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Insight on the application of graphene to sandy soils to improve water holding capacity

Approfondimenti sull'applicazione del grafene a terreni sabbiosi per migliorare la capacità di ritenzione idrica

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Riassunto

In questo studio, tramite esperimenti di lisciviazione in colonna è stata monitorata e modellata la variazione di alcuni parametri idraulici (vale a dire conducibilità idraulica, porosità totale ed effettiva, ritenzione specifica e dispersività longitudinale) indotta dall'introduzione di grafene in un suolo sabbioso calcareo e in un suolo silicoclastico. Sono state condotte prove di permeabilità a carico costante per calcolare la conducibilità idraulica di ciascuna colonna, mentre sono stati condotti esperimenti di lisciviazione per stimare la porosità totale e la ritenzione specifica e per ciascun trattamento sono state eseguite tre repliche. Le colonne sono state quindi portate a saturazione tramite una pompa peristaltica a basso flusso e sono state monitorate le concentrazioni di cloruro dell'eluzione. CXTFIT 2.0 è stato impiegato per la modellazione inversa gli esperimenti in colonna al fine di calcolare la porosità effettiva e la dispersività longitudinale. I risultati hanno evidenziato piccoli cambiamenti nei valori di conducibilità idraulica e porosità totale, indotti dall'aggiunta di grafene in entrambi i suoli sabbiosi. Si è invece registrato un forte incremento dei valori di ritenzione specifica nelle colonne ammendate con il grafene rispetto a quelle delle colonne di controllo. La modellazione delle curve di tracciamento effettuate con il cloruro ha mostrato che il grafene raddoppia la dispersività longitudinale nel terreno sabbioso calcareo rispetto al controllo, mentre la dimezza nel terreno siliciclastico rispetto al controllo. I risultati evidenziano che il grafene induce un miglioramento nella capacità dei suoli sabbiosi di trattenere l'acqua interstiziale ma allo stesso tempo altera anche i parametri di trasporto dei soluti, suggerendo la necessità di condurre ulteriori studi in condizioni di campo reali, per comprendere il destino di composti indesiderati nei suoli ammendati con grafene.

Abstract

In this study, the changes in relevant hydraulic parameters (namely hydraulic conductivity, total and effective porosity, specific retention, and longitudinal dispersivity) induced by the introduction of graphene in a calcareous sandy soil and a siliciclastic riverine soil were monitored and modelled via leaching column experiments. Constant pressure head tests were used to calculate the hydraulic conductivity of each column, while leaching experiments were run to estimate total porosity and specific retention, and for each treatment three replicates were done. Columns were then run under saturated conditions via a low flow peristaltic pump and monitored for chloride concentrations. CXTFIT 2.0 was employed to inversely model the column experiments and retrieve effective porosity and longitudinal dispersivity. Results highlighted small changes of hydraulic conductivity and porosity, induced by graphene addition for both soils. A marked increase of specific retention values was instead recorded in the amended columns respect to control ones. Chloride breakthrough curves modelling showed that graphene doubled dispersivity in the calcareous sandy soil compared to the control, while it halved dispersivity in the siliciclastic riverine soil with respect to the control. The results highlight that graphene induces positive shift in the capacity of sandy soil to retain porewater but at the same time it also alters solute transport parameters, like dispersivity, suggesting that further studies need to focus on using several exposure concentrations, durations and mode of exposure, and apply simulated field conditions or perform experiments in real field conditions, to understand the fate of unwanted compound in soils amended with graphene.

Introduction

Making the way societies produce and use natural resources more sustainable is important. Saving and reusing water resources is now essential, especially in the agricultural sector, which is the main user of this invaluable resource, accounting for approximately 70% at a global scale (FAO and UN Water 2021).

Enhancing crop areas efficiency are mandatory goals to improve food availability. Even soils that were not very productive up to now should be taken into consideration to increase their yield due to soils geological structure and composition.

In 2018 it was estimated that about 35% of the sandy soils were barren, 21% grassland, 21% shrubland, 11% savanna, 6% under forest, and only 4% cropland (Earth data 2018).

The application of soil improvers, organic and inorganic, can enhance the quality of sandy soils, increasing their productivity, helping to retain water and thus making them more resilient to Climate Change (CC).

