) studied the effect of high salinity ranges of water on the adsorption and the desorption
379 of two toxaphene congeners on marine sediments. As a result, no competition was reported.
380   Desorption can be inversely related to the sorption affinity of chemicals, which can be related to the electrolyte
381 concentration, as reported by Alva and Singh (1991). They investigated the adsorption/desorption capacity of four
382 herbicides as a function of ionic strength and cations. The results showed that desorption of all used chemicals
383 increased with increasing concentration of the electrolyte during the sorption process.

El-Nahhal and Lagaly (2005) studied the desorption process of linuron from the modified bentonites, and its rate was reduced in saline (NaCl) solution like the adsorption rate. Also, salinity had very little effect on the desorption of Analar-PPT in estuarine sediments (García-Ortega et al. 2011). Desorption of sorbed paraquat from the soil in the study carried out by Noicharoen et al. (2012) was reliant upon both the measure of paraquat adsorbed on the soil and salinity. A more noteworthy amount was desorbed from sediment containing the biggest measure of adsorbed paraquat. Likewise, just 1% of bound paraquat was remobilized from sediment in freshwater (0 g/l). Interestingly, a significant amount of paraquat (30%) was desorbed at a salinity of 20 g L^{-1} or higher.

Effect of salinity on pesticides' degradation

Chemical and physical degradation is a major process that influences the concentration of pesticides in a soil matrix and their availability for other possible processes (Huang et al. 2018).In most of the reported experiments, adsorption-desorption processes were completed considering short times (24-48H) but longer experimental studies were required. . Degradation happens in several ways and can be biotic and abiotic. Examples are catalyzed reactions, hydrolysis, photolysis, oxidative reactions, reductive reactions, hydrolytic reactions, and synthetic reactions (Pionke and Chesters 1973; Skipper et al. 1978; Wolfe et al. 2018).

The degradation of pesticides in the environment is influenced by many factors: physicochemical properties of the active compounds of the pesticides and environmental factors (Müller et al. 2007). Bacterial biodegradation is considered to be the most important way that pesticides break down (Pionke and Chesters 1973; Carpio et al. 2021). On a similar note, the influence of the sorbent's nature has a big impact when studying the effect of salinity on the degradation rate of pesticides. When in contact with water or soil, salinity has different behavior, which controls the fate of chemicals. These factors have been investigated by many researchers for several pesticides under various laboratory and natural conditions.

Chemical degradation is strongly influenced by organic matter and clay content (Yaron and Thomas 1968; Jones et al. 1982), pH (Huang et al. 2018), and temperature (Getzin 1981). All these factors and conditions that impact the rate of degradation emphasize the possible effect that salinity can have on the fate of some pesticides. The degradation of pesticides was studied by laboratory experiments under stabilized environmental conditions to calculate the half-life and the remaining pesticide concentration (Müller et al. 2007). The degradation rate is most commonly estimated by a simple first-order expression as a function of time, where the speed of degradation depends on what remains of the original concentration (Müller et al. 2007):

$$\frac{dC_h}{dt} = K.C_h \qquad (11)$$

where C_h is the concentration of pesticide, K is the degradation rate constant, h is the order of the reaction, and t is the time.

The impact of salinity on pesticide degradation has been studied, and results demonstrate the important effect that salinity has on the degradation of some pesticides in water and soil. However, the biological degradation has not been documented much because of the long period that pesticides require to be degraded by microorganisms (Oloye et al. 2021). Salinity can control the degradation of chemicals in some cases in water or soil matrix by either reducing or increasing the rate or even inhibiting the whole process. It is described to have a decisive effect on the microbial communities in the soil matrix, which are responsible for most pesticides' biodegradation. Salinization may affect the metabolism of the organisms present in the soil (de Souza Silva and Francisconi 2012; Abdul Rahman et al. 2021) and reduce their activities (Tripathi et al. 2006; Chowdhury et al. 2011; Mavi and Marschner 2012; Otlewska et al. 2020). The inhibition effect on the microorganisms in terms of amount and activity (Mavi and Marschner 2017) is explained by the osmotic stress from ionic cellular imbalance, which leads to excess use of energy to expel sodium ions from the cells (de Souza Silva and Francisconi 2012).

