

Review

Siliceous Natural Nanomaterials as Biorationals—Plant Protectants and Plant Health Strengtheners

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Abstract: This review aims to evaluate the scientific evidences for siliceous natural nanomaterials (SNNMs), natural zeolites, and diatomaceous earth, as biorationals. Both SNNMs are multifaceted agricultural inputs—plant protectants, plant biostimulants/plant strengtheners, soil improvers. The effects depend on the plant parts, where such siliceous natural nanomaterials (SNNMs) are applied. For stored grains, SNNMs act as plant protectants. Foliar applied SNNMs protect plants against biotic and abiotic stress—plant protectant and plant strengtheners. When applied to soil/roots, SNNMs stimulate root development and improve soil characteristics. These effects are related to the composition and porous (nano)structure of SNNMs. The large active siliceous surfaces of SNNMs are involved in: desiccation of the insects damaging stored grains, fungistatic effects against mycotoxigenic fungi and adsorption of their mycotoxins, desiccation of foliar pathogens and pests, stimulation of photosynthesis, release of soluble silicon species, improved soil characteristics. Similar to other biorationals from the category of basic substances with low risk, the SNNMs efficacy as plant protectants and plant health strengtheners is rather low. Complementary active ingredients should be used to enhance the effects of SNNMs on treated plants. For SNNMs applied as protectants of stored seeds, such strategy, of using complementary biorationals/low risk substances, proved to be highly effective.

Keywords: siliceous natural nanomaterials; natural zeolites; diatomaceous earth; plant protection products; plant strengtheners—plant biostimulants; soil improvers

1. Introduction

The siliceous natural nanomaterials (SNNMs) considered for this review, i.e., natural zeolites and diatomaceous earth/kieselguhr, are mineral natural products—volcanic ashes altered by water [1], and, respectively, biogenic sedimentary rocks [2]. Both SNNMs are generally recognized as safe (GRAS), being put on the market as dietary supplements (natural zeolites [3,4], diatomaceous earth [2,5]), feed additive (natural zeolites [6,7], diatomaceous earth [8–11]), filtration aid in beverage industry (natural zeolites [1], diatomaceous earth [12–14]).

Both SNNMs, natural zeolites and diatomaceous earth/kieselguhr, could be considered among biorationals categories when used in agriculture. The term “biorationals” refers to low-risk products which promote cultivated plant health [15]. Biorationals include plant protectants, plant biostimulants/plant strengtheners, and soil conditioners/soil improvers [15]. The main characteristic of biorationals is sustainability—low risk associated with lower stress impact on crop yield [15]. Their integrated use, in the frame of integrated pest management/integrated farming systems [16], is essential for a profitable agricultural production with low impact on global health.

The SNNMs considered for this review fulfill the criteria established for basic substances by Art. 23 of European Union (EU) Regulation 1107/2009 (concerning plant protection products) [17]: are safe, due to their long utilization without significant side effects; are without endocrine disrupting, neurotoxic or immunotoxic effects; and are not predominantly used as plant protection products. The products based on diatomaceous earth (under the name kieselguhr) are placed on the market as stored grain protectants [18]. This niche application is the only application connected to plant protection products—diatomaceous earth (DE) being predominantly used in the industry.

SNNMs were proved to have mainly plant strengthening effects. Such SNNM effects could be considered as being direct or indirect (mediated). Direct effects on plant physiology are related to the soluble silicon species, silicic acid, and its dimers/trimers, slowly released from diatomaceous earth [19,20] or natural zeolites into plant rhizosphere [21]. The mediated plant strengthening effects are induced by the soil/growing media improvements following the SNNMs application. SNNMs are typical soil conditioners, improving aeration and water holding capacity [22,23]. Recently, SNNMs, and especially natural zeolites, were considered solutions to emerging crops challenges, as part of geo-agriculture [24]. Two of the considered challenges addressed by geo-agriculture, i.e., environmental-sustainable fertilizers and enhanced crop drought resilience, could be considered as related to SNNMs plant strengthening effects too.

SNNMs effects related to plant protection against biotic stress, plant pathogens and pest, were reported. SNNMs products, known also as “inert dusts”, are used for decades as stored grain protectants, effective both against insects [25–27] and mycotoxigenic fungi [28,29]. There are also reports that demonstrate that foliar applications of siliceous natural nanomaterials protect plants against biotic stress. Diatomaceous earth sprayed onto canopy controls the population of aphids [30,31]. Similar effects, related to the control of leaves pest (leafminer *Tuta absoluta*), were observed for natural zeolites applied as treatment of tomato leaves [32].

The extended use of these biorationals in agriculture depends significantly on the legal status of siliceous natural nanomaterials as agricultural inputs. This legal status of biorationals—mandatory registration for plant protectants against biotic stress and variable administrative procedure before putting on the market for plant strengtheners—is different in different parts of the world. The different approaches are reflected also on SNNMs used in agriculture. SNNMs (diatomaceous earth) based products used for stored grain protection are registered as plant protection products in the European Union [18] and USA [33]. However, a different approach is for products with plant health strengthening effects.

SNNMs used for soil treatment/soil improvement do not have unitary requirement regarding registration. In most of the world countries, including USA (where these products are regulated on a state-by-state basis) soil conditioners/soil improvers are put on the market without prior registration/notification procedure. The regulations establish maximum level of contaminant and mandatory quality characteristics. The products which producers consider fulfilling the quality and safety requirements according to standards are put on the market at producer’s own responsibility—and post marketing control is done by governmental agencies. The legislation in force in EU for soil improvers, i.e., Regulation 1009/2019, establishes specific quality and safety requirements—maximum thresholds for contaminants, e.g., potential toxic elements, and requires demonstration of the claimed effects for access to the common market. However, there are still different approaches for soil improvers in different EU countries. For example, in Hungary, soil improvers are considered yield enhancers and are subject to National authorization according to decree 36/2006 of Ministry of Agriculture and Rural Development (FVM) [34].

Until, now SNNMs were not considered as plant biostimulants/plant strengtheners, despite the fact that their application as foliar treatment leads to effects specific to plant biostimulants (as it will be further discussed in this review). Plant biostimulants also have different legal status in different parts of the world. In EU, according to Regulation 1009/2019, plant biostimulants need registration [35]. The evolution toward an unitary approach of the plant biostimulants regulatory framework in different European countries (and the situation at international level) was reviewed three times during the

last years by a research group from Italian CREA (Consiglio per la Ricerca in Agricoltura e l'Analisi dell'economia agraria) [35–37].

The objectives of this review are to evaluate the scientific evidences for SNNMs as biorationals, i.e., plant strengtheners and plant protectants with low environmental impact; to analyze the best approach for their extended implementation in sustainable farming practices and to identify knowledge gaps and needs for further investigations. Arguments regarding inclusion of SNNMs in the different categories, plant protection products, soil conditioners/improvers or plant strengtheners–dual plant biostimulants, are further considered and discussed, after a short presentation of SNNMs structure peculiarities.

2. Siliceous Natural Nanomaterials Structure

Both SNNMs are siliceous compounds, with a porous nanostructure. Natural zeolites are crystalline hydrated polymeric tecto-aluminosilicates [38]. The polymeric structure is based on monomeric tetrahedral units–TO₄, where T is aluminum (Al) or silicon (Si) [1]. The monomeric tetrahedral units are linked by oxygen bridges [39]. The porous structure of natural zeolites is determined by its inorganic polymeric nature, the linked tetrahedron generating a nanohoneycomb structure, with tunnels and cavities [40].

