Prospects of 2D graphene nanomaterials in plant-based agriculture and their fate in terrestrial soils: A critical review

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Environmental Significance Statement

To feed the future global population with decreasing arable land, innovation in agriculture is a must to counterattack yield-hindering biotic and abiotic plant stresses. Application of nanomaterials as agricultural amendments has a huge potential to improve yields in conventional agriculture. This manuscript reports a state of art critical review that discusses the mechanistic understanding of the interactions of graphene with biotic and abiotic agricultural components as well as the fate and transport of graphene in soil environments. The understanding outlined in this manuscript will help the research community understand and better use graphene nanomaterials as agricultural amendments to ensure future food security.

“Prospects of 2D graphene nanomaterials in plant-based agriculture and their fate in terrestrial soils: A critical review”

Partho Das[1,3], C. Ryan Penton[2], Paul Westerhoff[1] and François Perreault[1,4]*

[1]School of Sustainable Engineering and the Built Environment, Arizona State University, Tempe, AZ.
[2]College of Integrative Sciences and Arts, Faculty of Science and Mathematics,
Arizona State University, Mesa, AZ, USA.
[3]Institute of Water and Flood Management, Bangladesh University of Engineering and Technology, Dhaka, Bangladesh.
[4]Department of Chemistry, University of Quebec in Montreal, Montreal, QC, Canada

*Corresponding author: perreault.francois@uqam.ca

Abstract:

To achieve a world without hunger, it is imperative to address the inefficiencies within the current agricultural system by adopting innovative and sustainable approaches. One such approach involves the use of graphene-based nanomaterials (GNMs), which have shown potential in alleviating plant stress, improving the performance of agrochemicals, enhancing fertilizer retention in the soil, and positively affecting plant productivity. This review explores the potential of GNMs as amendments in conventional agricultural practices and discusses the interactions with both biotic and abiotic components present in agriculture. Analysis of the literature showed that the biocidal action of GNMs in complex soil matrix tends to be lower when compared to short-term (1-3 h) toxicity test in pure culture media. Incorporation of 1ng/kg to 5g/kg GNMs in soil for an exposure time of 3 to 365 days showed a transient effect on soil microbial community, their activity, as well as soil function. When plant productivity is considered, addition of 50 mg/kg to 150 g/kg GNMs in soil showed positive impacts on plant productivity for exposure time of 3h to 120 days. However, it is important to note that outcomes of GNMs interaction in agriculture will depend significantly on factors such as the type of GNMs, application dose, exposure time, and experimental conditions. Additionally, in subsurface soil, GNMs are likely to bio-transform, which will alter their biotic/abiotic interactions. The understanding of how GNMs impact agriculture is still in its infancy, and there are discrepancies in study findings primarily due to the diversity and complexity across agricultural systems. There is need for mechanistically enriched research on GNMs interaction and fate in agricultural system that will pave the way to efficient design of GNMs application in improving yield and to obtain a food secured future.

Keywords: Agriculture, Food security, Graphene, Nanomaterial, Nanotechnology

1. Introduction:

Human population growth and worldwide reductions in arable land pose challenges for future food security (1). In order to meet the projected food demand, current agricultural production must increase by 50-80% by 2050 (2). However, the rate of increase in agricultural yield has principally declined since 1960, with the current average annual yield increase for major crops (rice, wheat, maize) being less than 1.5%. This slow rate of increase poses an issue for our future ability to meet the increased global food demand (3). Multiple factors can explain the slow increase in agricultural yields, such as inefficient delivery and plant utilization of both fertilizer and pesticides, crop losses due to diseases, extreme weather conditions intensified by climate change, soil salinization , depletion of freshwater resources, and degrading soil health (2,4). Addressing these inefficiencies while also providing a sustainable improvement in agricultural yield is difficult as soil agroecosystems are incredibly diverse and complex systems that vary between regions, crops, and types of soils (3). Considering this complexity, the path in achieving sustainable improvements in agricultural production may require the incorporation of both conventional and non-conventional approaches.

Nanotechnology embodies a non-conventional approach that has gained increasing interest over the last few decades (5). At the nanoscale, the properties of these materials are unique and exhibit promising characteristics (6) that can be leveraged to address agrochemical inefficiencies. Engineered nanomaterials can be broadly classified based on dimensionality, morphology, oxidation state, or chemical composition (7,8). Several nanomaterials, such as metal, metal oxides, and carbon-based nanoparticles have been tested as agricultural treatments since 2009 (9). Due to their very high specific surface area, excellent adsorption capacity, low production cost, and ability to serve as nano delivery agents for agrochemicals, two-dimensional carbon nanomaterials such as graphene or graphene oxide (GO) have been gaining increasing interest as agricultural nano-additives. Graphene based nanomaterials (GNMs) are classified as “nanomaterial enhanced fertilizers” (10) and have been shown to enhance plant growth and development in the soil environment. The application of GNMs to soils (alone or in mixtures of fertilizers) was shown to improve the efficiency of agrochemicals through targeted delivery and slow-release action (11–24). It is therefore a type of material that can be used in many forms to help improve agricultural yields. However, compared to the use of GNMs in industrial and manufacturing sectors, the application of graphene in agriculture is still in its infancy (25). This is partly due to a limited understanding of the interactions of GNMs with the different components present in an agricultural soil-plant system and their eventual fate once applied to the environment. Over the last two decades researchers have studied how GNMs are likely to impact environmental components (both biotic and abiotic). In a compilation of different studies on microbial interactions with GNMs, a recent study (26) observed that bioprocesses may be impacted by GNMs in both positive and negative ways. For example, a culture media-based study showed that GO at a concentration of 500 mg/L increased cell proliferation (27), whereas cell membrane damage and bacterial lysis were reported for a similar dose (500 mg/L) of GO in another study (28). Thus, it becomes difficult to generalize whether GO is a growth promoter or inhibitor, as the same dose can provide contradictory findings. Similar conflicting findings were also observed for the interactions with plants, where GNMs were shown to positively or negatively impact plant growth at similar GO doses (29). Given those inconsistencies, it's clear that further understanding is needed regarding the effects of utilizing GNMs in agricultural settings.

This review article aims to unravel some of the discrepancies surrounding the interactions and environmental fate of GNMs in agricultural soils. To do this, we systematically reviewed and discussed the interaction of GNMs with the different components present in a typical agricultural soil system. Guidelines for future GNMs development and mechanistically enriched research are needed in order to connect lab-based research with field-scale applications to provide a pathway towards the sustainable application of GNMs in agriculture.

2. What unique properties make graphene an interesting material for agricultural application?

GNMs are made of a sp^2-hybridized network of fused benzene rings existing as a single sheet or a few layers of sheets (30). These can be pure uniform networks, partially oxidized, or a heterogeneous mixture including combination of a crystalline structure made of parallel graphitic sheets and amorphous carbon defects. Some of the promising properties of GNMs are high electron conductivity (up to 50 000 $cm^2 V^{-1} s^{-1}$), thermal conductivity, mechanical strength ($E= 1$ TPa), and massive surface area (2630 $m^2 g^{-1}$) (31,32). Based on the number of layers or oxidation levels, GNMs can be classified into four major categories: graphite, single or few-layer graphene (FLG), GO, and reduced graphene oxide (rGO). The properties of GNMs vary among those different forms. For example, the electron conductivity of FLG can be up to 50 000 $cm^2 V^{-1} s^{-1}$, whereas GO is an insulator (31).

Graphene in its pure forms (e.g., FLG, graphite) is hydrophobic. However, the presence of oxygen on the surface in the form of surface functional groups (e.g., GO), converts it into a hydrophilic material as it can form hydrogen bonds with water molecules. Graphene can also be functionalized with other elements by both covalent and noncovalent modification techniques (33,34). Novel functional surface chemistries can be introduced to enhance performance in specific applications. Due to their high surface area, GNMs can adsorb and retain ions and nutrients essential to plants in agricultural soils and, with their high electrical conductance, they can improve the flow of electrons and thus impact microbial and biogeochemical processes such as nutrient cycling (e.g., denitrification). Altogether, these properties reveal GNMs as novel, multi-purpose nanomaterials that can be used to enhance agricultural efficiencies. Current methods of application of GNMs include direct soil amendment, water (hydroponic system) or growth media amendments, foliar application, stigma application, direct injection into the plant, and in combination with agrochemicals (both fertilizer and pesticide), which has shown a potential to increase the protection against biotic and abiotic stresses to improve agricultural yield.

