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Effects of a Municipal Sewage Sludge Amendment on Triasulfuron Soil Sorption and Wheat Growth

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The influence of municipal sewage sludge (SL) as a soil amendment on the sorption and activity of the herbicide triasulfuron (TRS, [2-(2-chloroethoxy)-*N*-[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]-carbonyl]benzenesulfonamide]) was studied. Weed control was checked in a greenhouse on a wheat (*Triticum turgidum* L. subsp. *durum*) crop. At the highest SL amount allowed by Italian regulation, TRS sorption onto soil increased by 7 times and weed control was unaffected. A vegetative bloom and an early heading phase were noted. To compare inorganic fertilization (N, P, and K) and SL amendment, a greenhouse fertilization experiment was carried out. The SL-amended crop developed larger leaf surfaces, higher biomass, and a forward heading compared to that fertilized with N, P, and K. The SL hormone-like activity was evaluated by measuring auxin- and gibberellin-like activity of sewage sludge.

KEYWORDS: Sewage sludge; triasulfuron; herbicide; sorption; fertilization; hormone-like activity

INTRODUCTION

The application of organic amendments to soils, for example, sewage sludge (SL), is a current environmental and agricultural practice to increase soil organic matter (OM) content (*1*, *2*). Sewage sludge, also referred to as biosolids, is the residue of wastewater treatment processes, in which liquid and solid are separated. The properties of sewage sludge depend on the wastewater treatment process and sludge treatment. Biosolids are composed of organic substances, macronutrients, a wide range of micronutrients, nonessential trace metals, organic micropollutants, and microorganisms (*3*). The safe disposal of sewage sludge is a major environmental concern. Soil application could be the most economical disposal method (*4*). However, it is essential to ensure that these materials do not cause any danger to the environment. The main limiting factors of SL applications to soils are related to the presence of organic and inorganic pollutants and microbial contaminants (*5*). European Union (EU) legislation concerning sewage sludge reuse in agriculture was introduced by Directive 86/278/EEC (*6*). This directive encourages the use of sewage sludge in agriculture and, at the same time, regulates its use to prevent harmful effects on soil. According to the above principle, the use of sludge in agriculture, without prior treatment, is not allowed. In Italy, the use of SL has been in force since 1992 and is regulated by D. Lgs. N. 99/92 (*7*), which puts Directive 86/278/EEC into action.

The application of organic amendments to soil can modify pesticide behavior, depending on both the amendant and pesticide properties. Generally, as a consequence of increased sorption of pesticides, a decrease of leaching and degradation is observed (*8*, *9*). This effect can reduce pesticide pollution, but can also lower pesticide efficacy (*10*). Moreover, organic amendants, by increasing the amount of soluble organic matter, can favor the desorption of scarcely polar pesticides (*11*, *12*).

Triasulfuron (TRS, [2-(2-chloroethoxy)-*N*-[[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl]benzenesulfonamide]) (**Figure 1**) is a selective sulfonylurea herbicide used at very low rates (15−25 g of active ingredient/ha) for weed control in cereals (*13*). The highest level of TRS sorption is measured on soils with low pH and high organic carbon content (*14*). The addition of municipal waste compost to soil enhances the sorption of TRS. This effect, due to stable interactions between TRS and the composted organic matter, reduces pesticide availability to soil microorganisms, resulting in a longer degradation time (*9*). This work was aimed at studying the influence of the amendment of soil with municipal sewage sludge on TRS sorption. Because the pesticide trapping in organic matter could reduce pesticide efficacy, a greenhouse test was carried out to verify TRS herbicide efficiency after soil amendment. Weed control was checked on a wheat (*Triticum turgidum*) crop. On the basis of the results

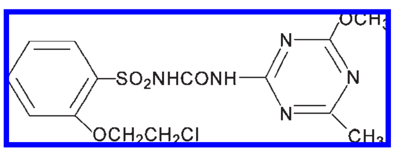

Figure 1. Triasulfuron chemical structure.

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Table 1. Selected Physical and Chemical Properties of SA and TU Soils

property	SA	TU
OM (%)	4.87	4.52
clay (%)	16.63	13.84
sand (%)	72.71	76.18
silt (%)	10.61	9.97
pH	8.50	5.50
N (‰)	1.62	1.30
P (mg kg^{-1})	5.49	2.38
Ca (mg kg^{-1})	1730	620
Mg (mg kg^{-1})	66	144
Na (mg kg^{-1})	50	52
K (mg kg^{-1})	90	90

obtained by greenhouse experiments, further investigations on fertilization and hormone-like activities of SL were carried out.