Diatomaceous earth are fossilized 3D nanopatterned cell walls of diatoms (microalgae), called frustules [41]. The frustules are formed by amorphous biosilica, SiO₂·*xn*H₂O, which is precipitated from a “soluble silicon pool”, a stabilized H₄SiO₄ solution [42] by several biomolecules associated with diatom cell walls, long chain polyamines (LCPAs), or proteins, such as cingulins and silaffins [43]. Such process of silicic acid polycondensation into amorphous biosilica seems to determine its high reversibility, i.e., fast release of soluble silicon species from diatom frustules [44].

The size of three-dimensional (3D) nanopatterned frustules is highly variable, from 500 nm to 50 μm [45]. The shapes are variable–drum like, triangular box, ellipsoidal circular box. The symmetry of frustule can be either pennate or centric [41]. Diatomaceous earth formed from fresh water contain lower amounts of crystalline silica compared to marine diatoms [46].

The common features determined by the common 3D nanostructure are: reversible dehydration, large volumes of free space, and high sorption capacity for various molecules and ions [40,46,47]. These features are essential for SNNMs effects for plant health promotion—Figure 1.

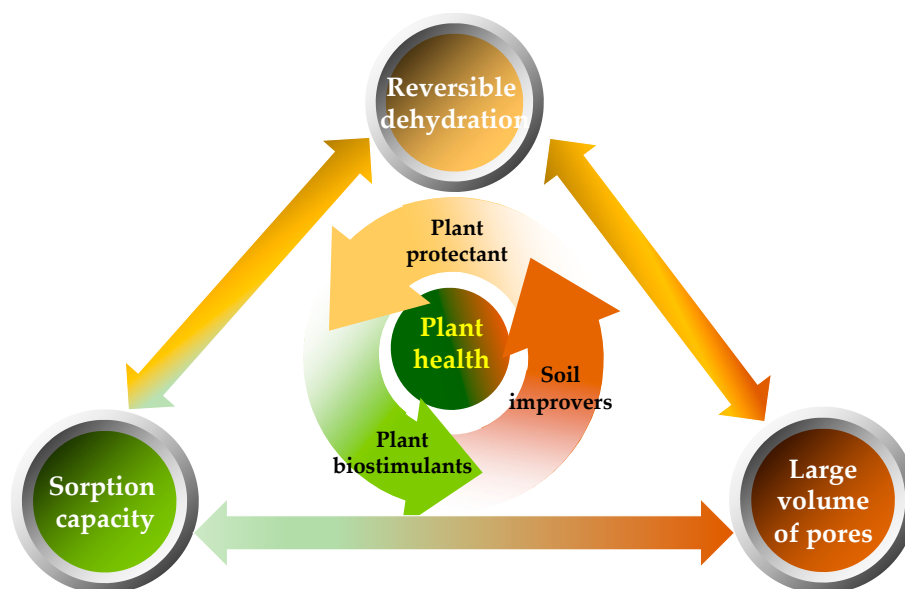


Figure 1. The common features of siliceous natural nanomaterials which are determinant for their application as plant protectant, plant biostimulants, and soil improvers.

Reversible dehydration, sorption capacity and large volumes of pores are essential for desiccant effects involved in plant protection against pathogens and pests, and exerted on stored grains [46] and/or on leaves [32]. Reversible dehydration and sorption capacity were involved in the activation of photosynthesis after foliar application of zeolites [48].

The (nano)structure, which includes large hydrophilic surfaces able to bind water/aqueous solutions and ions (sorption capacity, reversible rehydration) including for ions and a high proportion of (nano)pores, are responsible for the soil/growing media improvers effects [22,37]. The water holding capacity, pH, and cation exchange capacity (CEC) are improved following the addition of natural zeolites [22] or kieselguhr into soil or growing media [38]. Siliceous natural nanomaterials improve the nitrogen use efficiency, mainly due to their ability to fix and then slowly release nitrogen species, including ammonium from organic fertilizers [39]. Their ability to accommodate various cations into their nanostructures positively impacts the plant utilization of macro-nutrients, e.g., potassium [40], oligo-nutrients, e.g., zinc [41], and micro-nutrients, e.g., manganese [42]. Silicate interaction with phosphates improves corn yield and reduces phosphate leaching after natural zeolites application [43].

SNNMs features related to the siliceous porous nanostructure will be further discussed in relation to the main application as inputs in the cultivated plant technologies.

3. Siliceous Natural Nanomaterials as Plant Protectants

SNNMs are known for decades as protectant of stored grain products. As we already mentioned, products based on diatomaceous earth/kieselguhr are registered for stored grain protection as plant protection products in European Union [18] and USA [33]. Table 1 exemplifies several commercial products based on diatomaceous earth, which proved to be efficient for stored commodities (grains, flour) protection.

Table 1. Example of several commercial products based on diatomaceous earth.

Commercial Name	Type of Diatomaceous Earth (DE)	Others (Active) Ingredients	Dose (mg/kg)	Commodity	Tested Insect Species	Mortality	Ref.
Celatom® MN-51	Fresh water DE, dimension 15 µm, 83.7% SiO ₂ , less than 1% crystalline SiO ₂	none	500	wheat grains	<i>Sitophilus oryzae</i>	100%, after 14 days, 30 °C, 70% RH ¹	[49]
					<i>Tribolium castaneum</i>	100%, after 14 days, 30 °C, 70% RH ¹	
					<i>Rhyzopertha dominica</i>	100%, after 14 days, 30 °C, 70% RH ¹	
SilicoSec®	Fresh water DE, dimension 8-12 µm, 92% SiO ₂ , less than 1% crystalline SiO ₂	none	1500	Wheat flour	<i>T. castaneum</i>	100%, 32 °C, 55% RH ¹	[50]
			1500	Barley grain	<i>S. oryzae</i>	100%, after 7 days	[51]
			1500	Maize grain		>65%, after 14 days	
			800	Wheat grain	<i>Ephestia kuehniella</i>	>85%, after 14 days, 32 °C >65%, after 14 days, 75% RH ¹	[52]
			900	Wheat Barley	<i>T. castaneum</i>	>65%, after 21 days	[52]
		<i>S. oryzae</i>	100%, after 21 days, 30 °C, 55% RH ¹				
		<i>R. dominica</i>	90%, after 21 days, 30 °C, 55% RH ¹				

Table 1. Cont.

Commercial Name	Type of Diatomaceous Earth (DE)	Others (Active) Ingredients	Dose (mg/kg)	Commodity	Tested Insect Species	Mortality	Ref.
Protect-It®	Marine DE, median dimension 5.4 µm, 83.7% SiO ₂ , less than 0.9% crystalline SiO ₂	Silica aerogel 10%	300	Wheat grain	<i>T. castaneum</i>	100%, after 1 month, field test-variable temperature, 55% RH	[53]
			>400	Wheat	<i>T. castaneum</i>	100%, after 14 days, 30 °C, 65% RH ¹	[54]
PyriSec®	Fresh water DE, dimension 8–12 µm, ~90% SiO ₂ , less than 1% crystalline SiO ₂ (SilicoSec®, 95.7%)	1.2% natural pyrethrum (25%), 3.1% piperonyl butoxide	1500	peeled barley	<i>R. dominica</i>	84.2%, 26 °C, 55% RH ¹	[55]
			1500	wheat, whole barley, oats, rye, triticale, rice, maize		>95%, 26 °C, 55% RH ¹	
			300	wheat barley	<i>Oryzaephilus surinamensis</i>	100% after 7 days	[56]
			900	wheat barley	<i>T. castaneum</i>	100% after 21 days	
900	Wheat barley	<i>S. oryzae</i> , <i>R. dominica</i>	100% and 90%, 14 days 30 °C, 55% RH				
Dryacide™	Freshwater DE; 90% amorphous SiO ₂ ; mean particle size: 13–15 µm	none	400	wheat	<i>S. oryzae</i>	>95%, after 7 days, 30 °C,	[57]
			600		<i>T. castaneum</i>	>90%, after 14 days, 30 °C, 65% RH ¹	[54]
Insecto®	Marine DE, median dimension 8.2 µm, 87% amorphous SiO ₂	10% food-grade bait	400	wheat	<i>S. oryzae</i>	96%, after 14 days, 26 °C, 57%	[58]
			600		<i>T. castaneum</i>	90%, after 14 days, 30 °C, 65% RH ¹	[54]
Perma Guard™	Freshwater DE; median dimension 93% SiO ₂	none	400	wheat	<i>S. oryzae</i>	77%, after 14 days, 26 °C, 57%	[58]
			1000	wheat	<i>T. castaneum</i>	100%, after 14 days, 30 °C, 65% RH ¹	[54]

¹ RH—relative humidity.