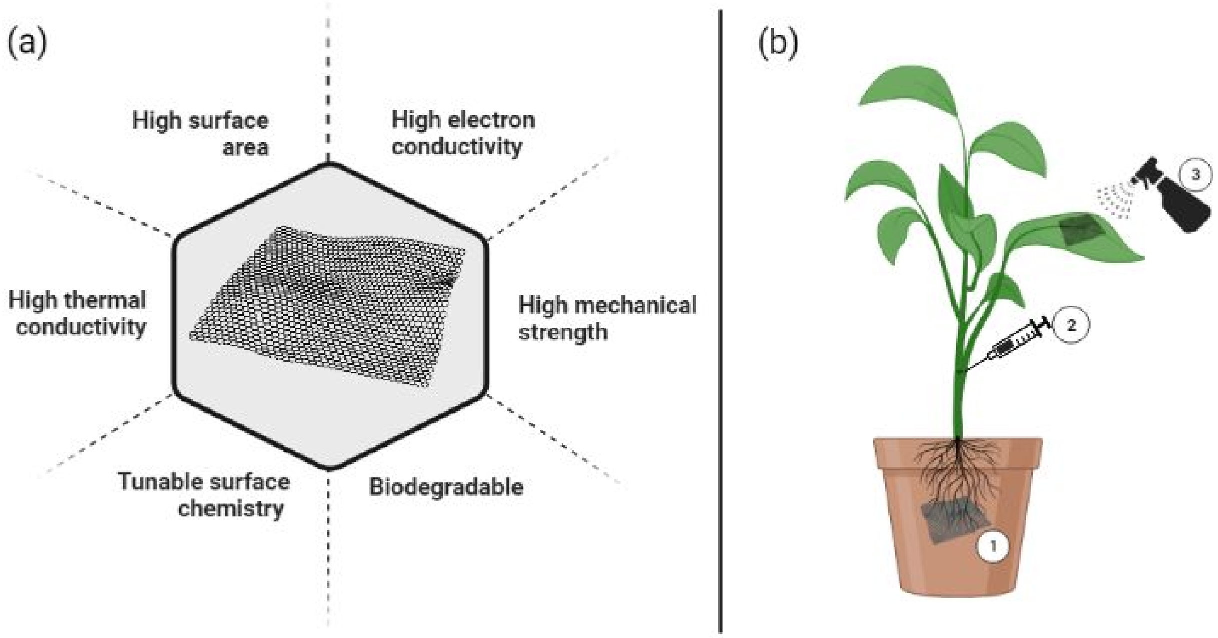

Figure 1: (a) Unique properties of graphene-based nanomaterials (GNMs) for considering application in agriculture. (b) Current GNMs application methods in plants (1) Direct application in soil or other growth media; (2) Direct injection; (3) Foliar and stigma (flower) application.

3. Graphene interaction with agricultural components:

Soil contains both biotic (e.g., bacteria and fungi as well as other microorganisms and soil fauna) and abiotic components (e.g., soil minerals, moisture, aggregates, oxygen status, water holding capacity) that interact across space and time. Given the potential use of graphene as a soil amendment in agriculture, the first consideration is how soil biotic and abiotic components interact with this added carbon-based nanomaterial. These interactions need to be evaluated based on GNM type, dose, exposure time, and experimental conditions (e.g., hydroponic vs soil) as each of these can alter the overall impact on the soil community and its associated processes. The identification of the GNM type, range of dose, exposure time, soil characteristics and plant type to which the maximum benefit can be obtained should be considered the overarching goal of future studies on utilizing GNMs as soil amendments in agriculture.

3.1 Graphene and soil biotic components interaction:

3.1.1 Graphene and soil organism interaction:

Soil is a dynamic ecosystem that harbors a complex community of micro-, meso-, and macro-flora and fauna. In agricultural soils, critical biogeochemical processes such as nutrient cycling and organic matter turnover largely depend on the activities of its biological components. Thus, it is important to assess how the presence of GNMs impact the different biological compartments and their activities within the soil.

3.1.1.1 Graphene and bacteria:

Among the biological components, bacteria are inarguably the most important unit in terms of their impact on soil nutrient cycles and major biogeochemical processes. The response of soil microbial communities to the addition of carbon-based nanomaterials (CNMs) has been explored by assessing various parameters related to microbial biomass, community structure, and enzyme activities (35–37). Most GNMs possess antibacterial properties associated with a range of mechanisms such as oxidative stress via the generation of reactive oxygen species, glutathione oxidation, DNA fragmentation, membrane damage, and cell entrapment (38). However, these toxic interactions have been principally reported for model bacterial species in culture media over short exposure times of 1 to 3 h (For GNMs dose: 10 to 1000 mg/L) (Table S.1.1). Several studies have reported how increased exposure time of 4 h to 48 altered the antimicrobial effect and often led to an enhancement in bacterial growth or activity (For GNMs dose: 25 to 500 mg/L) (Table S.1.1). Cellular response to GNMs is also influenced by the oxidation level of graphene. Higher C:O ratios have been associated with increased antimicrobial effects on *E. coli* in growth study employing GNMs dose of 1 to 500 mg/L (39,40). The size of the GNM sheets also plays a role, with smaller sheet sizes more lethal to bacteria (41). The presence of oxidation debris or elemental impurities can also negatively impact bacterial survival (42).These studies provide useful insights regarding the mechanisms of interactions of GNMs with bacterial cells, though in pure culture conditions.

The response of bacteria in an agricultural soil system after the addition of GNMs is expected to be quite different from culture media-based studies. This would likely be due to the interaction of GNMs with abiotic components such as clays, humics, charged species such as iron and aluminum and other constituents of soils, in addition to the different bacterial physiologies in soils compared to pure culture conditions. A recent study (43) reported a reduction in toxicity for GO in soil as compared to culture media. This effect was attributed to the adsorption of biotic and abiotic components of the soil to GO, which reduced its availability to interact with bacteria. Though culture-based studies mostly reported toxic interactions between GNMs and bacteria, in soil media both positive and negative impacts were observed for GNMs across a wide range of exposure times, doses, and GNMs types (Table 1). However, studies reporting the effects of GNMs on soil bacteria are sparse as compared to the large number of studies in artificial culture media. This imparts a challenge to clearly understanding conditions that distinguish beneficial from deleterious impacts on soil microbes. The complexity and heterogeneity of soil properties across soil types and landscape characteristics also add to this variability. Experimental conditions for studies that assessed the impact of GNMs on soil microbial communities ranged in doses from 1ng/kg soil (44) to 5 g/kg soil (45), in exposure times from 3d (46) to 1yr (47) and used various GNMs types, including graphite, graphene, GO, rGO, graphene nanoplatelet (GNP), and graphite nano additive (GNA) (Table 1).

The effect of adding any nanomaterial to a soil environment can be assessed by examining the change in microbial abundances. Study (48) reported an enhancement of soil microbial biomass (SMB) during the early stage of incubation (4 days) in soil when graphene was added at a rate of 10 to 100 mg/kg soil. This effect disappeared at longer incubation periods (e.g., 60 days) or higher graphene doses (e.g., 1000 mg/kg). On the contrary, GO didn't exhibit any significant impact on SMB at a comparable dose and exposure time (49). However, a study reported that after a relatively long exposure time (1 yr) of soil with graphene, a lower soil DNA abundance was recorded coupled with no change in soil respiration (50). A similar insignificant alteration of SMB was reported for rGO (51) and functionalized GO (52), indicating that the impact of GNMs on SMB varies with type and exposure time.

The presence of GNMs in the soil may also alter the composition of the soil microbial community (45,46,53). These changes may or may not impact the function of the soil microbial community, due to functional redundancy, the case when multiple microbes possess the same functional profiles. In terms of functional impact, GNMs have been reported to potentially impact the soil N cycle (54), where using gene abundance data, a suppression of soil nitrification gene abundances and an increase in soil denitrification gene abundances were reported in communities exposed to GNMs. Similar effects of GNMs on N cycling were observed in studies on sludge, wastewater, and freshwater sediments (55–58). However, it should be noted that GNMs imparted transient effects on soil microbial communities, with short exposure boosting microbial community abundances and their associated metabolic activities while long exposures revealed lesser beneficial impacts of GNMs (48,59).Thus, since the effect of GNMs on the bacterial community is known to be time dependent (46), information obtained from studies with longer exposure times can provide useful information considering the application of GNMs in agricultural soil. Moreover, how functionalized GNMs and GNMs with or without impurities impacts bulk soil and rhizosphere microbiome communities across various soil types for both short- and long-term period as well as information on resiliency of both beneficial and pathogenic biocomponents against the added GNMs need further exploration.