MATERIALS AND METHODS

Materials. Triasulfuron is the active ingredient of Logran. Triasulfuron (99.5% purity) and Logran were supplied by Syngenta Crop Protection Spa, Milano, Italy. Indoleacetic (IAA) and gibberellic (GA) acids were purchased from Sigma, St. Louis, MO.

All of the solvents were of HPLC grade (Carlo Erba Reagenti, Milano, Italy) and were used without further purification.

A semidwarf durum wheat (*T. turgidum* L. subsp. *durum*, 'Claudio' cultivar) was used in this study.

Two Italian soils, a sandy loam from Tula (Sardinia) and a sandy loam from Sassari (Sardinia), were used. The samples were air-dried and sieved to < 2 mm. The particle size distribution was measured by Purdue University Soil Testing Laboratory using the pipet method (*15*). The organic carbon content was determined according to the modified Walkley−Black (*16*) method. N was determined by using the Kjeldhal method. P, K, Na, Ca, and Mg were measured by atomic absorption after nitric−perchloric digestion. Soil pH was determined on slurries with a soil/water ratio of 1:1. Selected physicochemical properties of the two soils, Sassari (SA) and Tula (TU), are listed in **Table 1**.

Biosolids were collected from a municipal wastewater plant (Ploaghe, Sardinia). The treatment process includes screening and grit removal. Then, after nitrification and denitrification processes for nitrogen removal, the effluents are digested aerobically. Finally, the sludge undergoes thickening by flotation, disinfection with chlorine, and dewatering in a drying bed.

The SL amounts added to TU and SA soils were within the Italian limits for sludge agricultural use as regulated by D. Lgs. N. 99/92 (*7*), deriving from EEC Directive 86/278. The SL soil amendment was applied to TU and SA soils at two rates: 15.0 and 22.5 t ha^{-1}. The first is the maximum rate allowed under Italian regulation for soil with pH value < 6, the second one for soil with pH > 7.5.

Selected physicochemical properties of the biosolids are listed in **Table 2**. The contents of heavy metals, fecal streptococcus, fecal coliform, and salmonella were within the Italian regulatory limits.

Humic acids were obtained from SA (HA-SA), TU (HA-TU), and sewage sludge (HA-SL) according to the procedure of Stevenson (*17*). After precipitation, they were centrifuged, redissolved, precipitated three times, dialyzed against distilled water until salt-free, and, finally, freeze-dried.

Sorption on Soils and SL-Amended Soils. Sorption trials were carried out using a batch equilibration technique at 25 ± 2 °C. TRS sorption isotherms were measured on natural and SL-amended soils sieved through a 2 mm mesh screen. Soil-amended samples were obtained by mixing thoroughly TU soil (5 g) and SA soil (5 g) with 25 mg (equivalent to 15.0 t ha^{-1}) and 46 mg (equivalent to 22.5 t ha^{-1}) of air-dried sewage sludge, respectively. Triplicate 5 g samples of both untreated and amended soils were equilibrated in polyallomer centrifuge tubes with 10 mL of aqueous herbicide solution (3−24 μM). The tubes were shaken (end over end) for 24 h. Generally, 95% of the sorption took place within the first 5 h. After equilibration, the suspension was centrifuged at 19000*g* for 15 min, and the supernatant was pipetted off and analyzed immediately. The TRS amount adsorbed by soil was calculated from the difference between the initial and final concentrations of TRS in solution. The effect of SA soil solution pH on TRS sorption was examined by adding HCl to soil and equilibrating overnight with the solution of herbicide. The amount adsorbed was quantified with the same procedure described for natural soils.

Table 2. Selected Properties of SL

property	value	permitted value
Zn (mg kg^{-1})	33	2500
Hg (mg kg^{-1})	<0.1	10
Pb (mg kg^{-1})	31	750
Cu (mg kg^{-1})	143	1000
Ni (mg kg^{-1})	14	300
Cr (mg kg^{-1})	1.41	
OC (%)	43.2	
P (total, %)	5.31	
N (total, %)	6.11	
K (total, %)	0.32	
salt content (mequiv/100 g)	22	
pH	7.30	
humidity (% at 105 °C)	43	
ashes (% at 650 °C)	15.2	
fecal streptococcus (CFU[a]/g, %)	<2000	
fecal coliform (CFU/g, %)	<4000	
salmonella (CFU/g, %)	<400	

[a] Colony-forming units.