On the other hand, it is worth to test newly conceived improvers derived from wastes of industrial production with the view to reusing scraps which are becoming more and more widespread. To do so, in this study, engineered carbonaceous materials (ECM), namely graphene, was tested as possible soil improver to enhance the hydrodynamic characteristics of sandy soils which, in most cases, are inherently poor of Soil Organic Matter (SOM), have a low Available Water Capacity (AWC), a high permeability, and are often present in large coastal plains that are eligible for intensive agriculture (Dafny and Šimůnek 2016; Reichert et al. 2016).

Physical and hydrological studies on sandy soils demonstrated that preferential flow via macropore and funnel flow may occur, leading to a decrease in irrigation efficiency (Tarchitzky et al. 2007). The resulting non-uniform wetting front may in turn impact plant growth and microbial communities (Lozano et al. 2014) due to the uneven distribution of soil moisture.

Looking at European countries (Fig. 1), it is evident that AWC is inversely proportional to the percentage of sand in soils. Moreover, since sandy soils have a smaller porosity compared to other soils, they are more sensitive to changes for what concerns inputs in the water-cycle, like precipitation and irrigation), as well as outputs, like evapotranspiration (Fernandez-Illescas et al. 2001). Irrigation is often required to maintain an adequate water storage within the root-zone (Argo and Biernbaum 1995).

To reverse this trend, soil improvers are important tools that can be used to increase the sustainability of agrosystems. However, the high diversity of conditions where they can be applied may influence the results, which requires extensive

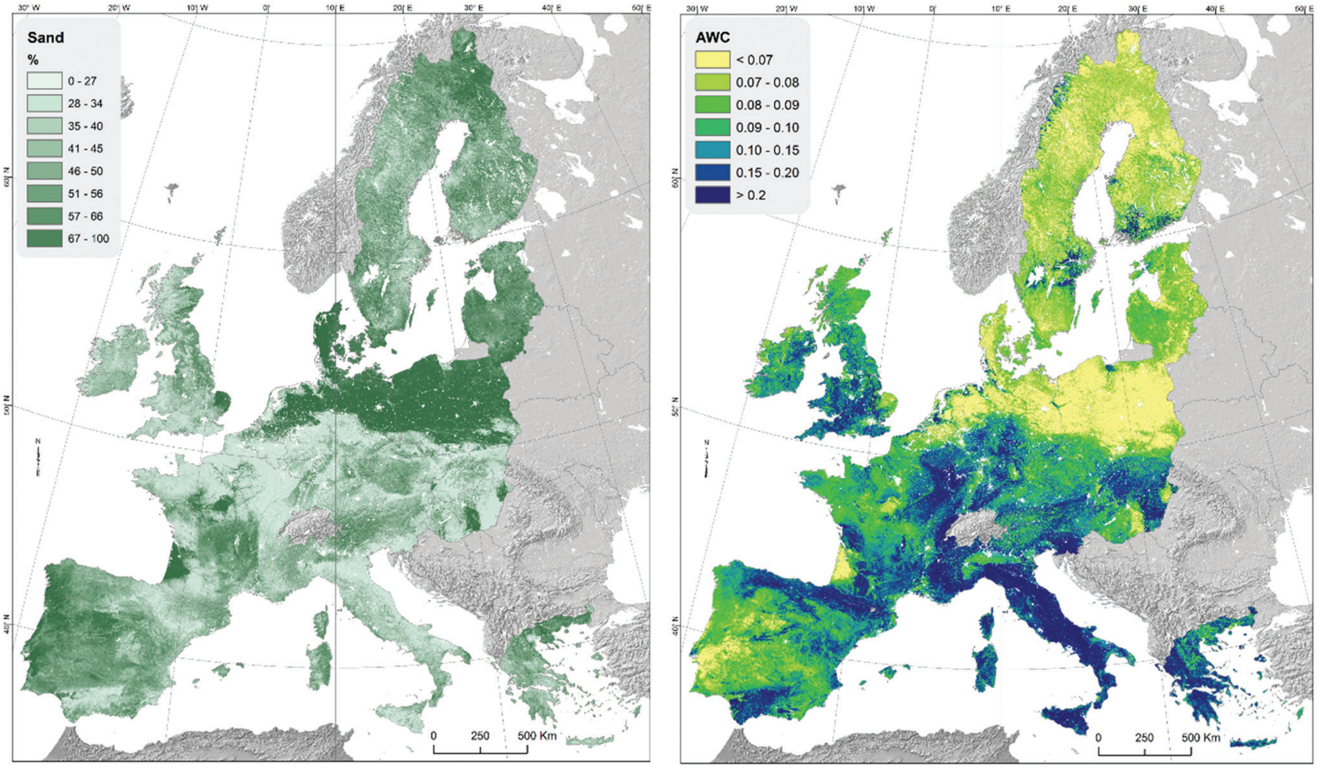

Fig. 1 - Percentage of sand (left panel) and available water capacity (right panel) in european countries, available at esdac.jrc.ec.europa.eu (European Soil Data Centre-ESDAC, European Commission, Joint Research Centre). For more information refer to Ballabio et al. (2016).