Table 1: Impact of GNMs on soil bacteria:

Type of graphene	Application dose to soil (mg/kg)	Exposure Time(days)	Impact studied-	Experimental matrix	Major findings	References
GO,rGO,GNP,GNA	5,1000	28	Gene abundance related to N cycle	Sandy loam	-Increased abundance of denitrifying genes (*nirK*, *nirS*, *nosZ*), decreased abundance of *amoA,* unchanged abundance of *nifH* gene	(54)
GO	10 to 1000	120	Abundance, enzyme activity and community	-	-GO decreased the abundance of microbes and altered the community structure. -Nitrate reductase, ammonia monooxygenase and urease enzyme activity were reduced. -GO inhibited urea hydrolysis and increased TN content.	(53)
GO, Graphite	10^{-6}, to 1	7 to 30	Community	Ultisol	-No significant impact on alpha diversity of microbial community -The composition of bacterial and fungal communities was influenced by GO or graphite at all doses.	(44)
Graphene	10 to 1000	7 to 90	Community diversity and enzyme activities	Cambisol	-For short exposure (7 to 15 days): Graphene increased the richness and diversity indices of the bacteria community -For longtime graphene exposure: Bacterial abundances increased (for low dose graphene) and decreased (for high dose graphene).	(59)
rGO	50 and 500	30	Biomass; community; enzymes; phytohormone	Loam Soil	-No significant impact on soil microbial biomass carbon. -Little shift of the predominant soil bacterial species, but composition of the bacterial community significantly altered. - phytohormones and antioxidant enzymes in rice roots significantly increased.	(51)
GO	100 to1000	7 to 21	Activity and community composition	Soil	-No change in soil bacterial biomass -Ag-GO decreased enzyme activities and inhibited nitrification.	(52)
GO	1000 and 2000	3 to 60	Community	Loam soil	-Altered the bacterial community in a time-dependent manner. - Increased enzyme activity except urease -Decrease the diversity of the bacterial community.	(46)
Graphene	1000	365	Biomass; activity; community.	Grassland	-No significant difference in SIR for control and graphene treated soil. -Significantly reduced extractable soil DNA ($P < 0.05$). -Altered bacterial communities.	(47)
Graphene	10 to1000	4 to 60	Function, structure and abundance	Anthrosol	-For short exposure of 4 days: Increased soil microbial enzyme activity and bacterial biomass. -For long exposure time of 60 days: No significant change in biomass and enzyme activity compared to control soil but suppressed bacterial populations (e.g., Nitrospira, Planctomyces).	(48)

GO	100 - 1000	7 to 59	Enzyme activity and biomass	-	-Microbial biomass showed increasing trend on 21, 31, and 45-days incubation. -High concentrations lowered soil enzyme activity up to 21 days of incubation. But showed increasing trend or no difference after 21 days.	(49)
GO	5	90	Community	Silty	- Bacterial community in the presence of GO became richer and more diverse. - Nitrogen fixing and dissimilatory iron reducing bacteria genus selectively enriched.	(45)
GO	10	56	Enzyme activity	Silty clay loam	GO enhanced soil arylsulfatase enzyme activity.	(60)
Graphene	200	28	Diversity, community, and metabolic activity	Commercial soil mix	-Increased microbial richness in both bulk soil and rhizosphere soil. -No significant impact on microbial Shannon diversity, beta diversity and microbial function in both bulk soil and rhizosphere soil. -Increased microbial use of both labile and complex substrates.	(61)
Graphene	10 to 1000	15 to 60	Richness and diversity of community	Haplic Cambisols	-Increased richness of bacterial community and relative abundance of dominant bacteria phyla. -Decreased the diversity of bacterial community and inhibited sone N cycling bacteria phyla. -Changes in bacterial community depended on incubation time rather than graphene dose.	(62)

3.1.1.2 Graphene and Fungi:

GNMs have been tested against a wide range of fungi to assess their antifungal performance across a variety of culture media (Table S.1.2). GNMs and GNM composites have demonstrated fungicidal effects or can be used to improve the performance of fungicides (63,64). For the effects of GNMs on fungi, studies reported the use of GNM doses ranging from 1 to 4000 mg/L and exposure times from 2h to 18 days (Table S.1.2). Most studies reported an antifungal effect while only a few reported no effect or positive effects (65–67). The observed positive effects may be associated with a “hormesis dose response phenomena”, where low doses stimulate fungal growth and high doses act as antifungal materials (68). The mechanisms of action proposed are associated with the inhibition of cell proliferation, damage to the cell membrane, the inhibition of spore germination, deformation of germination, and changes in volatile organic carbon and enzymatic production (28,69–71). Thus, there appears to be a dosage-dependent effect on fungi, thus revealing a possibilty of either increasing beneficial fungal-plant relationships or, at higher doses, acting as a suppression to fungal disease. To this end, a recent pot study (71) with wheat reported that the application of GO with irrigation water significantly decreased wheat growth inhibitory effects caused by the fungal pathogen *Bipolaris sorokiniana*. This promising finding illustrates one of the unforeseen potentials of GNMs in addressing yield-hindering fungal diseases in agriculture.

3.1.1.3 Graphene and Algae and Cyanobacteria

Along with the use as biofertilizers, eukaryotic algae (e.g., green algae), and prokaryotic cyanobacteria are naturally abundant in agricultural soils (72). Those photosynthetic microorganisms can have positive effect on soil structure, such as by improving soil aggregation and water holding capacity, increasing soil fertility, through carbon and nitrogen fixation, improving nutrient cycling such as P cycle, or by acting as plant biostimulants (72). With their beneficial characteristics it is necessary to address how GNM application will alter these communities. However, as noted with bacteria, current knowledge regarding GNM impact is based on toxicity studies carried out in pure growth media (Table S.1.3). In those toxicity tests, GNM concentrations ranged from 0.01 to 300 mg/L while the exposure time spanned 24 to 96 h. In general, there was dose dependent toxicity (73) while smaller sized particles exhibited more toxic effects as compared to relatively larger sized GNMs (74). The type of GNM was also found to be important in that the toxicity of GNMs that possess higher C:O ratios (more reduced form) was shown to be less toxic to an algal population (39) than more oxidized forms like GO. This impact on algae contrasted with that of bacterial cells where toxicity increased with the C:O ratio. The mechanisms reported for the toxicity of GNMs to algae include light shading, cell aggregation, nutrient depletion, oxidative stress-induced membrane damage, extracellular surface coating, and intracellular morphological changes (73,75–77). In all these algal media based studies it was obvious that the toxicity of GNMs also varied across algal species for the same GNM (39). The only information available for cyanobacteria revealed that they are more sensitive to GNM exposure, as compared to algae (76). However, the results of these direct toxicity studies may not apply to algae and cyanobacteria populations in agricultural soils due to the heterogeneity of the environment, influence of abiotic and biotic interactions, and system-level heterogeneity. Thus, further research is needed to assess the impact of GNMs on algae and cyanobacteria present in natural soil environments.

3.1.1.4 Graphene and soil invertebrates:

Soil invertebrates are an important indicator species of soil health and play important roles in terms of nutrient cycling through organic matter decomposition and nitrogen mineralization as well as by altering soil aeration which impacts aerobic and anaerobic microbial respiration. Several studies have assessed the impact of GNMs on earthworms in soil or filter paper systems whereas the uptake of GNMs has only been examined in water matrices. In a soil-based experiment, the exposure time ranged between 7 to 56 days with doses varying between 100 mg/kg to 30 g/kg (Table S.1.4). When compared to the proposed concentrations for the use of GNMs as a soil amendment in agriculture, the outcomes of studies using excessively high doses (30 g/kg soil) (78,79) may not be useful. However, study (80) evaluated the impact of GNMs at concentrations from 100 to 1000 mg/kg on earthworms, which is more representative of real application scenarios. Study (9) reported a median and mean dose of nanomaterial used in soil-based applications as 125 and 743 mg/kg for the timeline of 2009 to 2022, respectively). In a nematode based study, it was reported that a 130-day exposure to 10g/kg of GNMs resulted in an increase of bacterivores and fungivores but a decrease in several nematode community parameters associated with diversity, species richness, and structure (81). Thus, it is evident that a considerably high dose application scenario of GNMs may reduce the biodiversity of soil invertebrates. However, a knowledge gap persists in terms of the impact at reasonable application doses and exposure times on invertebrates in agricultural soils.

