Chemical and Biological Technologies in Agriculture

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Influence of chemical and mineralogical soil properties on the adsorption of sulfamethoxazole and diclofenac in Mediterranean soils

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Abstract

Background: The irrigation with treated wastewaters can be a way for the introduction of organic contaminants in soils. However, their adsorption onto soils can allow a control of their bioavailability and leaching. The adsorption is influenced by properties of contaminants (water solubility, chemical structure) and soils (organic matter content, pH, mineralogy). This study aimed to investigate the effect of mineralogical composition, organic matter content and others parameters of soils on the adsorption of sulfamethoxazole (SMX) and diclofenac (DCF), two contaminants of emerging concerns (CECs), in real cases (Altamura, Sibari and Noci soils).

Results: The isotherms data showed that the adsorption of the two CECs closely matched the Freundlich model, even if the DCF could also fit the linear one. The only exception was the adsorption of SMX on the soil of Sibari, for which Langmuir's model fitted better. In all cases, the K_d values were the highest for Altamura soil according mainly to its content of organic carbon. Positive correlations were found between K_d value of DCF and the soil organic carbon and Al oxyhydroxides content, suggesting their roles in its adsorption, while SMX showed only a slight positive correlation with the soil organic carbon content. Finally, between the two CECs studied, DCF was more adsorbed than SMX also because of the lower water solubility of the former.

Conclusions: The good interaction between DCF and soil organic carbon suggests the organic amendment of soils before the application of treated watewaters. The low adsorption of SMX onto soils suggests greater leaching of this compound which is, therefore, potentially more dangerous than DCF. For this reason, the application of a filtration system with appropriate adsorbent materials before the application of wastewater to soils should be expected.

Keywords: Soil, Soil organic carbon, Soil oxides and hydroxides, Adsorption isotherms, Contaminant of emerging concerns

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Graphical Abstract
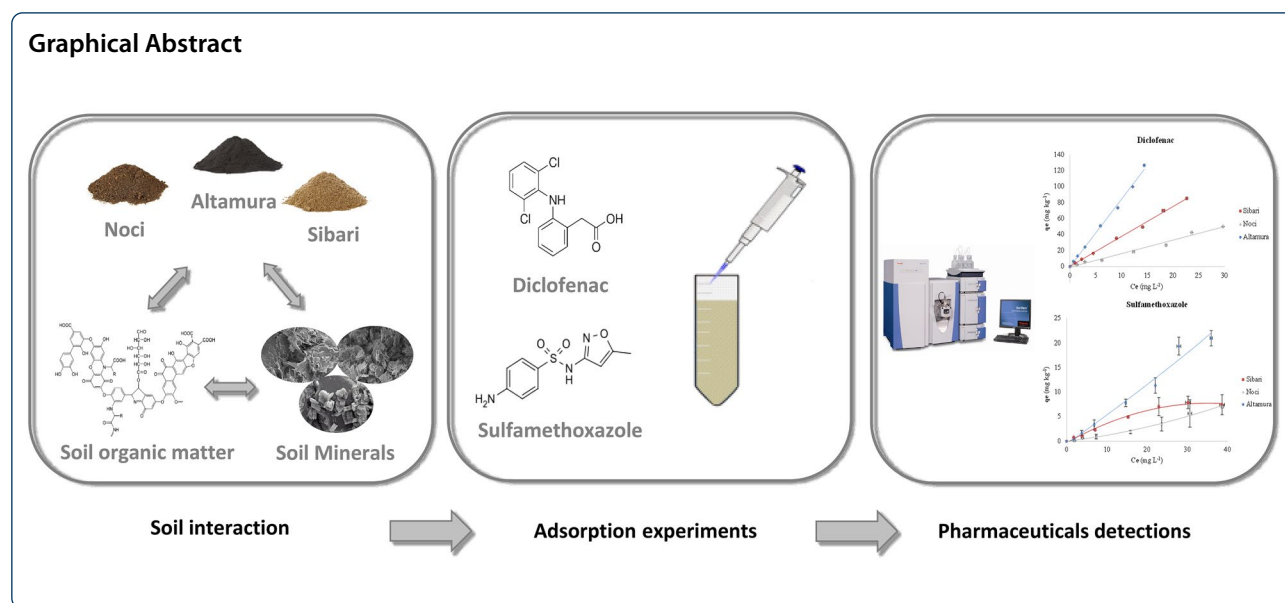
Background

The demand for irrigation water is increasing in agriculture, thus the re-utilization of treated wastewater is attracting always more attention. In the Mediterranean basin, already characterized by a scarcity of water, the use of wastewater could become more necessary, also to avoid the disproportionate use of surface and groundwaters [1, 2]. A recent estimate assumes the use of 3222 Mm^3 $year^{-1}$ treated wastewater in Europe by 2025 [3]. The use of treated wastewater also allows the supply of plant nutrients and organic matter reducing the application of fertilizers, although hundreds of contaminants of emerging concern (CECs) have been found in effluents [1–6], and in a lot of surface waters [7].

The CECs are dangerous also at very low concentration, because they can enter the food chain interfering with the proper function of vital organs and persist for a long time in the environment [8]. CECs can occur in their anionic, neutral or cationic form according to their pK_a and the pH value of wastewaters that previous studies have reported between 6 and 9 [9–13], and that of recipient soils.