Some studies demonstrated the negative impact that increasing salinity has on the biodegradation of some pesticide's active ingredients and it can change the resistance to the chemical contaminants of some communities that govern some soils (Jokar et al. 2022) . Yun et al. (2010) investigated the fate of chlorpyrifos using degradation with three different salinity levels. They showed that increased salinity led to a decreased degradation rate by increasing the half-life from 7.1 days to 10 days and 16.9 days when increasing salinity from 4.6 to 9.7 and 14.4 dSm^{-1}, respectively. This effect was explained by the fact that salinity attenuated microbial activity (Yun et al. 2010).Similarly, lin et al (2008) showed that increasing salinity from 0 g/l to 15 g/l inhibited atrazine degradation by decreasing microorganisms activity, mentioning an increased half-life from 18,8 days to 36,1 days. . The degradation of lactofen, a selective herbicide, and fungicide, is slowed down in salinized soil compared to control soil. Salinity affects the microorganisms responsible for the degradation of this pesticide (Liang et al. 2010). The half-life increased from 1.99 days to 2.54 days when increasing the salinity to 5 g/l with NaCl.

Similarly, the degradation of parathion in non-saline soils was quicker than in saline ones, which was explained by the rate of degradation decreasing within 6 days. The rate of degradation of parathion in non-saline soils was 76% compared to 14.5% in saline soils with an electrical conductivity of 0 dS^{-1} and 30.5 dS^{-1}, respectively

441 (Rajasekhar Reddy and Sethunathan 1985). The degradation of parathion as a function of salinity was mostly studied
442 in water. In this context, some results showed that salinity would have an effect (Walker 1976) or can present an
443 inhibiting factor (Kodama and Kuwatsuka 1980) as the degradation of parathion in seawater mainly occurs through
444 chemically mediated dearylation and dealkylation (Weber 1976). In soils, Reddy and Sethunathan (1985) found that
445 the inhibitory effect of salinity on the degradation of parathion in flooded soils was not due to hydrolysis but to
446 nitro-group reduction, which is the result of the activity of microbes.

447   The degradation of parathion was also studied by Kodama and Kuwatsuka (1980), who demonstrated that
448 salinity decreased the degradation rate. The percentage of residues increased with the addition of salt water from
449 30% to almost 85%when switching salinity condition from river to seawater.. The observation of bacterial activity
450 inhibition was consistent with previous studies (Kodama and Kuwatsuka 1980). Similarly, Yang et al. (2012) studied
451 the effect of salinity on the bensulfuron-methyl degradation and showed that the increase in salinity led to a decrease
452 in the degradation rate in riparian soil. Compared to no salt treatments, the half-lives were prolonged by 4.9% and
453 21.1% for 20% and 50% salt treatments, respectively. The addition of 50% of salt inhibited the activity of microbes:
454 the fluorescein diacetate hydrolysis rate decreased by 74.1%, the microbial adenosine triphosphate rate decreased
455 by 69.8%, and the basal soil respiration decreased rate by 63.4%.

456   Aside from bacterial inhibition, physical effects may influence the degradation. For instance, Mateus et al.
457 (2000) studied the rate of photodegradation of fenarimol under saline conditions (0.5 M) with solar radiation or a
458 photoreactor using different salt solutions (NaCl, NaBr, $BaCl_2$, and $ZnCl_2$). The results showed a decrease in
459 degradation rate by photolysis when adding salts, which changed from 0.67 h^{-1} in the absence of salt to 0.11 h^{-1} in
460 the presence of $BaCl_2$. This was due to the presence of halide ions. (Chaabane et al. 2007) studied sulcotrione, a
461 triketone herbicide, which exhibited a faster photodegradation with half-lives of 3.6 h and 10 h when changing from
462 no salinity to 24 g/l of NaCl, respectively. This was due to the presence of nitrate and nitrite at higher concentrations.