It was demonstrated that plant protection products for stored (dried) commodities, based on diatomaceous earth, despite their efficacy and safety, have several drawbacks which limit their large scale utilization. High dose determines reduction of the bulk density of the treated stored commodities [59]. Diatomaceous earth (Protect-It® and two products originating from Serbia) has a significant negative impact on the rheological properties of dough produced from flour resulted from treated triticale and rye grains [60]. The same treatment does not influence the rheological properties of flour resulted from treated wheat grains. As could be also noted from data presented in Table 1, the effects of diatomaceous earth as stored grains protectant are related to different insect species, commodities/grain type and the commodities/grain storage conditions, moisture, and temperature [59]. High humidity reduces efficacy, due to the fact that it influences the desiccant effect. High temperature increases insect metabolism and, in general, increases also the efficacy of the desiccant products. Among the tested insect species, *Tribolium confusum* was demonstrated to be the most tolerant [59].

To compensate the drawbacks, several approaches were considered. One approach was to develop alternative desiccant products based on zeolites. Initially the studies demonstrated that natural zeolites need higher application dose in order to match the efficacy of products based on diatomaceous earth [61]. *S. oryzae* and *T. castaneum* proved to be more tolerant to the tested natural zeolites compared to diatomaceous earth commercial formulation Protect-It® [60]. However, other studies proved that zeolites of different origins have a better efficacy [26]. Commercial zeolites used

as feed additive, originating from Greece and Slovakia, and as soil improvers, originating from Bulgaria, were tested for protection of wheat grains against *S. oryzae*, *T. confusum*, and *Oryzaephilus surinamensis* [26]. *O. surinamensis* was the most susceptible to tested zeolites and *T. confusum* the most tolerant. The same commercial zeolites proved to be effective against mold mite, *Tyrophagus putrescentiae* and the flour mite, *Acarus siro*, at all life stages [62]. Natural zeolites with 92% clinoptilite control bean weevils, *Acanthoscelides obtectus* [63]. The efficacy of stored beans protection depends on temperature and humidity. Natural zeolites registered as feed additives, originating from Slovakia and Serbia were proved to control saw-toothed grain beetle, *O. surinamensis*, and the rice weevil, *S. oryzae*, on wheat [64]. Natural zeolites, from Slovenia and Serbia, applied at 0.45 and 0.90 mg/kg, were demonstrated to be more effective than artificial zeolites against the maize weevil, *Sitophilus zeamais* [65]. The difference in efficacy was considered to be related to the difference in silica content.

The common features which determine good efficacy as feed additive or soil improvers, i.e., large active siliceous surface able to bind molecules, including water, and ions, are involved also in commodities protection against deleterious arthropods.

Another approach to reduce the drawbacks of the DE-based products was the combination with other natural products. Table 2 illustrates such combinations that were proven more effective than the SNNMs alone in controlling stored commodities pests.

Table 2. Enhanced siliceous natural nanomaterials (SNNMs) efficacy as stored commodities by complementary bioactive ingredients.

Type of SNNMs	Complementary Active Ingredients	Dose (mg/kg)	Commodity	Tested Insect Species	Mortality	Ref.
Diatomaceous earth (SilicoSec® 48% wt/wt)	Silica gel (24% wt/wt), bay leaves powder (20% wt/wt), corn oil (3% wt/wt), lavender <i>Lavandula x intermedia</i> essential oil (2% wt/wt), dried yeast up to 100%	600	wheat grain	<i>T. castaneum</i>	100%, 14 days, 28 °C, 60% RH ¹	[66]
				<i>S. oryzae</i>	100%, 14 days, 28 °C, 60% RH ¹	
				<i>R. dominica</i>	100%, 4 days, 28 °C, 60% RH ¹	
		600	barley grain	<i>T. castaneum</i>	>95%, 14 days, 28 °C, 60% RH ¹	
				<i>S. oryzae</i>	>95%, 14 day, 28 °C, 60% RH ¹	
				<i>R. dominica</i>	100%, 14 days, 28 °C, 60% RH ¹	
Diatomaceous earth (Celatom® MN-51)	Amorphous silica gel (20%), lavandin EO, Torula yeast powder	400	wheat grains	<i>S. oryzae</i>	100%, after 2 days, 28 °C, 65% RH ¹	[25]
Diatomaceous earth (Celatom® MN-51)	Amorphous silica gel (3%), pyrethrin, flax oil, lavandin essential oil (EO), and Torula yeast powder	125	wheat grains	<i>S. oryzae</i>	100%, after 2 days, 28 °C, 65% RH ¹	[25]
		125		<i>R. dominica</i>	81%, after 2 days, 28 °C, 65% RH ¹	
		100		<i>T. castaneum</i>	83%, after 6 days, 28 °C, 65% RH ¹	
Fresh water DE 89% amorphous SiO ₂ 4.0%, dimension 10 µm, crystalline silica 0.1%.	Abamectin, 0.25%	75	wheat grain	<i>S. oryzae</i>	100%, 14 days, 30 °C, 70% RH ¹	[67]
		150		<i>R. dominica</i>	>95%, 14 days, 30 °C, 70% RH ¹	
		125		<i>T. castaneum</i>	100%, 14 days, 30 °C, 70% RH ¹	
		75		<i>Cryptolestes ferrugineus</i>	100%, 14 days, 30 °C, 70% RH ¹	

Table 2. Cont.

Type of SNNMs	Complementary Active Ingredients	Dose (mg/kg)	Commodity	Tested Insect Species	Mortality	Ref.
Fresh water DE 89% amorphous SiO ₂ , 4.0%, dimension 10 µm, crystalline silica 0.1%.	Bitter bark omycin, 0.05%	125	wheat grain	<i>S. oryzae</i>	100%, 14 days, 30 °C, 70% RH ¹	[67]
		75		<i>R. dominica</i>	>95%, 14 days, 30 °C, 70% RH ¹	
		150		<i>T. castaneum</i>	100%, 14 days, 30 °C, 70% RH ¹	
		125		<i>C. ferrugineus</i>	100%, 14 days, 30 °C, 70% RH ¹	
Egyptian diatomaceous earth, 46.37% SiO ₂	Spinosad (98%), 0.5 mg/kg	100	wheat grains	<i>S. oryzae</i>	100%, after 14 days, 28 °C, 65% RH ¹	[68]
Egyptian diatomaceous earth, 46.37% SiO ₂	<i>Trichoderma harzianum</i> (Egyptian strain)	800	common beans	<i>Acanthoscelides obtectus</i>	>93%, after 7 days, 24 °C, 60% RH ¹	[69]
DEBBM, mixture of Canadian diatomaceous earth, freshwater DE 89% SiO ₂ and bitter barkomycin	Bitter barkomycin, 0.05% <i>Beauveria bassiana</i> 6.69 × 10 ¹⁰ conidia	30	wheat grains	<i>R. dominica</i>	>90%, 15 days, 25 °C, 55% RH ¹	[70]
Marine DE, median dimension 5.4 µm, 83.7% SiO ₂ , (Protect-It®)	<i>Beauveria bassiana</i> . 2700 mg/kg	190	wheat grains	<i>T. castaneum</i> larvae	>90%, 8 days, 26 °C, 75% RH ¹	[71]
Chinese diatomaceous earth, 93% SiO ₂	Garlic essential oil (purity ≥ 90%), 20 mg/kg	250	rice grain	<i>T. castaneum</i>	100%, 7 days, 27 °C, 70% RH ¹	[72]

¹ RH—relative humidity.