Various treatments have been studied to reduce the concentration of CECs in wastewaters, such as oxidation processes, considered powerful methods to eliminate them, even if they can produce unknown byproducts [14, 15]. Another way to reduce CECs is the study of their interactions with different types of solids, such as activated carbon [16], clay minerals [17] mesoporous silica [18], quartz sand [19] and natural zeolite [20]. However, all these materials require a regeneration process that can be expensive and/or difficult to implement.

Soils can play an important role in the adsorption of organic contaminants too. In fact, the adsorption of CECs on soils can reduce their mobility and toxicity, influencing their bioavailability, even if their behavior in soils is influenced by several properties [21], mainly the quality and content of organic matter (OM) that enhances their adsorption. In fact, soil OM, especially its humified fraction, presents many hydrophobic and hydrophilic portions characterized by different functional groups that can bond the organic contaminants through weak and/or strong bonds with different mechanisms [22, 23].

Even clay minerals influence the adsorption of CECs according to their quality and quantity. Non swelling clays, such as kaolinites, show moderate to low adsorption capacities for organic contaminants with respect to swelling ones, such as montmorillonites, due to greater specific surface area and consequently higher availability of adsorption sites in the inter-layers [24]. The adsorption of organic contaminants on clay minerals is affected by soil pH, because at neutral-alkaline values, they possess negative charges that favor the adsorption of cationic organic contaminants and contribute to electrostatic repulsions of anionic molecules [23, 24]. In addition, soil texture is another parameter that influences the adsorption of CECs, because high percentages of clay minerals enhance the adsorption of CECs onto soils [25, 26]. Iron, aluminum, and manganese oxyhydroxides have reactive oxygen functional groups and a high specific surface area that can help to adsorb CEC_s, reducing their leaching into water or absorption by plants [27, 28].

The organic contaminants behave differently according to their intrinsic features too [29]. For example, anionic pollutants are poorly adsorbed on clay minerals, move

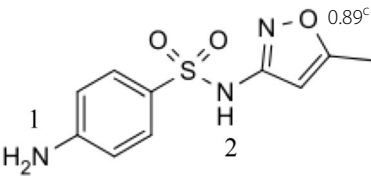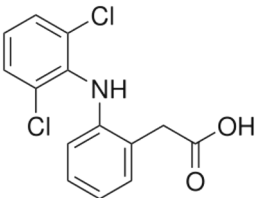De Mastro *et al. Chem. Biol. Technol. Agric.*   (2022) 9:34

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through the soil and easily reach groundwaters, rivers and seas determining environmental problems.

Sulfamethoxazole (SMX) is an antibiotic belonging to the group of sulfonamides largely used since the 1960s for medical treatment of animals and humans. This compound is not fully metabolized by animals and a great portion comprised among 50 and 100% of it can return to the environment either directly through the urine of grazing animals or via the application of manure [30]. In fact, Göbel et al. [31] estimated that a great portion of antibiotics (about 60–80%) returned to the environment, determining pollution issues. A previous study reported that SMX sorption dominated in soil at the beginning of soil-pollutant contact, and the biodegradation took over later because of the adaptation of the microbial community to the contaminant [32]. Nowrotek et al. [33] reported, as biodegradation products, several partially oxidized compounds and SMX conjugated with glutathione, which is an indicator of oxidative stress in bacteria and plants, attesting the adverse effect of this CEC on organisms. In addition, Poirier-Larabie et al. [34] detected SMX hydroxylamine as a major product in aerobic biodegradation. Several mechanisms of abiotic degradation of SMX were also proposed: (i) the hydroxylation of the benzene ring, (ii) the oxidation of the amine group at the benzene ring, (iii) the cleavage of the sulfonamide bond, and iv) the oxazole ring open. Unfortunately, even the transformation products of SMX concern for their toxicity [35]. From soil, the SMX can be easily leached due to its high solubility in water (610 mg L^{-1} at 37 °C) [36] associated with a low log K_{ow} value (0.89) [37], or it can be absorbed by plants and contaminate them. Herklotz et al. [38] conducted a study on cabbage grown under hydroponic conditions and found that the accumulation of SMX in roots was equal to 38.26 ng g^{-1} and higher than those of other CECs. Sallach et al. [39] in a study on lettuce irrigated with pharmaceutical spiked water found that the SMX was detected at concentration of 425 ng g^{-1}. Chitescu et al. [40] demonstrated that grass and watercress were able to take up SMX when the soil was contaminated with this compound at concentrations from 5 to 10 mg kg^{-1}. Due to its solubility, the SMX can also easily translocated to the aerial parts of plants. Finally, a long-term exposure to low concentrations of this kind of antibiotic is toxic for terrestrial and aquatic organisms [41].