Fig. 1 - Percentuale di sabbia (pannello a sinistra) e capacità idrica disponibile (pannello a destra) nei paesi europei, disponibile su esdac.jrc.ec.europa.eu (European Soil Data Centre-ESDAC, Commissione Europea, Joint Research Centre). Per maggiori informazioni fare riferimento a Ballabio et al. (2016).

field research when traditional soil improvers (like compost, biochar, and zeolites) are employed and even extensive laboratory studies when new materials, like ECMs, are considered.

It is known that carbon materials and their natural derivatives, have outstanding properties which make them suitable in many applications of advance technology, especially in field of nanotechnology. Nanomaterials (NMs) are atomic or molecular aggregates with variable sizes ranging between 1 and 100 nm (Roco 2003; Awasthi et al. 2016). NMs can be used for a multiplicity of utilizations to treat wastewater, enhance crop productivity and quality, reduce resource consumption, obtain clean energy, in catalysts, and for improving health (Nel et al. 2006). NMs play significant role also in agriculture via various practices, since they could be used as herbicides, pesticides, onsite detection of agro-pathogens and could be crucial also in soil fertility, irrigation management and improving crop yield (Duhan et al. 2017). In this light, the applications of NMs can add tremendous value in the current scenario of a global food scarcity (Singhal et al. 2022).

These widespread applications of two-dimensional NMs have attracted interest in the manufacturing of graphene and its derivatives, referred to as graphene-family nanomaterials (GFNMs). GFNMs include single- or few-layer graphene, graphene nanosheets, graphene ribbons, graphene oxide (GO), and reduced graphene oxide (rGO) (Sanchez et al. 2012). At lower concentrations, GFNMs were found to be effective in enhancing water uptake, water transport, seed germination, nitrogenase, photosystem and antioxidant activities, in activating water channels proteins, and promoting nutrition absorption, but those beneficial effects can be reverted when concentrations are raised over a threshold value (Chng and Pumera 2013; Verma et al. 2019).

The environmental risk of GFNMs is of low concern currently (Zhao et al. 2021). It is widely understood that the present level of GFNMs contamination is not dangerous (Johnson and Park 2012). Still, this may not be neglected that their concentrations may reach beyond safe limits very soon (Nicolodi and Gianello 2014). In fact, an increase in production of commercial products containing GFNMs in past few decades has led to its unrestricted development, fostered by the absence of regulatory guidelines (Gottschalk and Nowack 2011) and the limited analytical methods for GFNMs measurements in the environment (Goodwin et al. 2018). Hence the potential hazards of GFNMs on the environment and biological systems (Koo et al. 2015) should be evaluated before they are widely marketed, accounting for the risk in specific scenarios, the long-term effects of their application, and the role of different type (Kumar et al. 2019), size, structure (Khan et al. 2017), and mobility (Morales-Díaz et al. 2017) that different GFMNs may have on the environment.

This study highlights that graphene induces positive shift in the capacity of sandy soil to retain porewater but at the same time it also alters solute transport parameters suggesting that further studies are needed to deepen the understanding of the soil-graphene system in the environment. This will help in defining regulatory guidelines to assure that the employment of NMs in the environment can be safely monitored and controlled (Bhushan 2007).

Materials and Methods

Sandy soils, here defined as soils having an average sand content greater than 50% and a clay content less than 20% to a depth of 30 cm (Hengl et al. 2017), are widely distributed across the world covering approximately 31% of the emerged globe. Within this study, it was decided to test the response of two different sandy soils to the addition of graphene to assess the variation in their hydraulic properties. The selected sandy soils were a calcareous sandy soil (hereinafter referred to as "C") with a coarse texture and a siliciclastic riverine soil (hereinafter referred to as "S") with a medium-fine texture, both having a low organic carbon (OC) percentage (Tab. 1). They were selected as representative of the main sandy soils of Italy, covering between 16.5% and 19% of the whole national territory: Regosols, Leptosols, Fluvisols, and Arenosols according to the World Reference Base for Soil Resources, and Entisols according to the USDA Soil Taxonomy (Costantini and Dazzi 2013).