There are also other protective effects of SNNMs on stored commodities [10]. The desiccant effect contributes also to the limitation of the development of mycotoxigenic *Aspergillus flavus* on stored groundnut, *Arachis hypogaea* [73]. SNNMs are among the efficient and affordable mycotoxin binders [9,74]. The function of SNNMs as feed additive is related also to their ability to bind mycotoxins [8,75].

SNNMs were used to control also foliar pathogens and pests. Diatomaceous earth synergize the in vitro effects of *Thymus capitatus* essential oils against *Myzus persicae* [76]. A diatomaceous earth preparation, Fossil Shield [77], registered for controlling poultry red mite, *Dermanyssus gallinae*, was used to control cowpea aphid, *Aphis craccivora* on yardlong beans, *Vigna unguiculata* ssp. *Sesquipedalis* [31]. Fossil Shield, which contains 73% amorphous SiO₂, with particle dimensions varying from 5 to 30 µm, was proved to increase the efficacy of neem (*Azadirachta indica*) extract against cowpea aphids. The toxicity of the combination diatomaceous earth–neem extract on the coccinellidae beetle cowpea aphid predator, *Menochilus sexmaculatus*, was nevertheless lower than that of the recommended chemical insecticide triazophos. The same Fossil Shield was used to control *Myzus persicae* on globe artichoke *Cynara cardunculus* var. *scolymus* with good results [30]. Fossil Shield was applied also electrostatically, to control the mustard beetle, *Phaedon cochleariae*, on Chinese cabbage pak-choi, *Brassica chinensis* [78]. The efficacy in controlling mustard beetle was high, but the photosynthesis was reduced after dusting with diatomaceous earth. PyriSec®, the combination of diatomaceous earth, pyrethrum extract and piperonyl butoxide, used together with neem extract and biocontrol fungi *Paecilomyces lilacinus*, was proved to control cotton aphid, *Aphis gossypii* [79].

Diatomaceous earth formulation with average particle size of 2.6 µm was demonstrated to control the complex of wheat aphids, *Rhopalosiphum maidis*, *R. padi*, *Sitobion avenae*, *S. miscanthi*, *Schizaphis graminum*, in laboratory conditions. However, when the formulation was applied under field conditions,

the efficacy was poor, even at a dose of 150 kg/ha. The high quantity of dust influences also the treated plant, reducing chlorophyll content [80].

The EU FP7 project “Developing a pool of novel and eco-efficient applications of zeolite for the agriculture sector -ECO-ZEO” (<https://cordis.europa.eu/project/id/282865/reporting>) intended to develop products based on zeolites to control the following foliar pests and pathogens: *Ceratitidis capitata* (orange), *Cydia pomonella* and *Venturia inaequalis* (apple), *Lobesia botrana* and *Plasmopara viticola* (grape), and *Tuta absoluta* and *L. botrana* (tomatoes). Foliar applied zeolites were proved to be effective against *V. inaequalis* and *P. viticola*. However, for the rest of the targeted pest it needs additional active ingredients, such as azadirachtin or *Bacillus thuringiensis*. Until now, only the results obtained for controlling *T. absoluta* were published in peer-review journal [32].

The mechanism of action of SNNMs against foliar pathogens and pests is considered similar to that involved in stored grains protection—the desiccant effect. An effective desiccant effect requires formation of a particle film, covering the surface of aerial cultivated plant organs [81]. However, it was demonstrated that such desiccant effects could affect also the beneficial organisms, i.e., predatory insects [31]. Desiccant effects could negatively influence also plant pathogen antagonists or even the protected plant, by cuticle weakening. Until now, to the best of our knowledge, such effects were not investigated.

In conclusion, SNNMs effects as plant protectant is typical for basic substances, which are predominantly used as active ingredients for plant protection products. SNNMs need complementary products in order to have an acceptable level of pest/pathogen control. Under stored commodities conditions, wherein humidity could be controlled, SNNMs applied alone demonstrated an acceptable level of efficiency. However, even under such conditions, the existing drawbacks determine formulations with other active substances. Under field conditions SNNMs act mainly as adjuvant to other active ingredients with action against pests and/or pathogens.

4. Siliceous Natural Nanomaterials as Plant Strengtheners

Plant strengtheners are considered at present equivalent with plant biostimulants [15,37]. Europe is the leader of the plant biostimulants, with almost 40% of the world sale [35]. Several EU countries developed a legislative framework, separate from the EU legislation, which promotes low-risk agricultural inputs [37]. In Germany, such products were called plant strengtheners (*Pflanzenstärkungsmittel*), in Italy invigorants (*Corroboranti*), in Spain, means of phytosanitary defense (*Medios de defensa fitosanitaria, MDF*), in France, natural substances for use as biostimulants (*Substances naturelles à usage biostimulant*) [36]. The complete list of these different names is presented by Caradonia et al. [35]. However, there are some differences related to the definition of these agro-inputs. Plant strengtheners were defined in Germany as “substances and mixtures, including microorganisms, that are intended solely to serve the general health maintenance of plants” or “are intended to protect plants from non-parasitic damage”, without being a plant protection product [82]. The EU Regulation 1009/2019, Art. 47, paragraph (2) defines plant biostimulants as “a product stimulating plant nutrition processes independently of the product nutrient content with the sole aim of improving one or more of the following characteristics of the plant or the plant rhizosphere: (a) nutrient use efficiency; (b) tolerance to abiotic stress; (c) quality traits; (d) availability of confined nutrients in soil or rhizosphere.” Therefore, the definition of plant biostimulants by EU Regulation involves also the influence on nutrient and nutrient uptake, not “only general health maintenance of plants”, and enhanced tolerance to abiotic stress/protection from non-parasitic damage.

In the USA, the emerging legislative framework seems to consider soil improvers as a category of plant biostimulants. Last year, US Environmental Protection Agency (EPA) released a draft guidance regarding plant biostimulants which describes this category of agricultural inputs as “a naturally-occurring substance [...] that [...] improves the physical, chemical, and/or biological characteristics of the soil as a medium for plant growth.”

This discussion regarding legal framework is intended mainly to underline the need to consider both indirect/mediated and direct effects of the SNNMs on plants as being related to plant strengtheners/plant biostimulants effects. Such approach is not limited only to these siliceous natural minerals. Microbial plant biostimulants have both direct and indirect/mediated effects on plants. The bacteria from *Azospirillum* genera, largely recognized as plant biostimulants, produce siderophores, which modify the iron bioavailability into rhizosphere; therefore, fulfill the criteria of Art. 47 paragraph (2), because they enhance the “availability of confined nutrients in soil or rhizosphere”. Mycorrhizae fungi, other characteristic microbial plant biostimulants, influence not only directly the plant biology, but also indirectly, due to the production of glomalin. Glomalin improves soil structure and soil resistance to erosion and reduces the effects of heavy metals.

The organic, non-microbial plant biostimulants have also indirect effects. Humic and fulvic acids have typical indirect effects, improving soil characteristics and nutrient availability in the rhizosphere. Similar indirect effects are demonstrated also for other organic plant biostimulants applied to soil, such as protein hydrolysate. Both mentioned organic plant biostimulants classes exert also direct effects on plant physiology.