Diclofenac (DCF) is the most popular non-steroidal anti-inflammatory drugs in the world. Its large-scale consumption and its poor elimination during wastewater treatment processes determine its presence in wastewaters [42]. DCF has a low water solubility (2.4 mg L^{-1}), a log K_{ow} of 4.51 [43], and it is very likely to be ionized at high pH values. DCF can be adsorbed by the organic and inorganic components of the soils. For example, the $Al(OH)_2^+$ can act as a bridge between the negatively charged functional groups of DCF and negatively charged sites on soil surfaces [18]. In addition, DCF can form hydrogen bonds with the SOM, and cationic amino moieties can complex with the carboxyl and hydroxyl groups on SOM [43]. The abiotic degradation of DCF is negligible, while it can undergo to oxidation processes mediated by white-rot fungi and several genera of bacteria. Apparently, a complete mineralization of DCF does not occur, rather microorganisms transform DCF into a series of hydroxyl derivatives, such as 4-hydroxydiclofenac and 5-hydroxydiclofenac

Table 1 Properties of the selected pharmaceuticals

Compound	Molecular weight (g mol^{-1})	Class	Structure	log K_{ow}	Water solubility (mg L^{-1})	pK$_a$
Sulfamethoxazole	253.28[a]	Antibiotic		0.89[c]	610 (37 °C)[a]	1: 1.7[b] 2: 5.6[b]
Diclofenac	296.1[d]	NSAID		4.51[d]	2.36 (25 °C)[d]	4.15[d]

NSAID: non-steroidal anti-inflammatory drug

[a] Díaz-Cruz et al. [36]; [b] Chen et al. [53]; [c] Gao and Pedersen [37]; [d] Accessible at https://pubchem.ncbi.nlm.nih.gov/compound/diclofenac

[44] that can then be oxidized into quinone derivatives, without affecting the structure of the DCF rings [45]. Cortés et al. [46] conducted a study to identify the presence of DCF in soybean and wheat after the use of sludge and found that 2% of the DCF found in sludge was detected in plants. Zezulka et al. [47] found that DCF did not affect the seed germination and root elongation of onion, lettuce, pea and tomato, but reduced the growth and biomass production of pea and especially maize. DCF is mainly concentrated in plant roots, as reported by various Authors [48, 49] for crops such as *L. sativa*, *C. sativum*, *Spinacia oleracea*, and *Capsicum annuum* [48]. Nevertheless, given its toxicity at low concentrations in humans [50], the fate of DCF requires further investigation.

In this study, the adsorption of SMX and DCF onto three soils with different chemical and physical characteristics has been evaluated. The objective of the paper was to weight the effect of mineralogical composition, organic matter content and others parameters of soils on the adsorption of the two CECs in real cases. As far as we know, in previous studies, the soil as a whole has been little evaluated, as highlighted in a very recent review [51]. In addition, studies conducted on the adsorption of organic contaminants onto soils that consider also the mineral components of soils, such as oxyhydroxides, are also rare, as highlighted in another recent review [52]. This study can, therefore, help to understand the behavior of contaminants in situations closer to reality.

Methods
Chemicals
Diclofenac sodium (> 98%) and sulfamethoxazole (> 98%) were provided by Lab Instruments limited company (Italy). Chemical structures and properties of the selected pharmaceuticals are given in Table 1. Stock solutions of each CEC (100 mg L^{-1}) were prepared in methanol and stored at − 20 °C and proper working solutions (2.5, 5.0, 10, 20, 30, 40 and 50 mg L^{-1}) were obtained by appropriate dilutions of the stock solutions. Deionized water was prepared with a Milli-Q water purification system.

Soils
The experiments were conducted on three agricultural soils located in the Mediterranean area (Southern Italy). The three soils were chosen, because they were in different areas and showed different mineralogical composition and organic matter content. Noci was cultivated with a rotation of irrigated vegetables, Altamura was cultivated with rainfed cereals, while Sibari was a paddy field. In the near future, it is planned to irrigate these soils with treated wastewaters, in the framework of water recycling.

Three samples of each soil were cored from 0 to 20 cm layer, air-dried, ground to pass through a sieve with 2-mm openings and stored at 4 °C until use. They have been analyzed for their main chemical properties by conventional analytical methods described in Sparks et al. [54]. Particle size analysis was determined by the pipette method, total nitrogen by Kjeldahl method, organic carbon (OC) content by Walkley and Black method and available phosphorous by Olsen colorimetric method. Electrical conductivity was determined in distilled water using a soil/water ratio (W/V) of 1:2, while pH was determined in distilled water and KCl using a W/V ratio of 1:2.5.

The soil minerals were identified by X-ray diffractometry using a PHILIPS X'Pert pro diffractometer with Cu K α radiation and their abbreviations were in accordance with Whitney and Evans [55]. The soil samples were ground in an agate mortar and back-filled into a box mount to prevent orientation. The operating conditions were: 40 kV, 40 mA, divergence slit 1°, slit for diffuse radiation (antiscatter slit) ½°, programmable slit 0.2 mm, angular increment (step size) 0.02° 2θ, time for step 1 s, angular interval (range) 2–65° 2θ. The minerals were determined using the High Score software and PanICDS database and their semi-quantitative analysis was performed by measuring heights and/or areas of peaks on diffractometer patterns following the method by Schultz [56] and Shaw et al. [57], slightly reviewed by Laviano [58].

The elemental composition analysis, which included the determination of major elements expressed as oxides, was determined according to Franzini et al. [59–61] and Leoni and Saitta [62] and performed with an automatic Panalytical AXIOS-Advanced spectrometer equipped with an SST-mAX (Super Sharp end-window Tube) X-ray tube with Rh anode. Three-five g of each sample were mixed with about 2 mL of a solution of Elvacite® diluted to 20% in acetone, and pressed with a hydraulic press at about 10 tons in an aluminum cup with a diameter of 40 mm. The bottom of the cup was partially filled with boric acid to obtain the condition of infinite thickness for X-rays analysis regardless of its mass absorption coefficient. The loss on ignition (LOI) was obtained at 950 °C for 24 h.