463   Navarro et al. (2000) studied the degradation of endosulfan (α and β) in seawater and sediments. The dissipation
464 rate of the pesticide was compared between seawater and pure water and then in both sterile and unsterile marine
465 sediments. The dissipation in seawater was faster than in pure water. For α-endosulfan, the degradation in sterile
466 sediments was four times greater than in unsterile sediment, while for β-endosulfan, the dissipation in unsterile
467 sediment was double that observed in the sterile one. Overall, the dissipation rate of endosulfan in seawater was
468 higher than in pure water and greater in unsterile sediments than in sterile ones (Navarro et al. 2000). Biological
469 activity favored the degradation of the pesticide, and the characteristics of the two isomers played a role in
470 controlling the dissipation under different environmental and laboratory conditions.

471   Cotham and Bidleman (1989) studied the persistence of malathion, fenvelerate, and endosulfan under different
472 salinity conditions. Two experiments were conducted: one was carried out over 40 days with sterile and unsterile
473 seawater at a salinity of 34 ppt, and a second one carried with sediment cores in seawater at a salinity of 30 ppt. The
474 results showed that at pH 8, half-lives of malathion and fenvalerate in unsterile water increased from 2.6 days to 5.3
475 days and from 17 days to 41 days in sterile seawater, respectively. For endosulfan I and endosulfan II, the half-lives
476 decreased from 4.9 days and 2.2 days in unsterile water to 3.1 days and 2 days in sterile water, respectively. In the
477 seawater/sediment system, the half-lives of malathion, endosulfan I, endosulfan II, and fenvalerate were 2, 22, 8.3,
478 and 12 days, respectively. These results were supported by the fact that in marine systems, the degradation of
479 malathion, fenvalerate, and endosulfan occurs through hydroxide-catalyzed hydrolysis and microbial action.

480   Wang and Hoffman (1991) studied the degradation of malathion and parathion in coastal water to determine
481 their persistence and loss in the context of high salinity levels. They reported that in the Indian river, which has a
482 salinity of 24 ppt, 50% of the parathion degraded within 10 days, and 94% degraded in 30 days. With a salinity of
483 10-15 ppt, the persistence of malathion extended beyond 30 days, while parathion degraded more rapidly. Malathion
484 degraded through alkaline hydrolysis, but for parathion, biological interactions were the most dominant degradation
485 route.

486   Walker (1976) also studied these two pesticides to investigate their chemical and microbiological degradation
487 in an estuarine environment at salinity levels of 0 to 25 ppt. The decrease in malathion's degradation rate was
488 proportional to the increase in salinity levels, but parathion was more persistent across the same conditions, even at
489 very high salinity levels (25 ppt). Also, when in sediment, the degradation of both malathion and parathion was
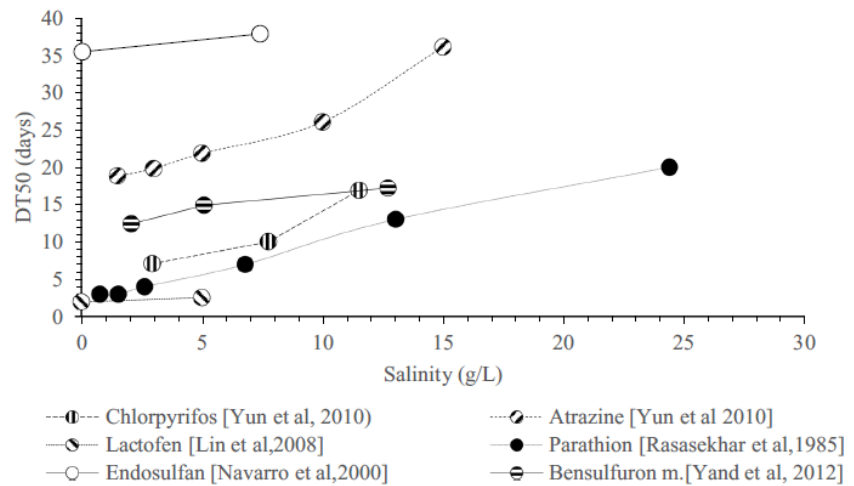490 quicker than in water and was enhanced by the microflora in the sediment.