The indirect/(soil) mediated effects of plant biostimulants overlap with effects of soil conditioners/soil improvers. The main difference is related to the dose. Plant biostimulants are applied in smaller quantities compared to soil improvers. The main class of organic plant biostimulants is produced from materials initially used as soil amendments (Figure 2).

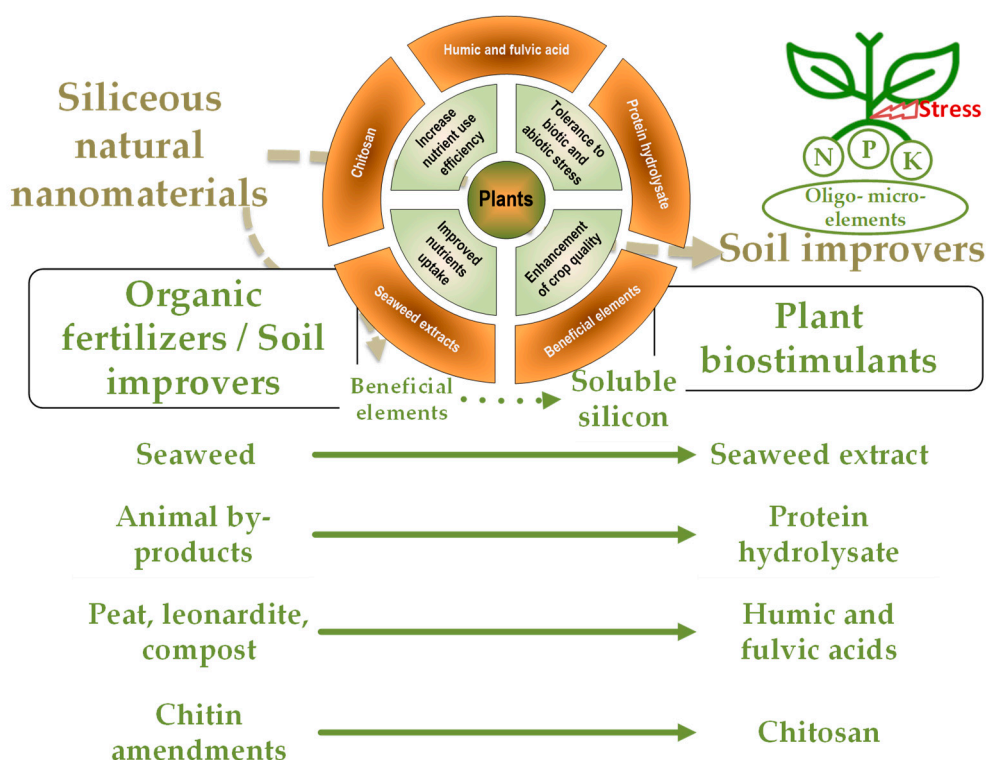


Figure 2. The relationship between organic fertilizers/soil improvers and the organic plant biostimulants and the similarities between their effects on plants and those exerted by the soil improvers based on siliceous natural nanomaterials.

Overall, the improvement effects on soils/growing substrate promote not only better plant nutrition, but also plant health and/or plant resistance to abiotic stress [83,84]. Increased yield, including under stress conditions, were found for plant cultivated on growing media/soil treated with SNNMs [84,85]. In the following subsections we will present and discuss the evidences of SNNMs indirect and direct

effects related to plant protection against abiotic stress, improvement of nutrient uptake and use efficiency, crop quality—i.e., plant strengthening effects.

4.1. Mediated Plant Strengthening Effects

SNNMs, and especially zeolites, were largely used for the improvement of poor soil, especially sandy and clay soil [86], and/or for the improvement of soil affected by salinity or heavy metal contaminations. Their effects on the crop are exemplified in Table 3.

Table 3. Effects of SNNMs applied as soil improvers.

Type of SNNMs	Crop	Type of Soil/Growth Substrate-Stress	SNNM Dose	Main Effect	Ref.
Zeolites (clinoptilite)	Corn, <i>Zea mays</i>	Typic Paleudults, fine sandy clay loam	280–350 kg/ha	Improved phosphorus dynamic and uptake	[87]
Zeolites	Rice, <i>Oryza sativa</i> L.	Clay loam-Drought stress	15 t/ha	Improved head rice rate; decreased chalk rice rate and chalkiness.	[84]
Zeolites	Fenugreek, <i>Trigonella foenum-graecum</i>	Semi-arid area - Drought stress	9 t/ha	Reduced effects of draught; Improved biological and seed yield	[88]
Zeolites	<i>Aloe vera</i> L. (syn. <i>Aloe barbadensis</i> Miller)	Drought stress	4 and 8 g/kg	Reduced drought stress effects; improved plant growth and yield	[89]
Zeolites (clinoptilolite)	Radish, <i>Raphanus sativus</i>	Growing substrate, Greenhouse experiment–Salinity stress	0.06 kg/m ²	Reduced salt uptake by plant; increased crop yield and quality	[90]
Zeolites	Onion, <i>Allium cepa</i> L.	Silt loam soil–Salinity stress	4 and 8 t/ ha	Decreased number of small onion bulbs	[91]
Zeolites	Rapeseed, <i>Brassica napus</i>	Soil–Cadmium (Cd)	10 g/kg	Reduced Cd uptake by plant; Improved plant physiology	[92]
Zeolites	Marjoram, <i>Origanum majorana</i> L.	Chromium-contaminated soil	5 g/kg	Alleviation of (Cr-induced) leaf senescence	[93]
Zeolites	Wheat, <i>Triticum aestivum</i> L.	Nickel (Ni)-contaminated soil	100 g/kg	Reduced Ni uptake by plant; Improved plant physiology	[94]
Diatomaceous earth (<i>Melosira granulata</i>)	Melon, <i>Cucumis melo</i>	Coarse texture, low nutrient and Si content	200, 400, 600, and 800 kg/ha	Increased nutrient uptake and nutrient use efficiency; increased yield and quality of fruits	[95]
Diatomaceous earth (biogenic silica, smectite, kaolinite and quartz), AgriPower Pvt. Ltd., Australia	Rice, <i>Oryza sativa</i> L., var. JGL 1798	Acidic, Neutral and alkaline soil–drought (and salinity) stress	150, 300, and 600 kg/ha	Improved water and nutrient-use efficiency; reduced stress effects; higher grain yield under stressed conditions; Si-uptake depending on soil type	[19]
Deionized diatomaceous earth (Zalpak area)	Wheat, <i>Triticum aestivum</i> L.	Growth substrate with known mineral composition–salinity stress	1 and 10 g/kg	Improved plant growth and yield compared with control, both with and without salinity stress	[96]

Data from Table 3 demonstrate: improved nutrient uptake, increased nutrient use efficiency, protection against abiotic stress (salinity, drought, heavy metals contamination) and enhanced crop quality. Such effects, similar with those described for plant biostimulants, are amplified by application of foliar treatment with known plant biostimulants. For example, zeolites were applied in combination with foliar treatment with melatonin [93], proline [94], selenium [91], or seed inoculation with metal-tolerant microorganisms [92]. In some cases, zeolites were more effective when applied together with amendments such as biochar [94].

Zeolites were much more studied compared to diatomaceous earth as soil amendments and Si sources for alleviation of abiotic stress-induced effects in plants, especially regarding salinity and heavy metal-induced stress. Only very recently, deionized diatomite was found to efficiently absorb Na^+ and Cl^- ions from aqueous solutions, presenting promising results in alleviating stress-induced negative effects on plants [96]. Although there are several studies investigating decontamination and removal of heavy metals from soils and wastewater by diatomaceous earth ([97–100]), we have found no study involving the capacity to reduce heavy metal-induced stress on plants.