Adsorption experiments
Soil's sorption of the two CECs was measured using a batch equilibrium method at room temperature (20 ± 2 °C). Briefly, five grams (dry weight equivalent) of soils were weighed into 50-mL Teflon centrifuge tubes and 25 mL of 0.01 M $CaCl_2$ solution was added into each tube to reach a soil/solution ratio of 1:5 (w/w). To suppress microbial activity during the experiment, 5 mg of

sodium azide were added into each sample. The soil samples were spiked with 20 μL working solutions to obtain initial nominal concentrations of 0, 2, 4, 8, 16, 24, 32, and 40 μg L^{-1} for each compound in the aqueous phase. These concentrations were consistent to those utilized by other Authors in real scenarios [3, 43]. The pH of the suspensions resembled that of soils suspended in distilled water because of the soil buffer capacity. The soil suspensions, closed with Teflon-lined caps, were continuously mixed by shaking and equilibrated for 24 h at room temperature (20 ± 2 °C). After shaking, the tubes were centrifuged for 10 min at 8820 g, and the supernatant was removed. An aliquot of the supernatant was passed through a Whatman 0.45 μm glass fiber microfilter (Fisher Scientific). A Thermo Scientific™ UltiMate 3000 UHPLC, equipped with a degasser, a high-pressure gradient pump, a WPS autosampler, a column oven, and Q Exactive mass spectrometer were used for data acquisition. Samples were injected, with injection volume of 10 μL, in Accucore™ aQ C18 Polar Endcapped (2.6 μm; 100 × 2.1 mm) column (Thermo Fisher Scientific) and maintained at 40 °C. The mobile phases were composed of 4 mM ammonium formate with 0.1% formic acid in LC–MS grade water and 4 mM ammonium formate with 0.1% formic acid in LC–MS grade methanol. The system used a Heated Electrospray Ionization source with the following parameters: sheath gas flow rate 35 arbitrary units (a.u.), aux gas flow rate 20 (a.u.), spray voltage 3.8 kV, capillary temp. 320 °C, S-lens RF level 50 and aux gas heater temp 220 °C. The Orbitrap instruments run a full scan in positive mode and the conditions were the following: AGC target 1e6, maximum IT 200 ms, scan range 70–900 m/z and instrument resolving power (FWHM at 200 m/z) 140,000 (set at 70,000 for experimental matrices). Nitrogen was used as the sheath and auxiliary gas. Data were acquired and processed with Thermo Xcalibur 4.0.27.10, Chromeleon, Trace Finder 3.3. For each CECs, 5 ppm mass tolerance was used for the extracted ion chromatogram (XIC). To calculate the sorbed concentration Cs (mg kg^{-1}), a soilless control (0.01 M CaCl$_2$ solution) with only the spiked chemicals was prepared. Finally, each adsorption experiment has been replicated three times.

Theoretical models

The linear, Freundlich and Langmuir models have been applied to find the more suitable adsorption process of DCF and SMX onto the three soils examined.

From the linear equation:

$$q_e = K_d C_e \tag{1}$$

$_d$ has been calculated as the angular coefficient of the line, while q_e (mg kg^{-1}) is the amount of compound adsorbed per unit of substrate and C_e is the equilibrium concentration of the sorbate in the solution (mg L^{-1}).

The Freundlich equation

$$q_e = K_F C_e^{1/n} \tag{2}$$

2) and, successively, 1/n has been obtained as the angular coefficient of the line, while K$_F$ has been calculated from its intercept.
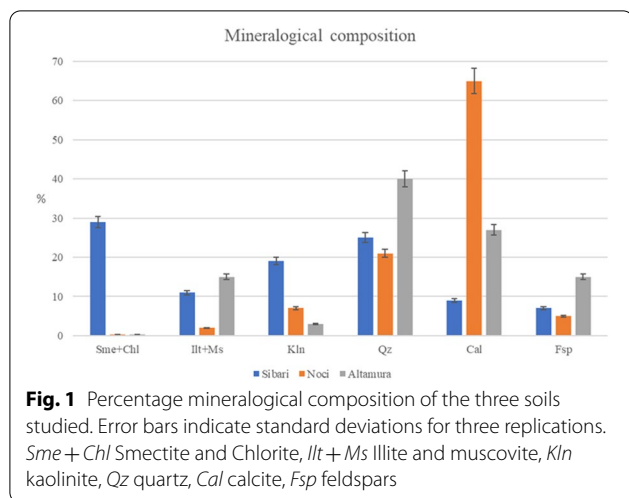
The Langmuir equation

$$q_e = (abC_e)/(1 + bC_e) \tag{3}$$

3). The value of the coefficient "b" has been calculated as the ratio between the value of the intercept and that of the angular coefficient of the linearized isotherm and represented the adsorption coefficient [63]. The value of the coefficient "a" has been calculated as the reciprocal of the value of the intercept and represented the theoretical maximum adsorption capacity [63]. The product between the coefficients "a" and "b" represented the K of Langmuir.

Linearized versions of Freundlich and Langmuir models produce coefficients of determination (r^2) that may not be appropriate for judging how well a nonlinear model fits the measured data. For this reason, the mean absolute error (MAE) has been determined and adopted instead of the coefficient of determination. The organic carbon partition coefficient (K$_{OC}$) has been calculated according to White et al. [64] as the ratio between the K$_d$ and the percentage of OC in soils, which is multiplied by 100.