491   As previously mentioned, biodegradation is the most competitive pathway of chemical degradation (Pionke and
492 Chesters 1973). Most of the studied chemicals in the literature were mostly degraded by microorganisms. This
493 reaction can be coupled with hydrolysis in some cases, which enhances the degradation rate. For the degradation of
494 parathion in seawater, biodegradation was not effective because of the toxicity of the pesticide to microorganisms
495 (Weber 1976). Nevertheless, the degradation was accelerated with increasing salinity levels, which doubled in
496 neutral salt solutions compared to distilled water.

497   Mingelgrin and Yaron (1974) studied the degradation of parathion in two sandy soils. For one soil, the
498 decomposition rate decreased after 5 and 15 days with increased concentration of $CaCO_3$, but after 21 days, the
499 decomposition increased. Using $CaSO_4$, the rate increased with increasing salinity, and the amount decomposed was

directly related to the amount of added salts. For the second sandy soil, both increasing concentrations of $CaCO_3$ and $CaSO_4$ enhanced the degradation of parathion.The interpretation proposed was that the decomposition of parathion was catalyzed by dry calcium salts via surface reactions. Variability of the results was due to the different soil components that intervened during decomposition through salts driven interactions. .

Bensulfuron-methyl biodegradation dynamic in a riparian area was governed by salinity, which increased when adding 10% seawater and decreased with 50% seawater. This is reported to be caused by the inhibitory effect that salinity has on the microorganisms responsible for the biodegradation of chemicals (Yang et al. 2012). Most of the studied pesticides' degradation under saline conditions decreased due to the influence that salts have on the microbes responsible for this process. Fig. 3 shows that DT_{50} of pesticides is between 0 and 60 days with salinity between 0 and 15 g/l.

Fig. 3 Examples of the effect of increasing salinity on the degradation of some pesticides

---◐--- Chlorpyrifos [Yun et al, 2010]   ---◑--- Atrazine [Yun et al 2010]
—◒— Lactofen [Lin et al,2008]   —●— Parathion [Rasasekhar et al,1985]
—○— Endosulfan [Navarro et al,2000]   —◓— Bensulfuron m.[Yand et al, 2012]

Thus, in most cases associated with cultivated soils, increasing salinity with NaCl or oceanic salinity type should result in an increase of the half-life degradation rate due to inhibition of microorganism activity by osmotic stress. Particular cases can be revealed when studying marine sediments, samples containing halophyte microorganisms, sterilized samples, or interventions with Ca^{2+} and K^+ salts. Similarly, when the main degradation process relies on physical processes like photo-degradation, degradation may be decreased or enhanced. In some cases, intervention with $CaCl_2$ or KCl may also be referenced.

Effect of salinity on pesticides volatilization

Pesticides' volatilization can be determined by Henry's Law Constants (HLCs), vapor pressure, and solid/air and water/air distribution coefficients (Fendinger and Glotfelty 1990; Guth et al. 2004). As these constants describe the partitioning of a chemical between liquid and gas phases, they can be used as solubility or volatility constants (Sander et al. 2020). For this reason, it is very important to distinguish between the two equations as they are different but equivalent:

$$H_s = \frac{Q_l}{Q_g} \qquad (12)$$

$$H_v = \frac{Q_g}{Q_l} \qquad (13)$$

where H_s is Henry's solubility constant (between liquid and gas; this concept is different from solubility in water), and H_v is Henry's volatility constant. Q_l is the liquid phase abundance, and Q_g is the gas phase abundance ($H_v = 1/H_s$).