Plant biostimulants were defined as a separate category of agricultural products, which promote cultivated plant growth and cultivated plant health without being nutrients, soil improvers, or plant protection products [101]. However, as we already mentioned, the intended use (e.g., protection of the cultivated plants against abiotic stress) is similar for both plant biostimulants and SNNMs used as soil improvers in soil affected by heavy metal contamination or sodicity, and/or from semi-arid area, with high drought risk. One of the main classes of plant biostimulants, humic acids, is described also as soil improver. Humic acid derived from lignite were used to improve the properties of poor soil–medium and coarse textured soil properties, in a pot experiment [102]. The quantity used for the pot experiment, 12.4 g per 5 kg of growth substrate is of the same order of magnitude with that of zeolites used to remediate the lead pollution in a pot experiment, wherein a maximum of 20 g per kg of growth substrate was used [103]. Humic acid amendment was proven to enhance corn tolerance to drought and phosphorus deficiency stress [104]. Humic acid amendment applied to soil, combined with foliar applied Zn and Se reduces Cd accumulation in tobacco [105]. The similarities with the effects described for SNNMs applied as soil improvers/soil amendment are significant. Therefore, in our opinion, there are enough arguments to consider the SNNMs application to soil/growing substrates, not only as soil improvers but also as a cultivated plant strengthening method.

4.2. Direct Plant Strengthening Effects

One potential direct effect of foliar applied SNNMs on treated plants is related to the activation of photosynthesis [81]. This effect was related to the capacity of SNNMs to concentrate CO_2 on treated leaves, near stomata [81]. SNNMs are well-known for their capacity to act as reversible CO_2 (chemo)sorbent [106,107]. Selective enrichment of the proximate stomata microenvironment should enhance CO_2 fixation, especially in C3 plants. This potential effect of zeolites on photosynthesis was demonstrated until now in only one publication [48]. A related siliceous nanomaterial, kaolin, was applied as reflective anti-transpirant [108] and photosynthesis and gas-exchange enhancer [109]. A particle film is formed by foliar spraying. The coverage of the canopy reduces leaf temperature, reflects the damaging UV-b radiation, enhances gas-exchange and improves photosynthesis in sweet orange [110], red grapefruit [111], olive [109] and grape [112]. Photosynthesis inhibition was noted after kaolin dusting on apple, hazelnut, and walnut. Similar effect was observed after diatomaceous earth application on Chinese cabbage [113].

The difference observed (photosynthesis enhancement versus inhibition) was explained to be a result of the water status in plant, based on recent experiments done on grape. On well-watered grape plants, kaolin reduces the photosynthetic performance [114]. On water stressed grape plants, kaolin functions as leaf protection agent [115]. Kaolin function as anti-transpirant and leaf protectant was recently reviewed [108]. Kaolin was considered an emerging tool to mitigate the effects of adverse abiotic stress on cultivated plants [116]. Despite the fact that foliar application of kaolin determines

effects very similar to those of plant biostimulants (higher plant tolerance to abiotic stress, enhanced crop quality), kaolin has not been considered yet as plant biostimulant.

This direction of photosynthesis stimulation by SNNMs under light and water stress is interesting and merits further investigation, also in relationship with the plant biostimulants mechanism of action. In general, plant biostimulants/plant strengtheners amplify the photosynthesis of treated plants under stress conditions [117]. Such effect was proven for microbial plant biostimulants [118,119], organic plant biostimulants [120], and inorganic plant biostimulants [121,122]. However, there is another aspect related to photosynthesis, which was not investigated enough in relation to plant strengthening/plant biostimulant effects. Boosting reactive oxygen species (ROS) production was constantly demonstrated after the application of various types of plant biostimulants [123–126]. ROS are involved in the response of plants to stress. The plants treated with plant biostimulants demonstrated an increased tolerance to imbalance determined by the increased ROS production [117,124,127–129]. Despite the fact that chloroplasts are well known as a source of ROS production [130], the research related to plant biostimulants mechanism of action has not considered chloroplasts involvement yet. It was demonstrated that chloroplasts are mediators of plant response to abiotic stress. For example, plant biostimulant *Trichoderma* strain increased the chloroplasts number and size in *Passiflora caerulea* leaves [119]. One explanation for this chloroplasts proliferation after plant biostimulant treatment could be in relationship with such mechanism of action, related to balanced ROS production by chloroplasts.

Other direct plant strengthening effects are in relation to soluble silicon species release from SNNMs. These will be further discussed, after a presentation of the present knowledge of the role of silicon in plant physiology.

Release of Soluble Silicon Species

In the last decades, an overwhelming body of evidences proved that Si is a *limiting factor* for crop production, particularly in soils that have a low soluble Si pool and for known Si-accumulating plants such as grass/cereals [131]. There are evidences suggesting that Si is essential, also, for non-grass species angiosperms [132]. Recently, it was hypothesized that silicon is essential for an efficient legume–rhizobia interaction and symbiotic nitrogen fixation [133,134]. Despite all of these evidences of silicon as limiting factor in cultivated plant productivity, silicon is still not considered an essential element/nutrient in plant, because it does not fulfill the plant nutrient criteria [135,136]. Rather, the soluble silicon effects on plants are characteristic for plant strengtheners/plant biostimulants [137]. Soluble silicon species promote plant health, improve plant resistance to biotic and abiotic stress [138–140], increase nutrient uptake and nutrient use efficiency [141], reduce heavy metals toxicity [142,143]. However, in order to accommodate the evidences related to the contribution of soluble silicon to plant yield, with the classical Liebig barrel and the nutrients included in it, silicon is for now considered only “*beneficial rather than essential plant nutrient*” [144].

Silicon has both morpho-structural and physiological/biochemical functions in plants [145]. Deposition of soluble silicon as silica layer beneath the cuticle generates a physical barrier for plant pathogens [146], phloem feeding insects [147], leaf eating larvae [148], and herbivores like locusts and small rodents [149]. The biochemical mechanisms of silicon action are not known yet, but there are evidences which suggest a regulatory function in plants. Soluble Si alleviate water stress (Sacala, 2009), nutrient imbalance (Ma and Yamaji, 2008) and lodging (Kashiwagi et al., 2008), due to activation of plant defense against abiotic stress. Silicon protects plants against saline stress by reducing the oxidative stress [150], chloride [151], and sodium uptake [152], and by enhancing potassium transport [153]. Similar effects, of reduced oxidative stress and reduced uptake of non-nutrient metal ions from soil solution, were demonstrated in relation with protective effects of soluble Si against heavy metals [142]. For the reduced uptake of heavy metals from soil are responsible also mechanisms of co-deposition of metals and Si, both externally, in the rhizosphere, and internal, inside plant roots [154]. A meta-analysis on soluble silicon alleviation of abiotic stress on several Angiosperm families revealed a similar

mechanism, which involves significant reduction in markers of oxidative stress, such as peroxy lipid (determined with reactive based on malondialdehyde, MDA) and H_2O_2 [139].