Sorption on Humic Acids. Herbicide sorption isotherms were measured on humic acid extracted from natural soil and sewage sludge. Duplicate samples of soil or sewage sludge humic acid (50 mg) were equilibrated in polyallomer centrifuge tubes with 10 mL of aqueous herbicide solution. TRS concentrations before equilibration ranged from 3 to 24 μM. The tubes were shaken (end over end) for 24 h. After centrifugation, the supernatant solution was removed and analyzed.

HPLC Analyses. The TRS concentration was determined by HPLC. The system was assembled as follows: a Waters 510 pump equipped with a Waters 2487 UV−vis programmable detector operating at 224 nm; Breeze chromatography software; a μBondapak C_{18} analytical column (10 μm, 4.6 × 300 mm) eluting with acetonitrile plus water (40 + 60 by volume, pH 2.7) at a flow rate of 1 mL min^{-1}. The retention time for TRS under the chromatographic conditions described previously was 10.5 min. The quantitative determination of TRS was performed by using an external standard. Calculations were based on the average peak areas of the external standard. The detection limit for TRS was 0.05 mg L^{-1}, as calculated from the concentration of herbicide needed to obtain a detector response approximately twice the background signal.

Greenhouse Experiments. Four plastic pots were each filled with 5 kg of sieved SA soil (< 2 mm). The air-dried sewage sludge was added to the soil in two pots, at a rate of 22.5 t ha^{-1} (46 g in each container; this amount is the maximum rate allowed by Italian regulation), and the mixture was homogenized. One pot containing amended soil (SA + SL) and one containing unamended soil (SA) were spiked with the calculated amount of TRS (0.1 mg kg^{-1}), giving the samples SA + SL + TRS and SA + TRS, respectively. Of the remaining two pots, the one containing unamended soil was considered as a control soil and the other containing amended soil was considered as an amended control soil.

Five seeds of wheat were sown in each pot, at 2 cm depth, and kept in a greenhouse, with day−night temperatures of 18−10 °C, a 12 h photoperiod, and 75% relative humidity. Distilled water was added daily to the pots to raise the moisture content to 70% of the soil water-holding capacity. All of the samples were prepared in triplicate.

One hundred and twenty days after planting, the aerial portion of plants was removed from each pot and the surface area of the flag leaf (FLA) was determined with an electronic leaf area meter. Then, plant material was washed with distilled water, oven-dried at 60 °C for 48 h, and analyzed for dry matter (DM) and for N content according to the Kjeldahl method (*18*).

To compare the SL fertilizer ability to that of chemical fertilizers (N, P, and K), a further greenhouse experiment was carried out. Five plastic pots were each filled with 7.7 kg of sieved SA soil (< 2 mm): SL was added to the first pot at a rate of 22.5 t ha^{-1} (71 g); the second pot was treated with N as

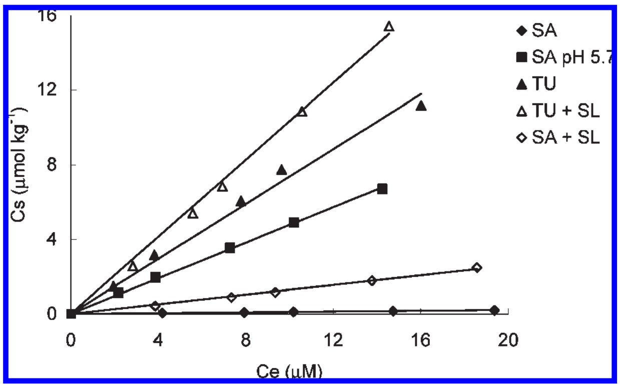

Figure 2. Triasulfuron sorption isotherms on natural (SA and TU) and amended (SA + SL and TU + SL) soils and on pH-modified SA (SA pH 5.7) soil.

urea (9.3 mg); the third pot was treated with P as calcium phosphate monobasic monohydrate (15.3 mg); the fourth pot was treated with K as potassium chloride (0.43 mg); and the fifth pot was treated with N + P + K (9.3 mg + 15.3 mg + 0.43 mg, respectively). The N, P, and K fertilizing elements were added to SA soil in amounts comparable to those in SL amount added to test soil and were mixed homogenously with soil. The samples were prepared in triplicate. Five seeds of wheat were sown in each pot and kept in a greenhouse, and the same procedure used in the presence of TRS was followed. Analogously, after 120 days, the aerial part of three plants was removed from each pot, and the surface area of the flag leaf, DM, and N content were determined.