When applied, the pesticide will be partitioned between the environment's phases: air, solid, and water (Müller et al. 2007). The flow of volatilization depends on several factors, such as pesticide properties, environmental factors, vapor pressure, soil texture, etc. This portioning is described by the following dimensionless form (Eq. 14):

$$K'_H = \frac{P_i}{C_{aq}} \cdot \frac{1}{RT} \qquad (14)$$

where K_H is Henry's constant, P_i and C_{aq} are the pesticide's concentration in the air and soil solution, respectively, R is the universal gas constant, and T is the temperature.

Based on the soil and pesticide properties, the interaction between pesticide and soil compartments implies the availability of the chemicals for one process more than the other. Some results show that the water content in the soil promotes volatility (Walker and Bond 1977). When the potential for adsorption of pesticides is high, volatilization increases in wet soils rather than in dry soils (Glotfelty et al. 1984, 1989). This means that the volatilization increases with the increase in the volume of water that the soil contains (Walker and Bond 1977). On a similar note, when pesticides do not have a strong adsorption potential, they can be immediately available for volatilization at the time of application (Bedos et al. 2002).

Among soil/water properties, salinity also has an effect on the rate of volatilization of some pesticides as it influences the solubility of organic compounds in soils and water. The composition of aqueous solutions has an effect on the values of Henry's constants (Sander 2015) and salinity intervenes by means of salting-in and salting-out, which influence the solubility of gases (Kampf et al. 2013; Kurtén et al. 2015). This effect can also be described by the Setschenow equation when the solubility of gas in pure water is larger in salt solutions (Setschenow 1889; Pitzer 1991):

$$log_{10}\left(\frac{H_0^{bp}}{H_{salt}^{bp}}\right) = K_{set} \cdot C_{salt} \quad \Leftrightarrow \quad \frac{H_{salt}^{bp}}{H_0^{bp}} = 10^{-K_{set} \cdot C_{salt}} \qquad (15)$$

where H_0^{bp} is Henry's constant in pure water, H^{bp} is Henry's constant in the salt solution, K_{set} is the molality-based Setschenow constant, and $C_{(salt)}$ is the molality of the salt. As far as we know, the impact of salinity on the rate of volatilization of pesticides has not been studied very much, but some papers discuss the impact of salts and other parameters, especially temperature, on Henry's constant. As salinity decreases the solubility of organic gaseous compounds, it is expected that the flow of volatilization will increase (Burkhard and Guth 1981).

Synthesis

The review highlighted the numerous effects that salinity can trigger on the fate of pesticides in cultivated soils. Salinity's effects on the solubility of pesticides' active ingredients in water benefit from oceanography studies that focused on the salting-out effect observed in estuaries. Thus, salinity's effects on solubility can be explained through a relationship with the octanol-water partition coefficient. For sorption studies, there are few works as they consider different ingredients, different materials (plastics, organic synthetic products, tortoise shells, marine sediments, treated clays, etc.), different ionic species such as KCl and CaCl$_2$ salts, which do not frequently have a high concentration in cultivated soils, and, lately, not focusing on the sorption on soils.

In cultivated fields, an upper salinity limit of 5 g/L for irrigation water is often considered. Thus, most plants would not tolerate higher salinity, and consequently, pesticide treatments would not be performed when cultivation cannot be effective. Nevertheless, salinity's effects on pesticide fate were found to be already significant in this range of salinity increase.

Soil hydro-dynamical changes that may result from varying salinity in the cultivation context are well documented. If sodium dominates the soil's CEC, fresh water (from precipitation or irrigation) may induce clogging that impairs vertical infiltration and restricts pesticide-solute transfer to groundwater. However, irrigation from salinized groundwater may prevent clogging and stabilize infiltration capabilities. Considering irrigated cultivation is constantly supplied with brackish underground water with sodium chloride as major ions and little input from precipitation, soil salinity may be tolerable by the plants if sufficient drainage takes place to stabilize the salt balance of the soil's root layer. This constraint is already prone to favoring groundwater contamination by pesticides without considering any direct salinity effects on adsorption or persistence.