3.1.1.5 Graphene and soil arthropods:

As important components of the soil nutrient cycle who can also play a role in pest control, soil arthropods are another group of soil biota of interest in agricultural soils. To date, there is very limited understanding regarding the interactions between GNMs on soil arthropods and mites (Table S.1.5). One study showed that the abundances of microarthropod groups including predators, detritivores, herbivores and fungivores increased in presence of GNMs (82) after 130 days exposure to 10g/kg soil. Total taxonomic richness, Shannon diversity index, and dominance index of the microarthropod community increased in the presence of graphene, indicating the formation of a more complex and diverse community that was induced by the presence of GNMs. In terms of agricultural relevance, it would be beneficial to investigate the potential interactions that would lead to the control of specific populations of arthropods, such as crop pests. In this context, it has been reported that GO can serve as a pesticide carrier with an improvement in the performance of a pesticide used against mites.

Considering the findings of the referenced published studies (Table S.1.1 to S.1.5), which assessed the impact of GNMs on soil biocomponents, it is evident that there is still limited understanding on how GNMs will interact with soil biocomponents at field-relevant doses across long exposure times in natural agricultural soils. Thus, there is a need to critically address how GNMs poses both short- and long-term impacts on biocomponents in complex agricultural soil with mechanistically answering how biocomponents community responds to the presence of GNMs if added as agricultural amendment.

3.1.2 Graphene and plant interactions:

Plant yield can be hindered by biotic stresses (e.g., pathogens, herbivory, competition), abiotic stresses (drought, salinity, temperature), and interactions between the two. Numerous studies have tested GNMs in context of their ability to alleviate stress and improve overall plant biomass production. Compared to other nanomaterials used in agriculture, such as ZnO and CuO, GNMs are not sources of macronutrients to the plant and microbial community. Therefore, potential GNM impacts on plant productivity may be through: (1) direct effects on plant gene translation and/or on gene regulation which alters plant physiology in a positive manner, (2) direct impacts on the microbial community composition or activity which improves plant nutrition through nutrient cycling and/or alleviation of stress responses, (3) indirect effects through reducing nitrogen losses and (4) a combination of these responses. In this section the current state of plant research employing GNMs are outlined including both positive and adverse effects along with an effort to provide mechanistic insights, where possible.

Although studies concerning the application of GNMs on plant growth/productivity are a relatively recent development, the limited studies do cover a wide range of plants. This includes forage crops (alfalfa(83,84), pearl millet(85), switchgrass(19), white clover(86)), shrub (*Paeonia ostii*(87), aloe vera(88)), herb (*Lepidium sativum* L. Calli(89), coriander(90)), flowering plants (catharanthus (91), *Plantago major L. calli* (92)*,* chive (93)*, Corylus avellana L* (94)*, Arabidopsis thaliana*(95))*,* cash crop (cotton(91)), cereals (rice(51,96,97), *Avena sativa L.*(98)*,* wheat (99–108), sorghum (19), *Zea mays* (109)), fruit (grapevines (110), watermelon (111), gala apple (112), peeper (113)), vegetables (cabbage (114), lettuce (12,114–116), tomato (13,113,114,117,118), spinach (93,114), faba bean (29,119), garlic (90), pea (120), zucchini (121)), pulse (lentil (122), soybean (123)), oil crop (*Brassica napus L*. (124,125)), pine family (red pine (126), *Changbai larch* (127)), and white moss (128) etc. In these studies, GNMs were applied directly to plant or seedling growth media (soil, nutrient growth solution, water) as well as a foliar application or direct injection to plant systems. GNM application to soil (as direct application or with irrigation water) (dose: 50 mg/kg to 150 g/kg or 12.5 to 500 mg/L), nutrient growth solution (dose: 0.1 to1000 mg/L), water or hydroponic system (dose: 30 to 2000 mg/L), leaf (dose: 10 to 1000 mg/L), stigma (dose: 5.5 to 22.1 ng/mm^2) or direct injection to stem (dose: 0.5 to 50 mg/kg) all resulted in beneficial impacts over exposure times that ranged from 3 h to 180 days (*see Table S.2*).

Addition of GNMs have been found to improve seed germination (13,19,23,29,93,99,119,129). This was reported to be due to improved water transport inside the seed by GMN penetration of seed husks and facilitation of water uptake. Enhanced seedling growth (90,100,101,130) and root-shoot development (109,111,112,117,126) was also reported and in most of the cases GNMs exhibited a 'hormesis effect' in seedling experiments. For instance, low concentrations (100 mg/L) of GO promoted growth whereas high concentrations (1000 mg/L) resulted in inhibition of seedling root growth (101). GNMs have also been reported to improve plant yield (12,88,131), possibly through improvement in photosynthesis, root growth, soil structure, available nutrient content or enzyme activities. Another study (111) reported injecting GO into plant stems which resulted in increased watermelon perimeter, sugar content and ripeness. Study (121) showed stigma application of GO upto 11.1 ng/mm^2 didn't alter sexual reproduction of *C. pepo*. Addition of GNMs (GNA, <1% wt of fertilizer) was also reported to decrease fertilizer requirements and decreased nitrate leaching in a greenhouse study (12). Our recent study with GNA (dose: 165 mg/kg) showed that this decrease in nitrate leaching is microbially related (132).Thus, along with plant yield improvement, GNMs have the potential to reduce the environmental impact of added agrochemicals by potentially reducing N requirements.

In addition to improved plant development, GNMs have exhibited the potential to reduce the impact of both abiotic and biotic stresses. For example, GNMs improved soil water retention (87,93) which is beneficial considering the abatement of nutrient leaching and reduction of irrigation water use in dry environments or under drought conditions (87,91,92). GNMs have also been reported to alleviate salinity stress (19,83,85,89,91,110). One study reported that the alteration in the expression of genes related to photosystems (I and II) were behind this enhanced salt and alkalinity stress tolerance (83) in a soil-based experiment with graphene dose of 0.5% to 2%). Conversely, enhanced antioxidant enzyme activity (85) for a foliar-based application study with GNMs (dose: 20 mg/L) was indicated as a correlation to reduced salinity stress. Enhanced antioxidant activity was thought to play a crucial role in overcoming nitrate/ammonium stress in seedlings when growth medium was supplemented with 50 to 250 mg/L of GNM (103,104). GNMs have also been reported to enhance leaf chlorophyll a/b ratios and thus minimize adverse effects under heat stress. Foliar application of GO (dose: 30 mg/L) were found as a safeguard against heavy metal (e.g., Cd) stress through the minimization of heavy metal effects on cellular organelles (116).

However, studies have also reported negative impacts of GNMs on plants such as through negative effects on plant growth and biomass accumulation (root or shoot) (96,98,114,124,125), altered photosynthesis (128), suppressed nutrient uptake (84,86,108), bioaccumulation (95,105,107,120), altered sexual reproduction (94) and oxidative stress (97,106,124). The mechanisms behind these adverse impacts include cellular structure damage (97,105,128), lower chlorophyll content (128), disruption of root structure (105), fragmented nuclei, membrane damage, mitochondrial dysfunction, increase of ROS (95), increases in phytohormones (51), and decreases in protein and polysaccharide content (107), downregulation of carbohydrate metabolism (133).These adverse effects not only depended on plant type, the specific type of GNM, exposure time or concentration but also the composition of the experimental matrix as the adverse effects of GNMs are decreased in a soil applications as compared to within hydroponic systems (98). This reduced phytotoxicity of graphene in soil compared to hydroponic system may be due to presence of aheterogeneous mixture of humic substances (134,135).