Table 2 Physico-chemical properties of the selected soils

Sample	pH		EC	OC	OM	P$_{ava}$	TN	Particle size fraction			Classification
	H$_2$O	KCl						Sand	Silt	Clay	USDA
			μS cm^{-1}	g kg^{-1}	%	mg kg^{-1}	g kg^{-1}	%			
Sibari	7.9 (0.03)	7.7 (0.10)	1135 (15)	16.4 (0.66)	2.8 (0.11)	18.1 (0.67)	1.6 (0.13)	20 (0.85)	26 (1.83)	54 (0.17)	Clay
Noci	8.2 (0.03)	7.9 (0.18)	205 (10.6)	10.6 (0.25)	1.8 (0.04)	30.2 (0.67)	1.1 (0.05)	10 (0.70)	45 (1.35)	45 (0.15)	Silty Clay
Altamura	7.4 (0.03)	7.3 (0.03)	133 (7.5)	47.0 (0.81)	8.1 (0.14)	4.7 (0.35)	4 (0.05)	10 (0.08)	55 (0.09)	35 (0.17)	Silty clay loam

EC electrical conductivity, *OC* organic carbon, *OM* organic matter, *P$_{ava}$* available phosphorous, *TN* total nitrogen. Values in parentheses are the standard deviations

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Fig. 1 Percentage mineralogical composition of the three soils studied. Error bars indicate standard deviations for three replications. *Sme + Chl* Smectite and Chlorite, *Ilt + Ms* Illite and muscovite, *Kln* kaolinite, *Qz* quartz, *Cal* calcite, *Fsp* feldspars

Statistical analysis

All analyses were performed in triplicate and results were tested against the normal distribution of variables (Shapiro—Wilk's test) and the homogeneity of variance (Bartlett's test) using the R software (version 3.2.3). The variables were normally distributed and showed homogeneity of variance; therefore, they were subjected to the Analysis of Variance (ANOVA), followed by Tukey test. Statistical significance was determined at $p \leq 0.05$.

Results and discussion

Soils

Some physico-chemical properties of soil samples are reported in Table 2.

The pH value was weakly alkaline in Altamura and moderately alkaline in Sibari and Noci, according to the USDA classification [65]. The electrical conductivity was significantly higher in Sibari with respect to the other soils. The OC and total nitrogen (TN) contents were significantly higher in Altamura in comparison to Sibari and Noci. The latter soil showed the highest content of available phosphorus (P_{ava}), compared to Sibari and, especially, to Altamura soils. The particle size distribution was different among soils, with Sibari, Noci and Altamura showing a clayey, a silty-clay and a silty-clay–loam texture, respectively.

Figure 1 and Table 3 report the mineralogical composition and the elemental analysis of soils, respectively, while in Fig. 2 are shown the XRD patterns of soil samples. All soils showed the presence of clay minerals such as illite and muscovite (Ilt + Ms) and kaolinite (Kln), together with quartz (Qz), calcite (Cal) and feldspars (Fsp) (Fig. 1). The high background at XRD low angles and the broad and intense 020 peak at 20 ° 2θ, particularly evident in Altamura soil, also suggested the existence of disordered phases of smectites and allophanes, that are not easy to quantify. The latter minerals are abundant in soils of volcanic origin according to IUSS Working Group WRB [66]; therefore, since soils from the same area of Altamura showed the presence of volcanic ashes [67], the aforementioned peak could be associated to the occurrence of allophanes deriving from volcanic eruption fallout. Altamura and Noci soils had the highest percentage of Qz and Cal, respectively, but both lacked smectite and chlorite (Sme + Chl), well represented in Sibari soil. In fact, the latter soil showed the highest percentage of clay minerals (59%) with respect to Altamura (18%) and Noci (9%). Finally, the content of clay minerals of Altamura and Noci soils did not resemble their corresponding clay fraction percentages, confirming the presence of disordered clay minerals.
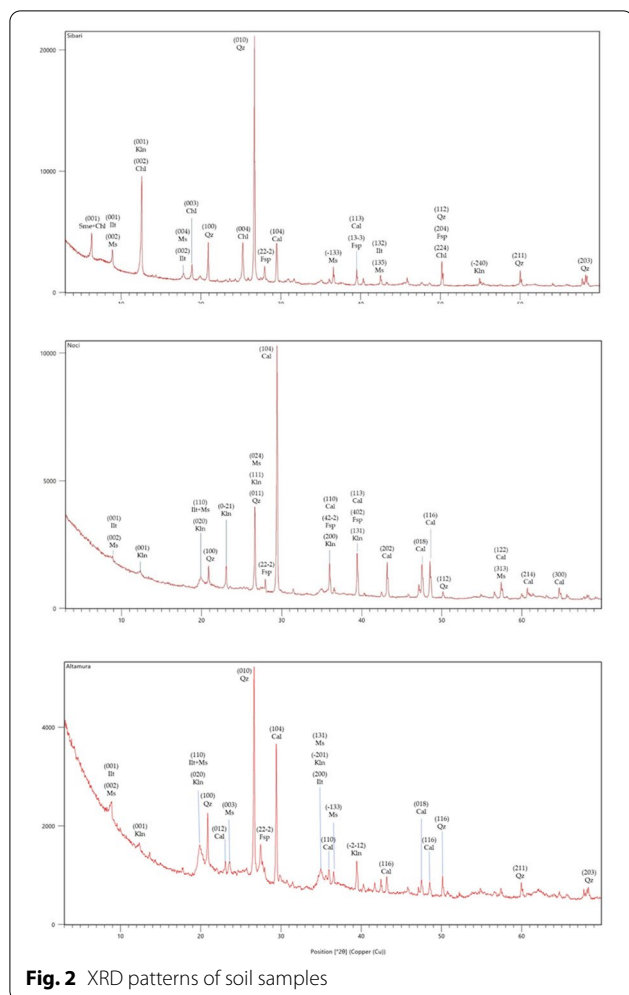
SiO_2 was present in all samples in concentrations ranging from 28.4 to 52.5% and can be ascribed to soil minerals detected, except for calcite. Al_2O_3 was mainly attributable to the presence of disordered oxyhydroxides, especially in Noci sample, where the minerals that contain Al_2O_3 did not exceed 14% (Fig. 1). In addition, no correlation existed between Al_2O_3 content and the amount of clay minerals plus feldspars ($r = 0.3472$), confirming the occurrence mainly of disordered phases compared to the crystalline ones. Fe_2O_3 was well represented in all samples, mainly as disordered phases, since no crystalline minerals containing Fe have been detected (Fig. 1). CaO content and the loss of ignition were consistent with the presence of calcite ($r = 0.9979$) and clay minerals (r = − 0.9771), respectively.