Graphene was a Directa Plus® scrap (GR006050) with a very fine texture, high OC, extremely low dry bulk density (DBD), and a platelet planar size of 0.3-5 µm. The mixtures of the calcareous soil "C" with graphene have been named Cg while the mixture of the siliciclastic soil "S" with graphene have been named Sg. Graphene was added in the top 10 cm of the soil columns at 0.015% dry weight, corresponding to an equivalent field dose of 0.03 t/ha.

Tab. 1 - Soils (C and S) and graphene grain size distribution, coefficient of uniformity (CU) which is the ratio of D_{60} over D_{10}, dry bulk density and organic carbon content. Standard deviation from triplicate samples is also reported.

Tab. 1 - Distribuzione granulometrica dei suoli (C e S) e del grafene, coefficiente di uniformità (CU) che è il rapporto tra D_{60} su D_{10}, densità apparente e contenuto di carbonio organico. Viene anche riportata la deviazione standard da triplicati.

	C	S	Graphene
Sand (%)	96.8±4.6	96.9±3.6	0.0±0.0
Silt (%)	2.5±1.6	2.7±0.1	1.8±0.2
Clay (%)	0.7±1.4	0.4±0.2	98.2±0.5
CU (-)	4.7±0.7	1.8±0.2	-
DBD (g/cm^3)	1.53±0.03	1.61±0.05	0.01 ± 0.01
OC (%)	0.55±0.4	0.48±0.5	>99.0

Soil specific retention (Sr) and total porosity (θ) were calculated using small columns of 10 cm height and 5 cm internal diameter, entirely filled with the mixture of the soils and graphene (Cg and Sg) which were fully saturated from below and then let drain under atmospheric pressure for 48 hours to reach the field capacity. Hydraulic conductivity (K; m/s) was estimated via constant pressure head tests while effective porosity (θ_e) and longitudinal dispersivity (λ_L; cm) were derived via breakthrough curve (BTC) experiments. In both cases acrylic columns 50 cm height and 5 cm internal diameter were employed. High density polyethylene chambers were installed in both column's inlet and outlet to uniform the flux. The column's filling was done via 1–2 cm soil additions packed with a Teflon piston before the next one was placed on top. The packed columns were completely saturated with distilled water (EC 15±2 µS/cm, pH 6.8±0.01, ORP 150±10 mV) and flushed via a peristaltic pump for at least 100 pore volumes to attain saturated conditions. The flow direction was upward to prevent the formation of trapped gas bubbles. Effluents were drained from the columns under gravity into conical flasks. Samples were taken from the conical flasks at constant time intervals and filtered with a 0.45 µm polypropylene filter.

Chloride (Cl^-) in the effluent samples was determined by an ion chromatography ICS-1000 Dionex™ equipped with an isocratic dual pump at a flow rate of 1.0 ml/min using an IonPac™ AS14A 4x250 mm column equipped with a pre-column and an ASRS-Ultra 4-mm self-suppressor with 9 mM sodium carbonate eluent. The detection limit for Cl^- was 50 µg/L.

To quantify the dispersive solute transport in the packed columns, the transport behaviour of a conservative tracer (Cl^-) was simulated using CXTFIT 2.1 (Toride et al. 1999), in the graphical user interface STANMOD (van Genuchten et al. 2012). The transport behaviour of Cl^- was described using the classical form of the advection dispersion equation (ADE):

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} - v\frac{\partial C}{\partial x} \qquad (1)$$

where C (ML^{-3}) denotes solute concentrations as a function of distance x (L) and time t (T). D (L^2T^{-1}) is the hydrodynamic dispersion coefficient, v (LT^{-1}) is the average porewater velocity. CXTFIT 2.0 estimates unknown model parameters by minimizing an objective function (the sum of squared residuals) using a nonlinear least-squares optimization approach based on the Levenberg-Marquardt algorithm (Marquardt 1963). The inverse problem is solved by fitting an appropriate mathematical solution to observed concentration data. The model parameter here determined was D and reported as λ_L (λ_L=D/v) with its confidence interval expressed as standard deviation in parenthesis, while v was derived from the Darcy law in the form of:

$$v = \frac{Q_s}{\theta_e} \qquad (2)$$

Results and discussion

Hydraulic conductivity (K) did not vary appreciably among soils C and S and their mixtures with graphene, namely Cg ans Sg (Fig. 2a). K values showed an average value of approximately $4x10^{-4}$ m/s which is typical for sandy soils (Cronican and Gribb 2004; Domenico and Schwartz 1990), with a large variation on the three replicas. θ values were higher for C (0.35±0.02) than for S (0.30±0.01), showing typical values of sandy soils (Heath, 1983). θ was slightly decreased (approximately by 10%) by the addition of graphene at the rates here employed (Fig. 2b). Sr values increased in Cg and Sg respect to controls C and S (Fig. 2c), and in Cg the increase in Sr was more evident (approximately 20%). Moreover, the addition of graphene increased the variability of Sr respect to both soils C and S.