Another aspect of GNMs application in agriculture is how much of the added GNMs will be uptaken and translocated inside the plant systems to examine the risk of GNMs entry into the food system. Employing ^{14}C or ^{13}C-stable isotope labelled GNMs (120,136), transmission electron microscopy (137), or inductively coupled plasma (138) elemental analyses, only a few studies assessed the uptake, translocation, and transformation of GO, rGO, or FLG in plant studies realized using liquid growth media (water or nutrient solution). In a pea (*Pisum sativum L.)* seedling growth study, (120) used ^{13}C labeled GO and rGO (concentration: 0.04 to 2 g/L; duration 20 d) in hoagland nutrient media and reported that GO is restricted to plant root but rGO was translocated to the leaves. Another study (136) studied the uptake, distribution, transformation, and depuration of ^{14}C labeled FLG (concentration: 250 μg/L; duration 21 d) in rice seedling growth experiment in a hydroponic system and reported an accumulation of FLG in both root and shoot at 695 and 54 mg/kg, respectively, of which 70% was retained by the plant after 14 days of depuration. In a similar hydroponic rice seedling growth experiment, (137) reported the translocation of FLG in chloroplasts, which resulted in an improvement in photosynthetic activity when the seedlings were exposed to a concentration of 100 μg/L for 7 d. By tracking metallic impurities present in graphene, (138) reported a root uptake of 14% and 48% GO and graphene by soybean roots in a growth study (concentration: 200 and 500 mg/; duration: 7 days). These studies demonstrate the ability of GNMs to enter the plant and alter physiological functions in a way that is influenced by the physicochemical characteristics of the GNMs. However, future studies are still needed to explore how differently GNMs will get uptaken from soil (if GNMs are added as soil amendememnt) followed by their transformation inside the plant system.

In summary, the impact of GNM application on plant physiological traits and responses to environmental stresses remains mixed as is most likely due to changes in the experimental variables. Furthemore, the overwhelming majority of studies have only investigated the effects of GNMs in controlled conditions. While these studies provide crucial insights into the direct impacts of GNMs on plants, it remains unlikely that these identified effects can be successfully replicated in soil systems. Therefore, it remains necessary to understand how the combined impacts of biotic and abiotic soil components influence plant responses to GNMs under varying agroecosystem management regimes.

3.2 Graphene and soil abiotic components interaction:

Soils are immensely complex system where the composition of the abiotic properties differs across spatial scales of <1mm to km. Numerous formations of abiotic soil, ranging from macro to microscale, play a crucial role in agriculture. Soil aggregates, for instance, are of significant importance as they create oxygen gradients, facilitating the storage of nutrients, water, and excreted metabolites that shape an active rhizosphere. Abiotic factors shape the diversity of life in soil, can reflect soil health with stored organic matter, and can influence the fate, transport, and activity of added GNMs.

3.2.1 Graphene and water:

Due to the movement of gravitational water through soil pores, application of GNMs in the topsoil layer may disperse to lower soil layers. However, this mobility depends on whether the added GNM is well-distributed in the soil pore water, the amount and frequency of water added, the presence of aggregates and roots, and the availability of preferential flow through pore channels. It will also rely on whether the added GNM is hydrophobic or hydrophilic. Pristine graphene, with no oxygenated surface functional groups, does not bind with water molecules due to the inability to form H bonds and thus is not well suspended in water (139). However, graphene nanomaterials with oxygenated surface functional groups like GO and rGO exhibit affinity towards water molecules which leads to fine dispersion in soil pore water.

3.2.2 Graphene and nutrients:

Macro- (nitrogen, phosphorus, and potassium) and micro-nutrient (copper, iron, manganese etc.) fertilizers are essential agrochemicals that support plant productivity. The high surface area and numerous functional groups expressed on GNMs have been investigated in their ability to adsorb and either retain (when used as a soil amendment) or deliver (when used as a fertilizer) nutrients to support plant growth. Thus, evaluating how different macro and micronutrients interact with GNMs that control the fate and bioavailability of added nutrients (as fertilizers) in agricultural soil systems is crucial.

Despite having a net negative charge, both functionalized and non-functionalized GNMs have been reported to adsorb the essential macronutrient nitrate which has high leaching potential in agricultural soil. For instance, nitrate adsorption by graphene with a maximum adsorption capacity of 90 mg/g has been identified (140). Functionalized graphene has demonstrated an excellent potential to bind nitrate to its surface. For example, the nitrate adsorption capacity of a functionalized anionic nanographene (ABGN) was reported as 182 mg/g (141) while another study (142) reported 80 to 90% nitrate adsorption by rGO coated magnetic nanoparticles. Concerning micronutrients, although plant requirements for growth is substantially smaller, they can impact important plant processes such as photosynthesis. The only identified micronutrient study, realized in a highly weathered soil (143), demonstrated that the addition of a small amount (<0.5%) of graphene oxide (GO) to biochar resulted in enhanced adsorption and retention of micronutrients (e.g., Zn). Thus, GNMs appear to harbor the potential to adsorb essential micro and macronutrients, enhancing their retention, especially for NO_3^-, within the soil rootzone.

In comparison with surface adsorption, GNMs have also been used to coat N fertilizer to induce a slow-release behavior (144). A GO based polymer composite was used as a coating material to improve the slow release of urea fertilizer (145). In a similar fashion, GNMs have been used to induce slow release from potassium and phosphorous fertilizers where study (24) reported a dramatic improvement in the slow release of potassium ions when KNO_3 pellets were coated with rGO. The induction of slow-release characteristics was also reported for GNM composites such as GO-chitosan (17) and GO-latex (146). Similarly, GO-Fe-P composites exhibited a slower P release as compared to a conventional P fertilizer (147,148). This has also been accomplished for micronutrients where (22) reported that the loading of GO on zinc (Zn) and copper (Cu) micronutrients resulted in a biphasic nutrient release (both fast and slow sustained release), as compared to commercial Zn and Cu fertilizers. Thus, for both macro and micronutrient fertilizers, GNMs have the potential to improve fertilizer use efficiency using current farming practices through either adsorptive properties or by inducing slow-release characteristics to current fertilizers. Being a low cost material, biochar applications ranged from 10 to 120 t ha^{-1}(54,149) much higher in comparison of nanomaterials application 0.4 to 1.7 t ha^{-1} (calculated based on the median value of 100 to 400 mg/kg soil for soil application of GNMs reported during year 2009 to 2022 (150) assuming a typical soil bulk density of 1.4 $g.cm^{-3}$ and soil depth of 30 cm). Thus, this low adsorbent (GNMs) to adsorbate (nutrient) ratio in the soil root zone, may limit the usefulness in employing GNMs for this purpose. Over the years, much emphasis has been only put on inorganic (e.g., zeolite) or polymer (e.g., cellulose) based materials as a coating material for controlled release fertilizer (151,152), and there is still a need to further research on utilizing GNMs as an efficient coating materials for fertilizer.

3.2.3 Graphene and pesticide:

Every year approximately 10-28% of global crop production is lost to crop pests (153). In addition, as much as 75% of the active ingredients of applied pesticides do not reach the target and are lost to the environment (154). To address these inefficiencies in both pesticide delivery and loss, nanomaterials have been tested as nanocarriers that encapsulate pesticide active ingredients (AIs) to achieve controlled, targeted, and synchronized release (155). GNMs with oxygenated surface functional groups have been tested to improve the efficiencies of both hydrophilic and hydrophobic pesticides. A simple mixture of Graphene–insecticide (3:1, mass basis) enhanced insecticidal activities of lambda-cyhalothrin (Cyh) and cyfluthrin (Cyf) on cotton bollworm by damaging the epicuticular spine cells and creating channels to facilitate the insecticide penetration into the cuticle (156). Another aspect of pesticides' efficiency, particularly for hydrophilic molecules, is loss during rain events. In a simulated rain wash experiment, (157) showed that a nanocomposite made of GO, polydopamine (PDA), and the hydrophilic pesticide hymexazol (Hy) exhibited a higher Hy persistence on the leaf due to an improved adhesion of the composite material, which was confirmed by dynamic contact angle measurements. Another study reported that a rGO-Cu-Ag nanocomposite exerted a significant decrease in *Xanthomonas euvesicatoria* (bacterial spot disease) activity in a greenhouse experiment with no phytotoxic effect (158). When conventional pesticides (pyridaben, chlorpyrifos and beta-cyfluthrin) were loaded on GO, higher pesticidal activity against mites was found due to the adsorption of GO on mites' cuticle (159). Similarly, fungicide (Carbendazim) loaded on GO showed improved antifungal activity due to cell structure damage and GSH oxidative stress (160). Due to the presence of oxygenated GO surface functional groups, loading a hydrophobic pesticide (emamectin benzoate) on GO significantly improved its hydrophilicity, resulting in sustained release of the pesticide, in addition to increasing the half-life under UV irradiation and enhancing the biocidal activity against *Mythimna separata* (armyworm) (161). Nanoparticles such as silver (Ag), which are often used as antibacterial agents, also exhibited antibacterial properties against *Xanthomonas oryzae* pv. oryzae (Xoo). The increases in antibacterial efficacy were four-fold higher when Ag-GO nanocomposites were applied compared to Ag only (162). The principal mechanisms behind this increase were improved ROS generation and inhibition of DNA replication by *Xanthomonas oryzae* pv.. These studies all point to beneficial effects in mitigating the losses of and the directed application of the approximately 4 million tons of pesticides used annually in agriculture (155).