In addition to this effect, pesticides' active ingredients that reach the soil may be affected by the soil solution's salinity, which may change characteristics from non-saline conditions for solubility, sorption, and degradation. In most cases that we referenced, sodium chloride salinity triggered a decrease in solubility and sorption capabilities, combined with higher volatilization and longer degradation time. Thus, soil water salinity has antagonistic effects on ingredient and metabolite transport.

For low-solubility ingredients, the main effect of sodium chloride salinity would be to reduce solute convective transport by decreasing solute concentrations. Thus, soil leaching capabilities would also depend on the product of infiltration fluxes according to the concentration. This effect is negligible for high-solubility ingredients as the treatment doses imply that saturation is never reached in the actual soil solution. In most studies that we referenced, sodium chloride salinity decreased the retention capability by sorption ($K_{foc}\downarrow$) and increased the half-life degradation time ($DT_{50}\uparrow$). Precisely, these two values are used to compute the Groundwater Ubiquity Score (GUS), an index that is widely used for contamination patterns of pesticide active ingredients.

Table 2 shows the range of effects that would result from a salinity change from 0 to 5g/L in terms of the GUS for a short list of ingredients. Unfortunately, we could not find simultaneous bibliographic data for K_{foc} and DT_{50} evolutions with the increase of sodium chloride salinity for the same ingredient. Computing arbitrary changes of

+10% and -10% for these two values, respectively, leads to a relative increase of GUS ranging from 3% to 12% for the ingredients listed (Table 2, last column). Applying interpolated values when identified from the bibliography for K_{foc} or DT_{50} (in bold in Table 2) resulted in a wider range of GUS that showed increased scores from +2% to +28%. Two ingredients, parathion, and atrazine, would cross the threshold values from low potential for movement toward groundwater to moderate potential and from moderate potential to high potential. Salinity effects on GUS greater than 10% were found typical of active ingredients with GUS in the range of 0.83 to 2.11 and octanol-water partition coefficient included in the range 10^3 - $10^{4.7}$.

Table 2 Salinity's effect on GUS index of some pesticides

	Log (K_{ow})	No salinity (PPDB values)				Salinity (5g/L)				Changes from 0 to 5g/L		
		Solubility	K_{foc}	DT_{50}	GUS	Solubility	K_{foc}	DT_{50}	GUS	$S_{(5g/L)} S_{(0g/L)}$	ΔGUS^{*}	$\Delta GUS^{10\%}$
		mg/L	L/Kg	days	index	mg/L	L/Kg	days	index	%	%	%
Endosulfan	4.74	0.32	18	86	5.31	0.03	16	**90**	5.36	10	+1	+4
Chlorpyrifos	4.70	1.05	3954	113	0.83	0.10	3557	**141**	0.96	9	+16	+12
Parathion	3.83	12.4	580	17	1.52	1.83	522	**29**	1.87	15	+23	+7
Lindane	3.50	8.52	477	523	3.59	1.46	429	575	3.77	17		+5
Linuron	3.00	63.8	559	48	2.11	13.64	**274**	53	2.69	21	+28	+6
Atrazine	2.70	0.035	174	29	2.57	0.00856	157	**36**	2.81	24	+9	+5
Bensulfuron	0.79	67	226	26	2.33	38.63	203	**36**	2.63	58	+9	+5
Imidacloprid	0.57	610	225	577	4.54	388	**222**	635	4.63	63	+2	+4
Paraquat	−4.50	620 10^3	10^6	2800	−6.89	*3844 10^3*	**0.8 10^6**	3080	−6.58	*620*	+4	+3

Underlined values correspond to the two pesticides that exceeded the threshold values of GUS due to salinity

In bold: values interpolated from bibliographic data: % of decrease of K_{foc} and increase of DT_{50} for 5 g/L is applied to PPDB values

In italic: doubtful solubility value from eq. 3

ΔGUS^{*} relative increase of GUS from 0 to 5-g/L salinity implying one parameter with an arbitrary 10% decrease of K_{foc}, or 10% increase of DT_{50}, and the other parameter interpolated from bibliography