Hormone-like Activity Determinations. The auxin- and gibberellin-like activity of the sewage sludge was assessed by checking the growth reduction of watercress (*Lepidium sativum* L.) roots and the increase in the length of chicory sweet Trieste (*Cichorium intybus* L.) epicotyls (*19*). The sewage sludge (1 g) was equilibrated overnight in a round-bottom flask with bidistilled water (1 L) at room temperature. After centrifugation, the SL supernatant was removed, the organic carbon content was determined (~10 mg L^{-1}), and the SL supernatant was stored in a refrigerator until use.

Watercress and chicory seeds were surface-sterilized by immersion in 8% hydrogen peroxide for 15 min. After five rinsings with sterile distilled water, 10 seeds were placed on sterile filter paper in a Petri dish. For the watercress, the filter paper was wetted with 1.2 mL of distilled water (control) or 1.2 mL of 20, 10, 1, or 0.1 mg L^{-1} of IAA for the calibration curve or 1.2 mL of 10, 10^{-2}, 10^{-4}, or 10^{-6} diluted SL supernatant. The experimental design for the chicory was the same as for the watercress except that the calibration curve was a progression of 100, 10, 1, and 0.1 mg L^{-1} of GA. The seeds were germinated in the dark at 25 °C in a germination room. After 48 h for watercress and 36 h for chicory, the seedlings were removed and root or epicotyl lengths measured. The results were recorded as concentration of IAA or GA of equivalent activity to diluted SL supernatant.

Data Analysis. Sorption data were fit to the logarithmic form of the Freundlich equation, $\log C_s = \log K_f + 1/n \log C_e$, where C_s (in μmol kg^{-1} units) is the amount of herbicide adsorbed by soil or humic acid, respectively, C_e (in μM units) is the equilibrium concentration in solution, and $\log K_f$ and $1/n$ are empirical constants representing the intercept and the slope of the isotherm, respectively.

Analysis of variance (ANOVA) was performed using SAS computer software. Means predicted by the *F* test to be significantly different from one another were distinguished by the Student−Newman−Keuls test. Simple correlations and their significance were calculated according to the method of Steel et al. (*20*).

RESULTS AND DISCUSSION

Sorption Studies. The sorption isotherms of TRS on natural (TU and SA) soils and SL-amended soils are shown in **Figure 2**. The empirical Freundlich equation fits well the behavior ($r \geq 0.9828$). The calculated constants K_f and $1/n$ and the correlation coefficients (*r*) for the linear fit are given in **Table 3**. In all cases the isotherms are linear with a slope value ($1/n$) of ~1, resembling the C-type curve described by Giles et al. (*21*). This shape suggests the partition of solute between solution and sorbent. The K_f values indicate that the TU soil sorption is greater than on SA soil. The two soils show similar chemical and physical features, except soil solution pH values, 5.5 and 8.5 for TU and SA soil, respectively. Most likely, the lower sorption measured on SA soil is due to the higher pH value of the SA soil solution. In a sorption trial carried out on SA soil with pH modified from 8.5 to 5.7 by the addition of hydrochloric acid, a strong increase of pesticide sorption was observed (**Table 3**). This finding agrees with the general trend observed for sulfonylureas (*14*, *22*).

Table 3. Freundlich Parameters for TRS Sorption on Soils (SD in Parentheses)

system	pH	K_f	$1/n$	*r*
TU	5.5	0.816 (±0.06)	0.97 (±0.04)	0.9972
SA	8.5	0.014 (±0.05)	0.92 (±0.05)	0.9927
SA[a]	5.7	0.537 (±0.08)	0.95 (±0.01)	0.9915
TU + SL	6.1	0.812 (±0.09)	1.08 (±0.05)	0.9828
SA + SL	8.1	0.094 (±0.06)	1.10 (±0.05)	0.9908

[a] SA soil with modified pH value.

Table 4. Freundlich Parameters for TRS Sorption on Humic Acids (SD in Parentheses)

system	pH	K_f	$1/n$	*r*
HA-TU	4.1	533.21 (±1.11)	1.15 (±0.10)	0.9892
HA-SA	4.1	610.24 (±0.22)	0.84 (±0.03)	0.9970
HA-SL	4.3	48.36 (±0.98)	1.46 (±0.04)	0.9929

The addition of SL to soil, although not significantly affecting the extent of pesticide sorption on TU soil, increases that on SA soil by about 7 times (**Table 3**). Because the SA soil was amended with higher sludge amounts than TU soil, it had a greater soil organic content and a lower pH soil solution (**Table 3**). Both of these effects may be responsible of the sorption increase observed on SA amended soil.