3.2.4 Graphene and soil mineral:

When GNMs are added as soil amendments, their availability may be compromised due to homo and hetero-aggregation processes (163). The GNMs added may also interact with soil minerals or major ions (e.g., $Ca^{2+,}$ Mg^{2+}) present in soil pore water. The presence of positively charged soil minerals and divalent cations largely control the homo-aggregation and hetero-aggregation behaviors of GNMs, especially those with oxygenated functional groups. Studies have assessed changes in aggregation and deposition of GNMs with soil minerals across a wide range of experimental conditions. In regards to GNM deposition on quartz, the most abundant mineral in soil, pH exerted no significant impact (164) whereas higher IS increased deposition (165). Thermodynamic analysis revealed that the interaction between quartz sand and GNMs (e.g., GO) is endothermic and non-spontaneous (164). This remains true for other negatively charged soil minerals such as montmorillonite (166). However, with positively charged soil minerals such as goethite, GNMs have been reported to bind strongly due to electrostatic, hydrogen-bonding, and Lewis acid base interactions (167,168). Studies have also reported similar heteroaggregation of GNMs with other positively charged minerals such as kaolinite, hematite, and layered double hydroxides (169–172).

Moreover, GNMs (with oxygenated functional groups) can undergo homoaggregation with divalent cations (e.g., Ca^{2+}, Mg^{2+}) by bridging between edges, intercalating between basal planes or by the crosslinking of H bonds formed on functional groups (173). Agricultural soil pore water contains abundant amount of those divalent cations and thus homoaggregation is expected between GNMs with oxygenated functional groups. Again, for GNMs without oxygenated functional group such as FLG, heteroaggregation with quartz was identified as a function of IS where higher IS condition resulted in higher heteroaggregation due to concurrent agglomeration and straining (174). Moreover, the presence of ferric oxide in soil is reported to enhance FLG adsorption in soil due to improved electrostatic attraction (175). In summary, GNMs can undergo aggregation and deposition on abiotic soil minerals with positive charge upon application as a soil amendment which will control their bioavailability and activity in agricultural soils.

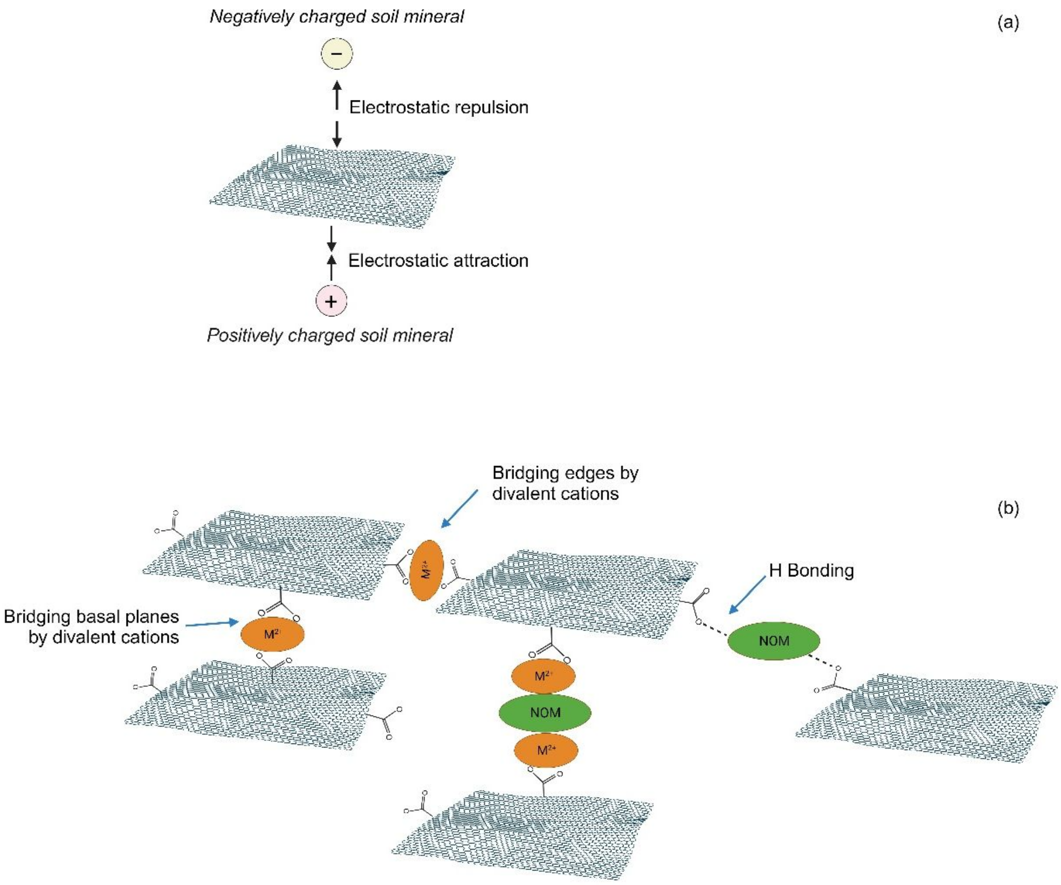

Figure 2: (a) Electrostatic repulsion or attraction between negatively charged GNMs and soil minerals (positive or negative charges). **(b)** GNMs (with oxygen functional groups), divalent cations (M^{2+}:Ca^{2+}, Mg^{2+}) and NOM bridging in aqueous solution (Redrawn from (173,176,177) with permission from the American Chemical Society, © 2013, 2014, 2015).

3.2.5 Graphene and soil organic matter:

Soil organic matter (SOM) or natural organic matter (NOM) can be present as dissolved organic matter (DOM) or particulate organic matter (POM) in soil pore water, or as other water insoluble forms, such as humus, within the soil matrix. NOM and sp2 carbon dominated structures like graphene can interact by electrostatic interactions, hydrogen bonding, and π–π interactions (178).Thus, the presence of NOM can significantly influence the stability of GNMs in aqueous media like soil pore water. For example, presence of model dissolved organic matter (e.g., Suwannee River Natural Organic Matter, SRNOM) was reported to enhance the stability of FLG due to a combination of electrostatic and steric interactions (179). Similarly, presence of NOM (Suwannee River humic acid (SRHA), alginate) can inhibit favorable interactions between GO and the positively charged soil mineral hematite (172).

The presence of oxygenated functional groups on GNMs drastically alters their interactions with NOM. For example, carboxylic, hydroxyl, and amine functional groups of NOM (e.g., humic acid, HA) can undergo H bonding with epoxy, hydroxyl and carboxyl groups of GO. The maximum adsorption capacity of HA on graphite and graphite oxide was reported as 16.5 and 190 mg/g, respectively (180). Another study (165) experimented GO attachment on three model NOM (Suwannee River humic and fulvic acids, alginate) and concluded that GO attachment was highest on alginate. Study (181) reported an increase in soil DOC adsorption capacity once graphene is incorporated in calcerous sandy soil. Moreover, NOM can bridge with divalent cations and GNMs with oxygenated functional groups. This bridging is more prominent for GNMs with higher oxygenated surface functional groups (GO>rGO) (176). The stabilization and transport of GO were found to be positively correlated with the molecular weight of NOM (182). Thus, the interactions of GNMs with both water soluble and insoluble soil organic matter is necessary to consider when evaluating the fate and reactivity of added GNMs within an agricultural soil system.

In summary, along with improving efficiency of essential agrochemicals (fertilizer and pesticide), GNMs seems to physio-chemically interact with abiotic agricultural soil components which can potentially compromise its effect due to its aggregated state and soil organic matter is a key factor on this aspect. Furthermore, biological interactions with GNMs will also play important role in its overall fate and transformation in agricultural soil.