The importance of soluble Si in plant physiology results, also, from its role on simultaneous and non-antagonistic activation of the different pathways related to defense system [155]. Plant systemic defense against biotic and abiotic stress is regulated by several pathways: of salicylic acid (SA), of jasmonic acid (JA) and of abscisic acid (ABA) [156–158]. In general, SA is associated with resistance to biotrophic pathogens and sucking/phloem feeding insects, and JA is associated with resistance to the necrotrophic pathogens and cutting and chewing insects/herbivores and ABA is related to abiotic stress. The SA and JA pathways are antagonistic, generating a balancing between resistance to biotrophic pathogens/phloem feeding insects and necrotrophic pathogens/cutting and chewing herbivores. Various types of abiotic stress (extreme temperatures, solar radiation, and chemical pro-oxidant agents) interfere with SA/JA/ABA pathways, including through modulation of the level of reactive oxygen [159] and nitrogen species/nitric oxide [160]. All of these interactions could determine an increased plant susceptibility to biotic stress factors controlled by other pathway than the activated one [156,157]. Soluble Si balances these cross-talking pathways related to plant defense and prime broad-spectrum resistance to biotic stress [155]. A flow of soluble silicon through cytoplasm and further deposition on cell wall/plant extracellular matrix seem to be essential for silicon priming in plants [161]. Deposition of silicon into plant cell wall is mainly done as amorphous silica, which interferes with further biorefinery processes [162].

The soluble Si species up-taken by plants from the soil solution is mono-silicic acid, H_4SiO_4 [163], through an active transport system [146]. The mono-silicic acid concentration in soil ranges from 0.1 mM to 0.6 mM [163], which is less than 10–60 folds its saturation point [164]. The soluble Si pool in soil results mainly from the recycled Si accumulated in plants (phytogenic Si), $SiO_2 \cdot nH_2O$, an amorphous, hydrated, and highly porous material, produced by silicic acid molecules mutual polycondensation [131]. Chemical weathering of silicate minerals from parental rock does not replenish soluble soil Si pool, despite the fact that silicon is the second mineral in earth crust [165], but rather determines soil desilication [144]. The moderate mobile H_4SiO_4 is immobilized due to the reaction with immobile Al and Fe ions resulted from weathered parental rock and formation of secondary clays [166]. Therefore, the main source of soluble silicon in the soil is considered the bio/phyto silica–amorphous silica/opal $SiO_2 \cdot nH_2O$, deposited in plant cell wall.

Release of soluble Si from phytogenic Si is done by microorganisms responsible for plant residues decomposition [167]. Despite the fact that Si solubilizing microorganisms from phytogenic Si could be very useful plant biostimulants (accelerating soluble Si pool replenishing) there are practically no studies into this direction. It was reported that arbuscular mycorrhizal fungi (AMF) collected from saline sites accumulate Si and transfer it to host plants [168], but this is in relation with an enhanced uptake of soluble Si (like other nutrients) by AMF, and it is not related to an accelerated soluble Si release into soil.

There are practically no studies related to phytogenic Si solubilization by microorganisms. In aquatic systems biogenic Si dissolution is promoted by microbial consortia [169], by degradation of the organic matter wherein biogenic Si is embedded. A similar mechanism is most likely to be responsible for phytogenic Si solubilization in soil environment. However, besides the enzymes responsible for lignocellulose degradation, microbial metabolites, which enhance silicon/ H_4SiO_4 dissolution from amorphous phytogenic Si, should be also involved. Such microbial metabolites have not been identified yet, but it is known that H_4SiO_4 equilibrium in solution is influenced by alkaline cations, organic acids, and polyamines [164]. Among the environmental friendly additives used to prevent silica fouling in water pipes, catechuic acid (3, 4-dihydroxybenzoic acid), gallic acid (3, 4, 5-trihydroxybenzoic acid), dopamine, citric acids, and amino acids were the most effective [170]. Putrescine and their homologues [171], spermidine and spermine [172], and other long chain biogenic polyamines [164] influence silicon species equilibrium in unsaturated solutions. Such substances could be produced by several plant beneficial microorganisms.

Among these metabolites, several are directly related to the effects of plant biostimulants. Catechuic acid derivatives are well known as one of the main category of siderophores responsible for plant growth promotion effects of rhizobacteria [173,174]. Gallic acid accumulates in wheat treated with salt tolerant rhizobacteria [175]. Rhizobacteria producing polyamines (Pas) stimulate plant growth—*Azospirillum* producing cadaverine [176], *Streptomyces* producing putrescine [177], *Bacillus* producing spermidine [178]. Therefore, Si solubilizing microorganisms could represent an effective category of microbial plant biostimulants. However, until now there is no systematic investigation focused on the effects of SNNMs applications as soil conditioners on Si solubilizing microorganisms.

Soluble silicon species are formed mainly from diatomaceous earth. Its structure is formed mainly by amorphous silica, $\text{SiO}_2 \cdot x\text{H}_2\text{O}$ and is similar to that of phytogenic silica. Zeolites release soluble silicon species mainly by weathering. The flow of silicon through plant tissues supports the formation of amorphous silica—plant opal, $\text{SiO}_2 \cdot x\text{H}_2\text{O}$. Silicon deposition, generating apoplastic obstruction [136] was hypothesized to be the main mechanism of action which protects plants against biotic and abiotic stress—Figure 3.

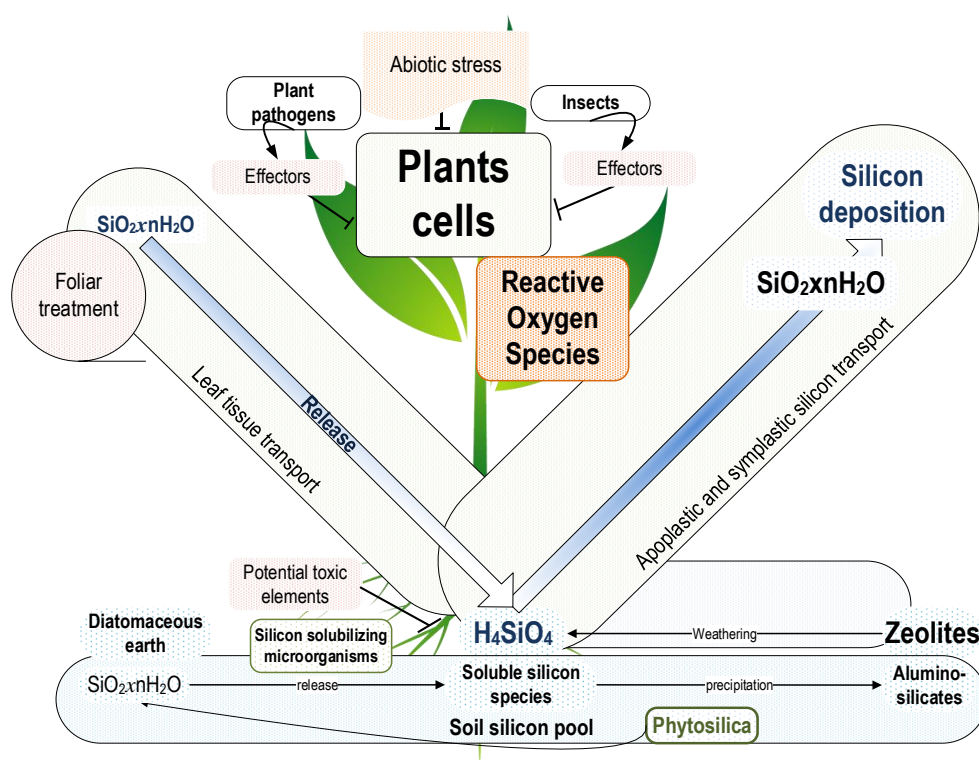


Figure 3. Siliceous natural nanomaterials as soluble silicon sources for plants. Diatomaceous earth, formed mainly by amorphous silica, is similar to phytogenic silica and releases silicic acid by hydrolysis. Zeolites form silicic acid mainly by weathering. In the root silicon block potential toxic element uptake. In soil, the moderate mobile H_4SiO_4 is precipitated with immobile Al and Fe ions and generates clays. The apoplastic and symplastic soluble silicon flow sustain the silica deposition, after concentration into aerial parts. This process balances reactive oxygen species enhances plant tolerance to abiotic stress and blocks the action of pest and pathogen effectors.