It is well-known that humic substances are among the most active soil components in pesticide retention. Therefore, TRS sorption on the humic acids, extracted from TU and SA soils and from SL, was tested. The pesticide showed much more affinity for TU and SA soil humic acids than for the humic component of sewage sludge (**Table 4**). Generally, the humic components of organic amendments exhibit lower degrees of polycondensation, polymerization, and humification than native soil humic substances (*23*). Most likely, the scarce sorption ability of SL low weight humic fraction may be responsible for the low K_f value observed on HA-SL. This suggests that the increase of TRS sorption on amended SA soil is not due to an increase of soil humic matter content but rather to a decrease, although little, of soil pH value.

Greenhouse Experiments. Greenhouse experiments were carried out to check if TRS sorption on SL-amended soil could modify TRS bioactivity. Weed control was checked on a durum wheat crop. The SA soil was chosen as a test soil because of its higher TRS sorption capacity compared to natural soil, due to the amendment. The herbicide controlled the weeds both in natural soil and in SL-amended soil. Only in one pot containing the unamended soil (**Figure 3**, SA + TRS) was a weed belonging to the Geraniaceae family (*Geranium rotundifolium*) observed. This weed is not present in the Logran label among those controlled by its active ingredient. The SL soil amendment has a visible effect on the vegetative growth of the wheat plants (**Figure 4**). In fact, the flag leaf area and the dry matter and N contents per plant were

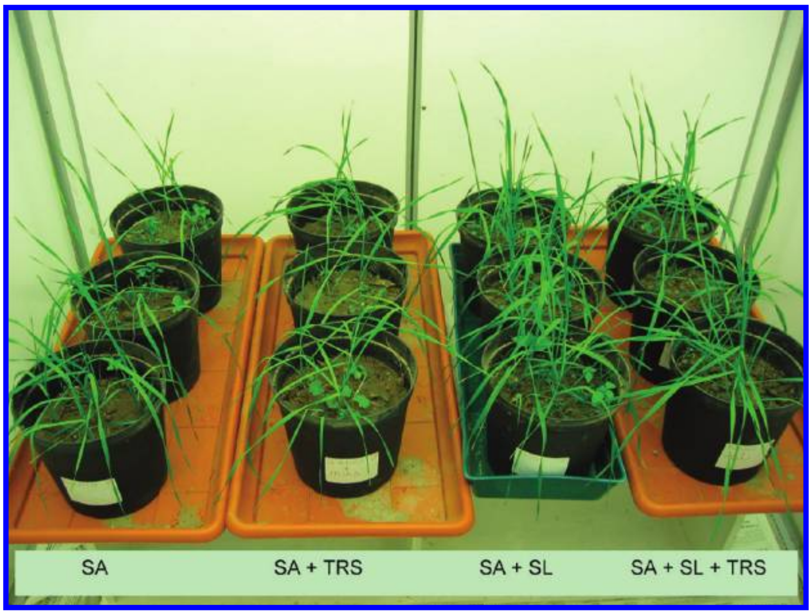

Figure 3. Herbicide control. Pot sequence from left to right: SA soil, SA + herbicide, SA + sewage sludge, and SA + sewage sludge + herbicide.