Table 3 Analysis of variance and mean values of the major elements (wt%) of the selected soils

Sample	SiO$_2$ %	TiO$_2$	Al$_2$O$_3$	Fe$_2$O$_3$	MnO	MgO	CaO	Na$_2$O	K$_2$O	P$_2$O$_5$	LOI
Sibari	52.5 (a)	0.81 (a)	17.4 (ab)	7.3 (a)	0.19 (a)	2.85 (a)	6.0 (c)	0.72 (a)	2.28 (a)	0.17 (a)	9.8 (b)
Noci	28.4 (c)	0.65 (b)	15.5 (b)	5.3 (b)	0.13 (b)	0.83 (c)	22.9 (a)	0.23 (b)	1.37 (b)	0.02 (b)	24.6 (a)
Altamura	37.6 (b)	0.80 (a)	19.4 (a)	6.7 (ab)	0.18 (a)	1.15 (b)	12.4 (b)	0.36 (b)	2.36 (a)	0.13 (a)	19.0 (a)

LOI Loss of Ignition

The values in each column followed by a different letter are significantly different according to Tukey's test

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Fig. 2 XRD patterns of soil samples

Fig. 3 Adsorption isotherms of Diclofenac **a** and Sulfamethoxazole **b** onto the three soils analyzed. Standard deviation is reported as horizontal and vertical bars on each point ($n = 3$)

Adsorption isotherms

The adsorption isotherms of DCF and SMX are shown in Fig. 3a, b, while in Table 4 are reported the parameters calculated fitting sorption data at the equilibrium in the linear (Eq. 1), Freundlich (Eq. 2) and Langmuir (Eq. 3) linearized models, and the value of K_{oc}.

The values of MAE calculated for all equations indicated that DCF was adsorbed onto the three soil according to the Freundlich model (Table 4). Anyway, since the values of 1/n of the Freundlich model were very close to 1, a linear adsorption would fit well (Fig. 3a) and the curves can be considered C-curves, indicating a constant distribution of DCF between the solid phase and the aqueous solution [68]. This was also confirmed by the almost equal values of r^2 of the two above mentioned models. In addition, Lin and Gan [43] and Graouer-Bacart et al. [69] observed a linear relationship between the amount of DCF adsorbed onto soil and that in solution at the equilibrium in several soils with different characteristics but sharing alkaline pH.
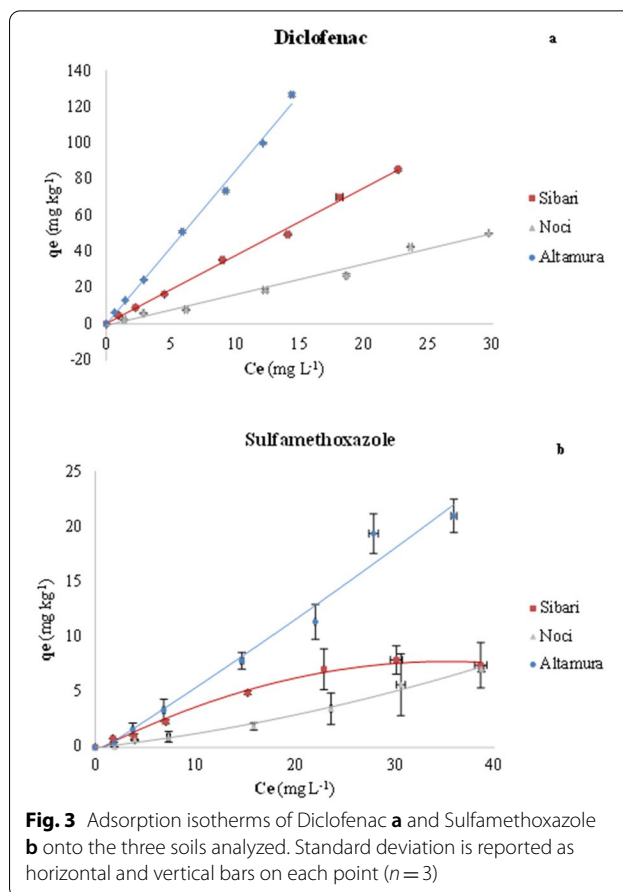
DCF showed a higher adsorption onto soils compared to SMX as can be seen from the higher K_d values reported in Table 4. Altamura soil showed a K_d value (8.4) higher with respect to Noci (1.7) and Sibari (3.7) and, due to the high correlation between the soil organic carbon content and the K_d values ($r = 0.989$), soil organic matter confirmed its crucial role in the adsorption of this CEC. Various Authors have reported that the content of soil organic matter (SOM) influenced positively the sorption of contaminants onto soils [22, 70, 71]. In this regard, DCF is able to form hydrogen bonds with the surface acceptor functional groups of SOM with its –NH group, as reported by Filep et al. [72]. In addition, SOM also contains electron-deficient aromatic moieties with highly polar substituents that can interact with the two aromatic rings of DCF to form stable charge-transfer complexes [68].