The main difference among the C and S columns, as regard the modelled Cl^- BTCs, is the spreading of the centre of mass which is much more pronounced in columns C and Cg respect to columns S and Sg (Fig. 3). This was likely due to the higher CU of C (Xu and Eckstein 1997), which increased the mechanical dispersion (Gerke and van Genuchten 1993; Mahmoodlu et al. 2021). Conversely, the transport processes in the S and Sg columns were advection dominated. In fact, the fitting was slightly better in the S column than in C column due to its higher homogeneity (Moradi and Mehdinejadiani 2018). In Cg λ_L nearly doubled (5.82±1.45 cm) compared to its control C (2.6±0.29), while in Sg it was halved (0.31±0.05) compared to its control S (0.65±0.06), suggesting that in well sorted soils the effect of graphene was to decrease the BTCs spreading, while in poorly sorted soil the effect was the opposite. On the other hand, θ_e was unaffected by the addition of graphene in column C (from 0.20±0.001 to 0.20±0.016) while it slightly decreased in column Sg respect to S (from 0.26±0.001 to 0.24±0.001). As regards the parameters' calibration, the inverse procedure allowed to calculate the confidence intervals of the estimated λ_L values, which were always below 25% of the estimated value; this indicated that the estimated parameter values were reasonably well identified.

The use of graphene as soil improver could have positive implications for food production, water saving, and the environmental sustainability of agricultural activities. Specifically, graphene proved to improve hydro-physical properties of the amended sandy soils, for instance augmenting water retention capacity and aeration which may favour the cultivation of wider areas, where not very productive soils (like sandy ones) are present, thus fostering agricultural productivity (SDG 2.4: Ensure sustainable food production systems and implement resilient agricultural practices that increase productivity, that help maintain ecosystems, that strengthen capacity for adaptation to CC, and that progressively improve land and soil quality). Moreover, the increased water retention capacity will lower the demand for irrigation of sandy soils, thus increasing water-use efficiency (SDG 6.4: Substantially increase water-use efficiency across all sectors to address water scarcity) and making them more

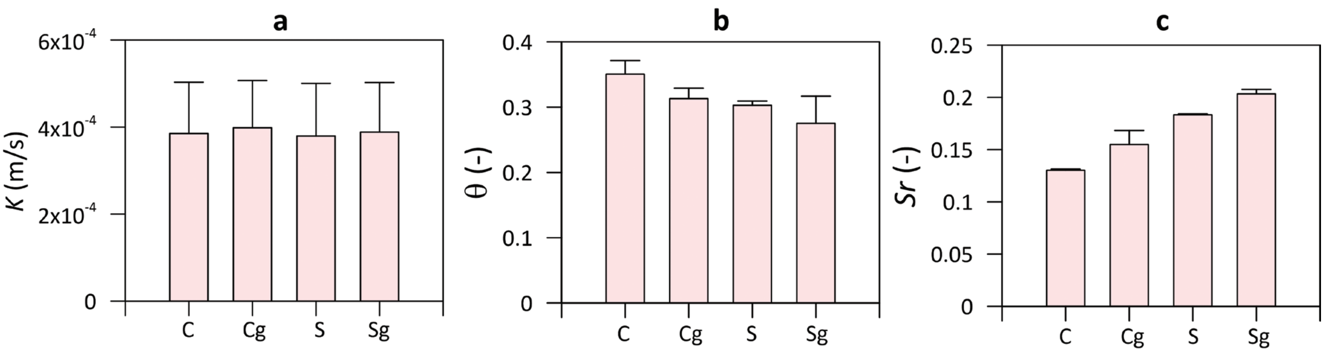

Fig. 2 - Hydraulic conductivity (a), porosity (b), and specific retention (c) measured in control columns filled with C and S soils and in the columns filled with the mixtures of soils and graphene, namely Cg and Sg. Error bars denote standard deviations calculated on three replicates.