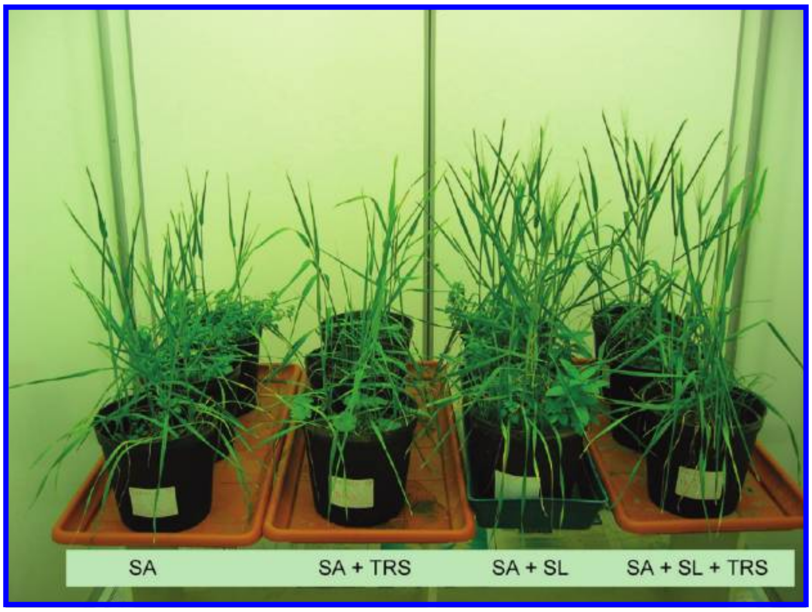

Figure 4. Wheat vegetative bloom. Pot sequence from left to right: SA soil, SA + herbicide, SA + sewage sludge, and SA + sewage sludge + herbicide.

significantly higher in the SL soil treatment (**Table 5**). Generally, the positive effect of the sludge amendment on plant growth is attributed to the increase in nutrient availability (*2*). Therefore, a greenhouse fertilization experiment was carried out to compare the effect of inorganic fertilization (N, P, and K) in comparison to SL amendment. The N, P, and K fertilizing elements were added to SA soil in amounts comparable to those contained in SL added to test soils. The inorganic fertilizers were supplied to soil both separately and together (see Materials and Methods).

Also in this case, the sewage sludge amendment was more effective in increasing the biomass and leaf surfaces than N, P, and K fertilizers, together and/or separately (**Table 6**). The SL-treated wheat plants showed, again, an anticipation of heading time of ~20 days. On the other hand, the plant's growth in unamended soil did not show any anticipation of heading time. This unexpected finding is not attributable to SL fertilization, but could be the result of SL hormonal activity. Therefore, trials were carried out to test SL hormone-like activity.

Table 5. Flag Leaf Area (FLA), Dry Matter (DM), and N Content in the Different Treatments[a]

system	FLA (cm^2)	DM (g $plant^{-1}$)	N (mg $plant^{-1}$)	N (% DM)
SA	9.83b	1.15b	7.23b	0.62a
SA + TRS	10.63b	1.68b	11.40b	0.68a
SA + SL	15.80a	3.29a	21.87a	0.66a
SA + SL + TRS	16.07a	3.36a	22.07a	0.66a

[a] Mean values sharing the same letter do not differ significantly from one another (SNK test at $P < 0.05$).

Hormone-like Activity of SL. Because hormones, particularly auxin and gibberellin hormones, have a specific role in seed germination (*24*), we checked whether the SL water extract could influence seed metabolism in the same way. The trials carried out on 2100 seeds imbibed with aqueous SL extracts suggested that IAA- and GA-like activities took place. In fact, in the presence of SL water extract, the root system showed a reduction in length

Table 6. Effect of SL and NPK Fertilization on Wheat Flag Leaf Area (FLA), Dry Matter (DM), and N Content in the Different Systems[a]

system	FLA (cm^2)	DM (g $plant^{-1}$)	N (mg $plant^{-1}$)	N (% DM)
SA + SL	17.97a	3.87a	26.60a	0.68a
SA + NPK	12.09b	1.53b	10.30b	0.68a
SA + N	10.35c	1.37bc	8.40b	0.61a
SA + P	8.90d	1.17c	8.00b	0.68a
SA + K	8.17d	1.13c	7.87b	0.70a

[a] Mean values sharing the same letter do not differ significantly from one another (SNK test at $P < 0.05$).

compared to the control, as affected by IAA. In contrast, the SL water extract induced longer epicotyls compared to the controls involving GA-like activity. In particular, 1 g of SL was comparable to 0.4 μg of IAA and to 0.8 μg of GA.

Humic substances can affect plant growth, and the effect depends on the origin, concentration, and molecular weight of humic fraction. In particular, the low molecular weight fraction is regarded as very active not only in the absorption of nutrients but also in hormone-like activity (*25−28*). Most probably, in our case the low SL degree of humification is responsible for the positive effects on plant growth.

In conclusion, the SA soil amendment influences TRS retention by preventing the groundwater contamination risk. Moreover, the adsorbed herbicide retains unchanged its bioactivity. The SL amendment of soil affects positively wheat growth and anticipates heading phase. In Mediterranean conditions the earlier heading phase may play a major role in improving crop wheat performance by preventing the negative effect of terminal drought during the grain-filling phase.

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