Another positive correlation has been observed between Al_2O_3 and K_d values ($r = 0.976$), suggesting that disordered Al oxyhydroxides contributed to the sorption of DCF, since they show a high specific surface, a net positive charge over the entire normal range of soil pH values [68] and can interact with the anionic form

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Table 4 Adsorption parameters for Diclofenac and Sulfamethoxazole onto the three selected soils

Soil	Linear model		Freundlich model				Langmuir model					K_{OC} (L kg⁻¹)
	r^2	K_d (L kg⁻¹)	r^2	MAE	K_F (L kg⁻¹)	1/n	r^2	MAE	b (L mg⁻¹)	a (mg kg⁻¹)	K (L kg⁻¹)	
Diclofenac												
Sibari	0.9966	3.7	0.9954	**2.19**	4.4668	0.93	0.9884	8.38	0.0423	118.6	5.0174	225.6
Noci	0.9821	1.7	0.9809	**2.61**	1.8197	0.95	0.9842	4.06	0.0174	110.0	1.9168	160.4
Altamura	0.9953	8.4	0.9983	**2.52**	9.1201	0.95	0.9976	7.26	0.0321	308.3	9.8861	178.7
Sulfamethoxazole												
Sibari	0.9072	0.21	0.9600	1.76	0.4328	0.84	0.8886	**1.09**	0.0478	9.3633	0.4477	12.8
Noci	0.7187	0.36	0.9014	**0.32**	0.0281	1.64	0.8436	2.62	0.0651	0.3444	0.02242	34.0
Altamura	0.9755	0.64	0.9792	**1.17**	0.2188	1.32	0.9281	7.84	0.0500	3.8636	0.1932	13.4

MAE mean absolute error of q_e

The model that fits better is in bold, according to the lower MAE value

of DCF occurring at alkaline soil conditions. Yu and Bi [73] reported that Fe oxides dominated the DCF adsorption with respect to SOM in soils with pH 4.5 and 6.0. In the present study, disordered Fe oxyhydroxides were not correlated with K_d values of DCF ($r = 0.487$), while SOM and disordered Al oxyhydroxides apparently contributed equally to the DCF adsorption.

The K_{oc} values of DCF (Table 4) were not proportional to the organic carbon content of each soil suggesting that a part of the soil organic matter was not available for the adsorption, possibly because involved in surface linkages with minerals.

Although the latter CEC was not very soluble (Table 1), its adsorption on soils was moderate, as reported also by several Authors [21, 69, 74], and that result could be ascribed to the alkaline pH of soils that determined the dissociation of the contaminant and the electrostatic repulsion between the negative charges of soil particles and the negative charge of DCF [75], as confirmed by the strong negative correlation between soil pH and K_d values ($r = -0.996$).

Finally, a strong negative correlation was found between the P_{ava} and the K_d ($r = -0.978$), suggesting that DCF adsorbed as inner-sphere surface complexes competing with phosphate for the same adsorption sites, and that worsened the adsorption capacity of Noci soil for DCF due to its higher P_{ava} content.

The values of MAE calculated for all equations indicated that SMX was adsorbed onto Noci and Altamura soils according to the Freundlich model (Table 4), suggesting the formation of adsorbed solute multilayers or the activation of new sites, which became available after the saturation of those with higher energy [76]. In contrast, the adsorption of SMX onto Sibari soil fitted better with the Langmuir model (Table 4), and the corresponding L-curve shown in Fig. 3b was the result of the

relatively high affinity of soil particles for the adsorbate at low surface coverage mitigated by a decreasing amount of adsorbing surface remaining available as the surface excess increased [68]. The values of K_d for SMX were very low (0.21, 0.36 and 0.63 for Sibari, Noci and Altamura, respectively) and similar to those found by Kodešová et al. [77]. The relatively higher sorption of SMX onto Altamura soils can be justified by the higher organic carbon content of this soil compared to those of the other two soils. In fact, the only positive correlation was found between the value of k_d of soils and their organic carbon content ($r = 0.877$). According to [70], SMX binds to dissolved humified organic matter via aromatic conjugate and hydrophobic interaction, and a small amount of polar bonding due to its hydrophilic sulfonamide and anilino groups [78]. However, the behavior of SMX is particular, since Liang et al. [78] reported that this CEC exhibited strongest co-adsorption and competitive adsorption in presence of high molecular hydrophobic dissolved organic matter, but the competitive adsorption was dominant. In presence of low molecular weight dissolved organic matter the polarity of the CEC and that of the organic matter resulted in a low sorption via hydrogen bonding and exchange coordination reaction. In both cases, the adsorption of this contaminant was low.