4. Fate and transport of GNMs in soil

Upon application, GNMs are likely to end up in agricultural soils. Thus, it is essential to identify controlling factors that will determine the extent of the mobility of the GNMs in subsurface soil system as well as the possible transformation due to biotic and abiotic interaction to understand better the environmental fate and interaction with different biotic or abiotic components in agricultural soil.

4.1 Mobility of GNMs in soil and porous media:

Laboratory column studies have assessed the transport mechanism of GNMs (e.g., GO, rGO, FLG, Graphene composite) in varied experimental conditions that have manipulated pH, IS, organic matter, mono/di valent cation, low molecular organic acid, surfactant, root exudates, flow rate, column media (grain size, clay mineral, iron oxide, biofilm, EPS), temperature, and the chemical properties of different GNMs (Table S.4). The transport of GNMs (e.g., GO) has been explained by preferential flow phenomena caused by heterogeneity in porous media (183), extended DLVO theory (184), and an advection–dispersion-reaction model (185). GNMs property such as lateral size, presence of oxygenated functional group has been identified as two important factors while considering GNMs mobility in porous media. The lateral size of GNMs influenced its overall mobility due to blocking and straining phenomenon (186) while GNMs with lower oxygen content (rGO compared to GO) exhibited decreased mobility in saturated quartz sand (187). After transport through a porous column, the size of the applied GO increased due to aggregation (188).

Flowing solution characteristics such as pH, IS, organic matter, divalent cations, low molecular organic acid, and surfactants are reported to affect GNMs mobility in porous media. The mobility of GO in porous media has been shown as independent of pH (189) of the flowing solution. However, in the case of rGO, flowing solution with a higher pH exerted higher mobility due to steric hindrance (187) while GO mobility has been shown to be enhanced in lower IS conditions (184,185,189–191) with one exception where a lower IS resulted in decreased mobility (188). The presence of organic matter (e.g., SRHA) was found to increase the mobility of GO or rGO (187,189) while NOM characterized by higher aromaticity and higher MW significantly influenced GO transport (182). Another form of dissolved organic matter in soil are root exudates (e.g., citric acid, oxalic acid, simple sugars, hormones, signaling molecules) that vary in composition among plants as well as well as with plant development. GO mobility increased when root exudates were present (192) and cation valance significantly impacted GO mobility. In a mixed Na–Ca electrolyte system, (193) discovered that higher Ca^{2+}/Na^{+} ratios exerted prominent effects on GO mobility. They also reported that GO nanoparticles aggregated (resulted in higher particle size) by Ca^{2+}-derived cross-link interactions which impacted mobility. Moreover, the presence of low molecular organic acid in the flowing solution resulted in enhanced transport of GO where steric hindrance and competitive deposition was reported as controlling factors for GO retention (194). Another study reported that the mobility of GO increases with increasing concentration of cationic surfactant (195). Therefore, while the presence of ions in pore water tends to decrease GNM mobility, the presence of various organic macromolecules may, conversely, support mobility within soil pore water.

Beyond water chemistry, experimental conditions such as flow rate and temperature also impact GNM mobility in soils. One study showed that a higher flow rate increased GO attachment efficiency on quartz sand media due to enhanced approach and subsequent deposition (196). However, the impact of this flow velocity was reported as a function of IS, with negligible impact of flow velocity in low IS conditions and increasing GO mobility with increasing flow rate at high IS condition (189). Temperature was also found to impact the transport of GNMs as a function of the IS of the flowing solution. A high IS condition influenced GO transport whereas a low IS condition showed limited impact (197). At higher temperatures, retention of GO was higher (198) and was due to decreases in repulsive electrostatic forces between sand and GNMs, which resulted in lower mobility (199).

Porous media characteristics such as moisture content, grain size, minerals (clay, iron oxides), presence of EPS were shown to influence GNMs mobility. One study (185) reported that the increased retention of GO was associated with lower moisture content. Grain size and clay minerals were reported to control GNM transport where there was higher retention of GO with smaller grain size media due to straining actions (188,191,200). The presence of clay minerals (kaolinite, montmorillonite, and illite) improved GO retention due to the presence of positive deposition sites on clay edges (201). Similarly improved GO retention was reported when quartz sand contained iron oxides (goethite, hematite and ferrihydrite) that resulted in enhanced binding of GO by cation bridging (202). The presence of EPS exerted a negligible impact on GO transport (203) but biofilm presence improved the retention of GO due to surface roughness and physical straining due to reduced porosity (198,203,204). Finally, experimental flow direction (upward or downward flow) didn’t significantly impact GO mobility, indicating gravity doesn’t influence GNMs mobility in porous media (205).

Though all those studies identified crucial parameters that affect GNMs mobility in porous media systems, most of those studies employed hydrophilic GNMs except for a few studies that included FLG, Nitrogen-doped graphene, and rGO−Pd nanosheets (174,199,206). Another limitation is that the majority of these studies were carried out in saturated columns using uniform column media (e.g., quartz) which does not represent actual flow in the soil vadose zone. Thus, further study is needed that employs non-oxygenated GNMs and heterogeneous agricultural soil media under unsaturated flow conditions to better approximate natural environment and representative pore water chemistry.

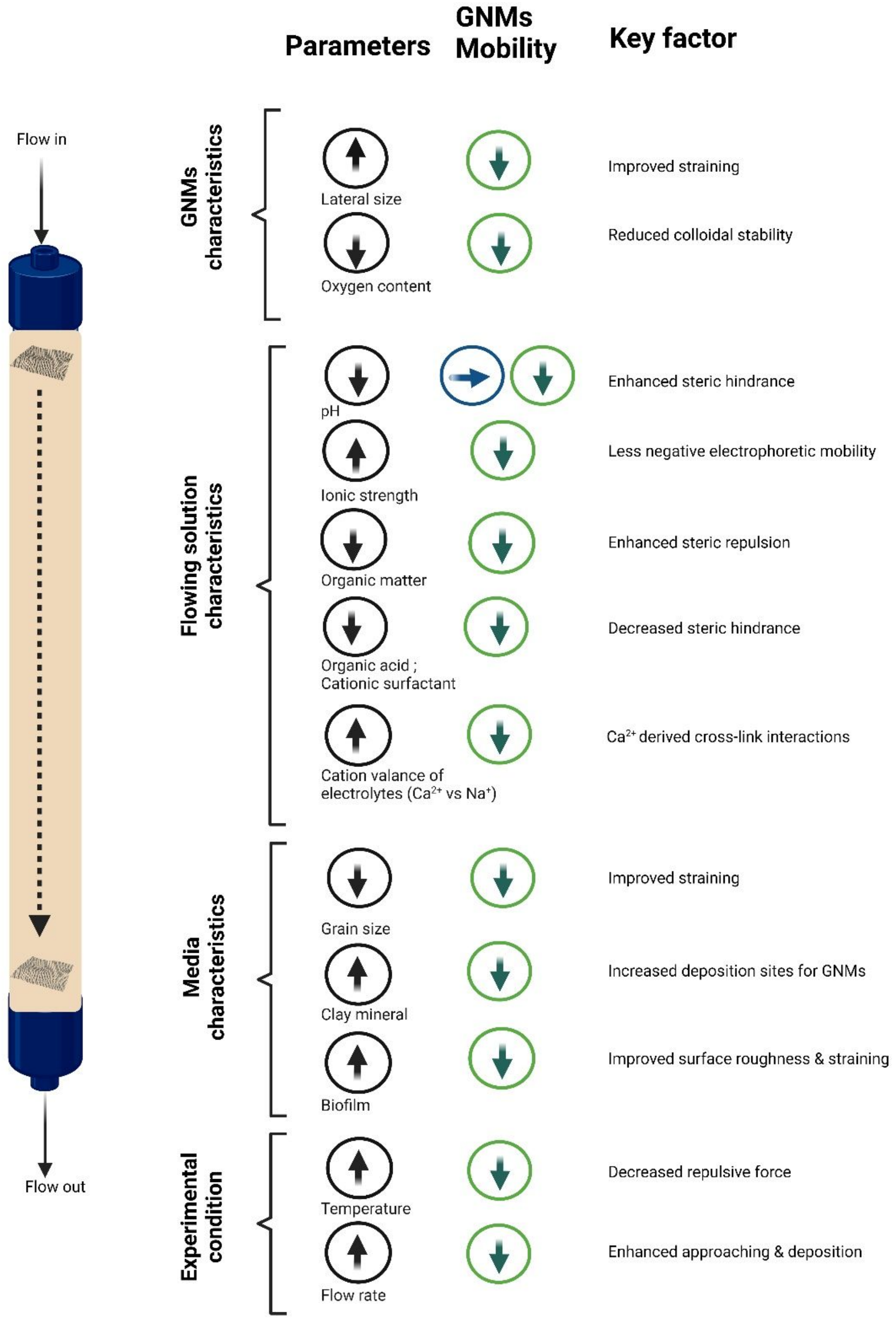

Figure 3: Factors affecting mobility of graphene-based nanomaterials (GNMs) in porous media. Here, ↑ indicates increase, ↓ indicates decrease and → indicates no change.