Fig. 2 - Conducibilità idraulica (a), porosità (b) e ritenzione specifica (c) misurate nelle colonne di controllo riempite con i suoli C e S e nelle colonne riempite con le miscele di suolo e grafene, ovvero Cg e Sg. Le barre di errore indicano le deviazioni standard calcolate su tre repliche.

resilient to CC (SDG 13.1: Strengthen resilience and adaptive capacity to climate-related hazards and natural disasters).

Finally, since the ECM used in this Ph.D. study comes from graphene production's scraps, the recycling of these materials as soil improvers will help addressing SDG 12.5 (Substantially reduce waste generation through prevention, reduction, recycling, and reuse).

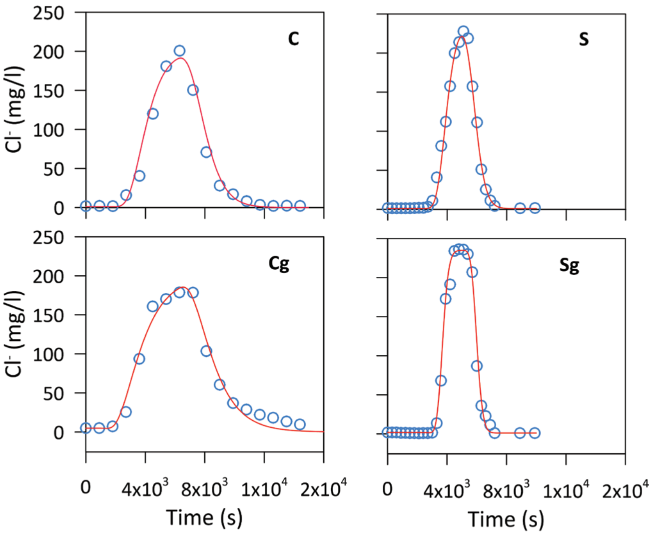

Fig. 3 - Observed (blue circles) and modelled (red line) Cl^- BTCs in control columns C and S and in the columns with the mixtures Cg and Sg.

Fig. 3 - Valori della BTC per il Cl^- osservati (cerchi blu) e modellati (linea rossa) nelle colonne di controllo C e S e nelle colonne con le miscele Cg e Sg.

Conclusions

This study highlights that graphene could be reused as improver in sandy soils at the rate of 30 kg/ha. Thus, sandy soils benefit from the addition of graphene that can effectively increase their capacity to retain porewater without inducing clogging. In particular, hydraulic conductivity, total and effective porosity, specific retention, and longitudinal dispersivity were assessed via monitoring and modelling of solutes breakthrough curves in column experiments using the ADE included in CXTFIT 2.0 (Chen et al. 2011; Mastrocicco et al. 2011; Joanna and Kazimierz 2013; Alessandrino et al. 2022b). While hydraulic conductivity, total porosity, and effective porosity were relatively unaffected by graphene, specific retention and longitudinal dispersivity were highly altered by the introduction of graphene. Graphene's addition led to an increase in specific retention (nearly 20%) which in turn increases the capacity of sandy soils to retain the porewater. λ_L doubled in the calcareous sandy soil and halved in the siliciclastic riverine soil, after graphene's addition.

In conclusions, the results of this study seem promising for the application of graphene to improve soil hydro-physical properties. Despite some potential positive aspects, graphene can have negative effects on the growth of some plants of agricultural interest (Begum et al. 2011) thus, there is still the need to further investigate the fate and transport of graphene in the environment from a multidisciplinary point of view before its eventual employment in the field, as recently emphasised by Alessandrino et al. (2022a; 2022b).

Accordingly, for new ECNMs like graphene, this study could represent a starting point for more in-depth future studies that will have to address: (i) the effects of graphene at the mesoscale and in the open field to have a clear understanding of how this material behaves in the environment, (ii) the behaviour of the graphene-soil system at different dosages of graphene, (iii) its potential toxicity (to humans and animals) in a long-term exposure in the open field, for example caution should be taken regarding exposure to respirable particles that may cause adverse health effects that are not yet known, and (iv) the economic sustainability of the addition of graphene to sandy soils in the open field which was not the objective of this study and, as far as the authors are aware has never been considered so far.

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Competing interest

The authors declare no competing interest.

Author contributions

Conceptualization, Methodology, and Formal Analysis: LA and MM; Investigation, Data Curation, and Writing-Original Draft: LA; Visualization, Supervision, and Writing-Review and Editing: MM.

Additional information

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