Due to the alkaline pH of the studied soils, SMX was in its negatively charged form (Table 1) and hardly at all adsorbed because of the electrostatic repulsion between soil particles and SMX⁻, in particular the clay fraction, that showed a strong negative correlation ($r = -0.987$). In addition, SMX did not show good correlations with Al and Fe oxyhydroxides ($r = 0.653$ and -0.124, respectively), suggesting that it behaved as other anions that adsorb mainly as outer-sphere surface complexes [68]. For the same reason, the correlation between K_d of SMX and P_{ava} was negative but low (r = -0.661).

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As per DCF, the K_{oc} values calculated for the three soils (Table 4) were not consistent with the organic carbon content of each soil. Anyway, the aforementioned considerations and the high water solubility of SMX (Table 1) resulted in a negligible adsorption of SMX onto the three soils analyzed.

No correlation has been found between each of contaminant and Mn and Ti oxides, even if they are able to degrade phenolic compounds [79], amines [80], azo compounds [81], steroid hormones [82] and pharmaceuticals [83]. Some recent studies showed methods to enhance the oxidation capacity of oxidants in removal of organic compounds. For example, Tian et al. [84] used $KMnO_4$ and biochar to obtain highly oxidative intermediate Mn species capable to transform SMX in less toxic compounds in aqueous solutions. The same Authors also tested the potassium ferrate (K_2FeO_4) and biochar in the removal of CECs and found that 75 and 65% of SMX and DCF, respectively, were oxidized at pH 8 within 20 min [85]. Wang et al. [86] also reported that ferrate removed DCF from water, even if its oxidation generated several byproducts that, synergistically, showed higher toxicity than DCF, and needed time to be further oxidized to non-toxic compounds. The behavior of certain oxides could be influenced also by the pH of the medium. The CECs studied are adsorbed and degraded better in acidic conditions due to their speciation depending on pH and the surface electrical charge of oxides [87, 88]. Therefore, the results of the present study related to soil oxyhydroxides could be ascribed to the low content of these oxyhydroxides in the studied soils and their inaccessibility for the CECs, because already encrusted with soil organic matter and/or interacting with cations and anions [89]. In addition, the pH of the soils was alkaline and stable due to the buffer capacity ensured mainly by soil organic matter and clay minerals [90, 91].

The Altamura soil was the best in adsorbing the two CECs because of its higher organic carbon and, possibly, with the contribution content and high specific surface disordered phases The Noci soil was the worst in adsorbing the two CECs studied because of the lower percentage of organic carbon and the very high content of calcite, as reported by El Arfaoui et al. [92, 93] in similar soil conditions.

Conclusions

This study aimed to identify the role of chemical and mineralogical soil properties on the adsorption of two CECs on real soils. The results highlight that DCF has been adsorbed moderately while the SMX negligibly, regardless the soils. Crystalline and disordered clay minerals have little influence on the adsorption of CECs mainly because of their negative net charge at alkaline pH that does not help the interaction with

the anionic form of the CECs considered. Disordered Al oxyhydroxides seem to contribute to the adsorption of the sole DCF, but with a lesser extent with respect to the soil organic carbon. In this regard, the discrete interaction of DCF with the organic matter could be exploited using organic amendments, such as high-quality compost, digestate or biochar, before the application of treated wastewater, to enhance the adsorption capacity of the recipient soils and to prevent the introduction of this CEC into the food chain. In contrast, SMX is particularly dangerous if present in wastewater, since it apparently is not adsorbed onto alkaline soils. In this case, the utilization of wastewater containing such contaminant should be avoided or a filtration should be considered upstream the irrigation system using appropriate adsorbent materials. In addition, the fertigation using commercial liquid organic fertilizers, such as humic acids, seaweed extract, etc., and treated wastewaters should be studied to understand if the effect of such good agricultural practice can enhance the adsorption of CECs.

CECs with characteristics similar to the contaminants considered in the present study, presumably should have almost the same behavior in alkaline soils. In addition, considering that treated wastewaters can contain any kind of CECs, all proposed practices could be useful to mitigate pollution and utilize safely such wastewaters for irrigation.

Author contributions
GB, CCo, FDM and AT conceived and designed the experimental strategies and manuscript. FDM, FM, CCa and MP performed all experiments and analyses. AT, FDM, MP and FM have organized all data to insert in the publication. GB and CCo have supervised all experiments and analyses. AT, FDM and FM have performed the statistical analysis. AT, FDM, MP and FM have written the original draft of manuscript. GB and CCo have revised and validated the results. All authors read and approved the final manuscript.

Availability of data and materials
The data set used and/or analyzed during the current study are available from the corresponding author on reasonable request.

Declarations

Ethics approval and consent to participate
This manuscript is an original research and has not been published or submitted in other journals.

Consent for publication
All authors agreed to publish in the journal.

Competing interests
The authors declare that they have no competing interests.

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