$\Delta GUS10\%$ relative increase of GUS from 0 to 5-g/L salinity implying arbitrary 10% decrease of $K_{foc}c$ and 10% increase of DT_{50}

S solubility

Conclusion

This study aimed at understanding and discussing the effect of salinity on the fate of pesticides in irrigated areas. Therefore, the literature on this topic has been reviewed. The results from field studies and laboratory experiments have demonstrated that salinity has a big role in influencing the transport and transformation of pesticides. The body of literature reporting the role of salinity on the fate of pesticides in the environment is not very massive and it is in most cases not very recent. Nevertheless, the review identified that most pesticides' active ingredients show behaviors following the colligative properties of solutes when salinity increases, depending on the polarity and the presence of specific ionic radicals. In general, increased salinity can degrade the effectiveness of pesticides by reducing their solubility in water. This can cause the pesticides to bind to soil particles and become less available for uptake by plants or contact with pests. In addition, high levels of salt can also lead to increased breakdown of some pesticides, especially those that are sensitive to hydrolysis or oxidation. Considering the role that plays the salinity on the adsorption of pesticides, researchers reported a decrease in the adsorption capacity of soil by competition for adsorption sites between pesticide and electrolytes. Indeed, adsorbed cations reduce the negative charge of soil particles, reducing the ability of the pesticide to be adsorbed. It has also a big effect on the solubility by increasing the solubility of the chemicals in the soil solution, making it more mobile and available for plant uptake or leaching to groundwater. It can also affect the degradation rate of the pesticide by decreasing microbial activity in the soil, reducing the ability of microorganisms to break down the pesticide. Moreover, salinity can result in the formation of insoluble organic complexes that can sequester pesticides, making them unavailable for degradation. Salinity can also affect soil pH, which can in turn affect the adsorption of pesticides. For instance, in alkaline soils, some pesticides may become more soluble and less adsorbed onto soil particles. Overall, the effect of salinity on pesticides' fate will depend on the specific pesticide and soil conditions. Some active ingredients have counterintuitive and unique behaviors that may contradict the simplified overview given above. Similarly, due to the lack of systematic studies, the salinity behavior patterns of all the active ingredients in use in irrigated systems need to be explored. Some ingredients would likely show particular combinations in terms of solubility, sorption, volatilization, and degradation that would drastically change their fate when exposed to a certain change of salinity conditions with unseen consequences. Experimental laboratory data should be established to describe behavior of active ingredients and their metabolites known as water contaminants in front of salinity effects. Knowledge of soil sorption and degradation changes for the range of sodium chloride contents compatible with most plant survival is required.

635   . In conclusion, the topic has been insufficiently treated by agronomists and soil scientists, despite its importance
636 from the perspective of stresses on global water resources' volume and quality due to over-exploitation, rising sea
637 levels, and climate change, as well as the dependence on irrigated crop production on active chemicals. It is
638 important to consider soil salinity levels when applying pesticides to ensure proper adsorption and effectiveness
639 while minimizing negative environmental impact. Given the current knowledge of the effect of salinity on the fate
640 of pesticides, we consider that well-detailed and characterized experiments are required to understand, extrapolate
641 and anticipate long-term changes in most active ingredients and metabolites' behavior in soils. With sufficient
642 experimental data acquired, pesticide water and soil modeling should be able to render the salinity-driven behavior
643 changes emphasized by this review. More generally, potential effects of salinity on the fate of all organic pollutants
644 in cultivated soils should be considered as an emerging concern.

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Statements and declarations

Author contribution All authors contributed to the establishment of this study. Data collection was performed by Mariem Khouni, whereas data analysis was performed by Mariem khouni, Claude Hammecker, Olivier Grunberger and Hanène Chaabane. The first draft of the manuscript was written by Mariem Khouni, and all authors commented and corrected previous versions of the manuscript. All authors read and approved the final manuscript.

Data availability The datasets used and/or analyzed in this study are available from the corresponding author on request.

Declarations

Ethics approval There are no ethical issues involved in this study.

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