Other hypothesized mechanisms recently reviewed [122,135] refer also to the transport of soluble silicon species through plant tissues and polycondensation after concentration into the aerial parts due to transpiration.

SNNMs supply plants with soluble silicon. Application of 600 kg/ha of diatomaceous earth, in combination with standard fertilization practice promotes rice growth and increases yield [19]. A commercial preparation of diatomaceous earth, Agrisilica[®] (AgriPower, Sydney, Australia), which is formed from *Melosira granulata* frustules, with 26% silica, was demonstrated to increase the yield

of melon when applied in dose of 600 and 800 kg/ha to the coarse soil from Northeastern Brazil [95]. The same commercial product determined an increase of sugar beet yield, up to 40%, in Morocco [179], and proved to be an efficient source for sugarcane in sandy soil in Brazil [180]. Applied at 150 kg/ha, diatomaceous earth increased the potato tuber yield by 38.7% [181]. A commercial preparation of diatomaceous earth (Perma-Guard, Inc., Kamas, UT, USA) was used to compensate the water stress in potted ornamentals, black-eyed Susan, *Rudbeckia hirta*, dahlia, *Dahlia Cav. × hybrida* and daisy, *Gerbera jamesonii*. Si-rich mineral zeolite protects barley plants grown in hydroponics against cadmium stress [21].

Application of SNNMs as source of soluble silicon species could compensate the decrease of phytogenic Si inputs into soil, impacted by anthropogenic biomass removal [182,183]. Additional studies are necessary for a better exploitation of this potential SNNMs application.

5. Conclusions and Further Perspectives

Evidences regarding siliceous natural nanomaterials as biorationals for integrated farming systems were presented. However, there are gaps in knowledge that limit their large scale utilization. Figure 4 illustrates such gaps related to SNNMs effects on (micro)organisms associated to microbiocenosis delimited by plant organs, in relation to their main effects.

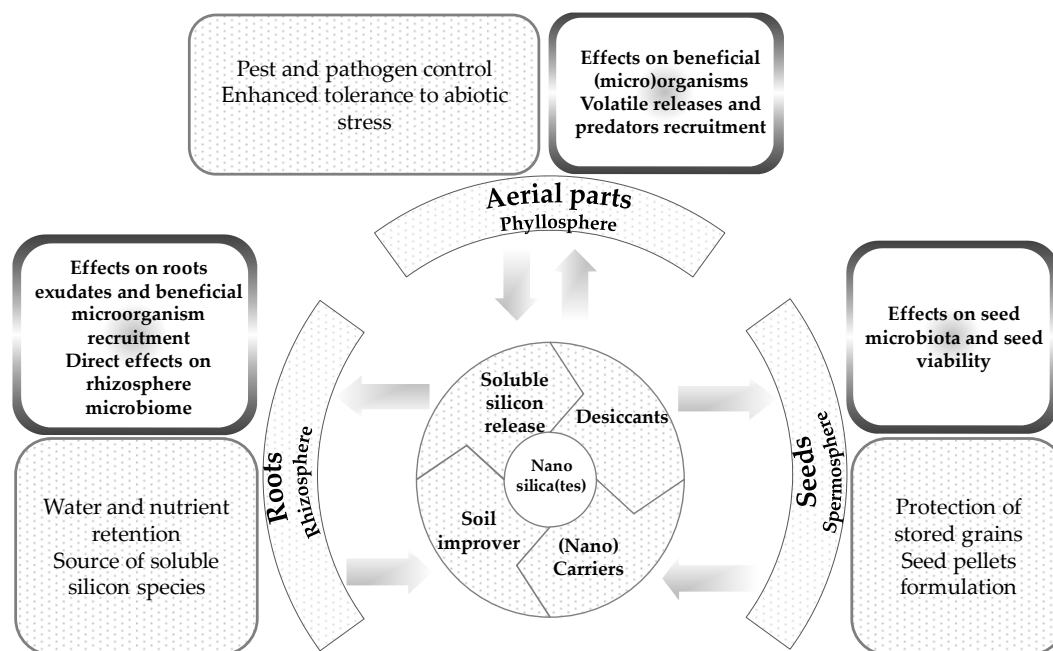


Figure 4. The main effects of siliceous natural nanomaterials and the gaps in knowledge related to their effects on (micro)organisms associated to microbiocenosis delimited by plant organs. The gaps are shown in black boxes.

Similar to other biorationals from the category of basic substances with low risk, SNNMs efficacy as plant protectants and plant health strengtheners is rather low. Complementary active ingredients should be used to enhance the effects of SNNMs on treated plants. For SNNMs applied as protectants of stored seeds such strategy, of using complementary biorationals/low risk substances, proved to be highly effective.

Natural zeolites are excellent soil improvers, especially in poor soil. However, their effects are not limited to the improvement of chemical and physical characteristics. Natural zeolites seem to influence also the recruitment and promotion of beneficial rhizosphere microorganisms, but there is a limited number of studies and information. Recently, it was reported that the application of natural green tuff stimulates the development of several phylotypes belonging to *Bacillales* [184]. Further

studies are necessary to understand the mechanisms behind such effects on beneficial microorganisms. Three-dimensional (3D) SNNMs porous structures, especially of diatomaceous earth, could provide shelter for bacteria against grazing protozoa. Reversible sorption and ion exchange capacity could modulate bioavailability of bioactive molecules, such as antibiotics, quorum sensing signals or siderophores, and respectively, of essential or potential toxic elements.

SNNMs foliar application is still on its infancy. The combination with foliar fertilizer should benefit from the excellent ion-exchange capabilities of zeolites. To the best of our knowledge, SNNMs were not used as carrier for foliar fertilizer until now. As foliar application, diatomaceous earth could be exploited better as anti-transpirant and leaf protector by cleaning the fossilized frustules to their initial state of transparency. The frustules of diatoms are transparent “house” for photosynthetic organisms, protecting them against damaging UV radiation [185] and stimulating photosynthesis [186]. The abrasiveness of SNNMs applied on leaves could be used to promote the release of volatile signals and predators recruitment.

Particle film formation is an agricultural technology which was demonstrated to protect plants against both biotic [187,188] and abiotic stress [108]. Recently, it was demonstrated that micronized chabazitic zeolites, applied together with microorganisms, present superior particle forming ability and enhanced efficacy in controlling tomato diseases [189]. Diatomaceous earth synergizes the effects of *Metarhizium flavoviride* against western flower thrips, *Frankliniella occidentalis*, an invasive pest [190]. Therefore, the potential for synergy between SNNMs and phyllosphere plant beneficial microorganisms, in connection to particle film formation technology, seems to be significant and requires more attention.

Diatomaceous earth are not only grain protectant, but are also bioactive carriers for seed coating. Applied together with vermicompost and soy flours, diatomaceous earth promotes seedling growth of a cover crop mixture grass-legumes, perennial ryegrass, *Lolium perenne*, and red clover, *Trifolium pretense* [191]. Further studies regarding the effects on seed viability, seed priming, and on microbial plant biostimulants applicable as seed inoculant could generate new solutions for sustainable farming.

The combination of SNNMs with microbial plant biostimulants has significant potential to be synergic for plant health strengthening effects. The microbial plant biostimulants should promote the release of soluble silicon species. Soluble silicon should enhance the microbial plant biostimulants effects related to nutrient use efficiency, enhanced plant tolerance to stress and crop quality.

Natural zeolites and diatomaceous earth have complementary features—e.g., high ion-exchange capacity and, respectively, the ability to release soluble silicon. Their optimal combination could lead to additive/synergic effects, which should promote their use as biorationals.

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