4.2 Transformation of GNMs in soil:

Considering the trends of increasing production and application of GNMs, it is highly likely that GNMs will ultimately end up within the soil system. Once GNMs are added to soil, intentionally or unintentionally, their physical and chemical characteristics will be altered due to both biotic and abiotic interactions. The transformation of GNMs within aquatic ecosystems has been reported to takes place due to irradiation, chemical reactions involving enzymes, ROS, reducing agents and microbes (30,32). However, current understanding regarding the transformation of GNMs in soil is scarce due to analytical limitations in the detection and quantification of GNMs within a complex soil matrix (30).

GNMs biodegradation and transformation by bacteria, fungi, or enzymes have been studied in culture media based experiment by raman spectroscopy, transmission electron microscopy (TEM), atomic force microscopy (AFM), scanning electron microscope (SEM), fluorescence imaging and X-ray photoelectron spectroscopy (XPS) techniques (207–212). In addition, different studies have characterized the biodegradation and transformation of GNMs in granular media, such as soils or sand, using raman spectroscopy (213) or radioisotope techniques (163,175). It appears that some forms of GNM are resistant to direct microbial attack and utilization as a carbon source. Indeed, a short term (3 week) study in soil reported an absence of degradation of GNMs (GO) due to microbial mineralization (163). This may be due to the physical structure of the GNM used or the lack of microbial populations capable of mineralization. Indeed, biodegradation of FLG to GO was found to occur through saprotrophic fungal enzymes (207). Phenol oxidase and peroxidase are widely distributed fungal enzymes that indiscriminately attack large, heterogeneous molecules such as lignin. Another study (208) reported the degradation of both oxygenated and non-oxygenated GNMs by lignin peroxidase (LiP) enzymes. In addition, H_2O_2 and ferric oxides have been used as catalysts in order to enhance heterogenous Fenton reactions that degrade FLG to CO_2 gas (175). While the ability to attack large molecular weight molecules is associated largely with fungi, some soil bacteria possess enzymes that are also capable of this action. In support, a study (209) reported that GO can serve as a source of C for soil bacteria. In contrast to bacterial and fungal mineralization, GNMs added to a soil ecosystem can be utilized as terminal electron acceptors through interactions with the resident soil microbial community. This is supported by several culture-based studies where GNMs (e.g., GO) acted as terminal electron acceptors as a part of the respiration process in both aerobic and anaerobic environments

(210,211,214). Thus, the oxidation state of surface functional groups can be altered through the accepting of electrons generated by microbial respiration. It should be noted that the ability to transfer electrons to external electron acceptors is not a universal trait among bacteria and is largely constrained to anaerobic microbes located in soil aggregate anaerobic microsites. Lastly, while soil bacteria are negatively charged, π−π interactions and H bonding may overcome the electrostatic repulsion between GNMs and bacteria (166), allowing for adhesion to bacterial cell surfaces. Moreover, another study (212) found that insects such as the larvae of the yellow mealworm (*Tenebrio molitor*) can degrade and mineralize GO by either biomass assimilation in or mineralizing into CO_2. Moreover, plant based constructed wetland system has also been reported to introduce defects in GO (213,215). These documented interactions of GNMs with abiotic and biotic soil components, coupled with the possibility of degradation of some GNM types over time, partially alleviates potential concerns regarding their persistence in the environment.

In summary, more innovation (e.g., ^{13}C or ^{14}C isotope labelling technique) is required to overcome current analytical limitations in detecting and quantifying GNMs in both agricultural soil and water matrix that will eventually improve current understanding on fate and transformation of GNMs in soil which is crucial to obtain mechanistic understanding on GNMs interaction in native agricultural soil eventually pave the way of efficient design of GNMs incorporation in conventional agriculture.

5. Future perspective and conclusion:

This review discussed the current state of understanding regarding how GNMs may interact with biotic and abiotic components of soil if added as an amendment in agricultural soils. Primarily based on culture studies, graphene has been characterized as a material that can have antimicrobial effects. However, the biocidal effects of GNMs are likely quite different in a soil system as compared to culture-based experiments. To this end, multiple studies have pointed to lower toxicities when added to soil as well as a “hormesis effect” where small GNM additions results in stimulatory effects to the soil biological components. Manipulating this stimulatory effect requires GNM dose management, the use of appropriate application methods and the use of a compatible type of GNM. Ultimately, it appears possible that proper GNM management can lead to new methods to address management goals such as the reduction of abiotic and biotic stresses on plant growth/productivity. The application of GNMs may also improve the efficacy and lower the doses of agrochemicals (fertilizer and pesticide) that are needed in order to maintain or enhance agricultural yields. Applied GNMs are also likely confined to the application area as accumulated research has shown that the risk of

GNM on groundwater contamination is quite low due to interactions with soil organic matter, minerals and biological components. Despite the potential for far-reaching positive impacts, GNMs have not been adopted as amendments in conventional agricultural systems. We perceive the principal constraints that currently hinder the development of graphene application in agriculture as being:

(i) A lack of a broad base of foundational knowledge the impact of GNMs on soil ecosystem components (plant-microbe). The limited studies that have been performed have reported both positive and negative effects on plant growth and the soil microbiome, principally through correlations without mechanistic explanations. This reflects the early stages of biochar research before an adequate number of studies were performed that showed how the impacts of biochar change with soil type, pyrolysis temperature, source material type, etc. Thus, additional knowledge is needed that addresses different GNM types, soil types (especially across C contents) and relevant agricultural plants.

(ii) A lack of information regarding the impact/fate of GNMs in field-based studies where multiple interactions take place that may confound lab- or microcosm based results. Considering GNMs application in conventional farming practices, the application rates may differ from short scale lab studies due to significant variation in soil type and structure, abiotic and biotic stress as well as diverse climate that can potentially alters GNMs beneficial function.

(iii) An emphasis, for agricultural-focused studies, on experimental designs that use the soil matrix, rather than pure culture, and investigate changes in the function and composition of the soil microbiome. There are likely direct toxic effects, potentially to some microbial groups while not to others. Thus, it is likely that GNM addition may manipulate that soil microbiome. Whether this alteration is beneficial, such as through an increase in the size of plant growth promoting rhizobacteria (PGPR) populations, or negative, remains unknown.

(iv) A need for studies that detect and quantify applied GNMs within a heterogeneous soil matrix to monitor its persistence and fate. This may be accomplished by labeling the C input (^{13}C or ^{14}C) for GNM production followed by stable isotope probing (SIP) in order to determine if incorporation within microbial biomass is a possible fate.

(v) Graphene production is still in its infancy and thus cost is a current barrier. Positive impacts of GNM addition on plant production in an agricultural system will need to be balanced with the carbon costs and encumbrances of nanomaterial production and application which include the costs of source material, packaging, transportation, and application. Ultimately, since cost-benefit analysis is the driving force that underlies agroecosystem management, it remains necessary to reduce GNM production costs while simultaneously rigorously showing that significant positive impacts on plant production/health are possible. This cost-benefit analysis also needs to be done in comparison with other conventional materials, like biochar, that may be used in similar applications.

(vi) Finally, being the oldest sector, incorporating any new intervention in conventional agriculture is a challenge. As many nanomaterials have been reported as toxic to living beings, there is both negative perception among growers and/or regulatory concern for having 2D carbon-based graphene as an agricultural amendment. Adequate mechanistic understanding of interaction with biotic and abiotic components and knowing the fate and transformation within agrarian ecosystem will pave the way to efficient design and incorporation of this 2D carbon-based nanomaterial in conventional farming which has potential to achieve a food secured future.

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