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(54) Title: NON-CHELATED DIVALENT METALLIC SULFUR-NITROGEN COMPOSITIONS

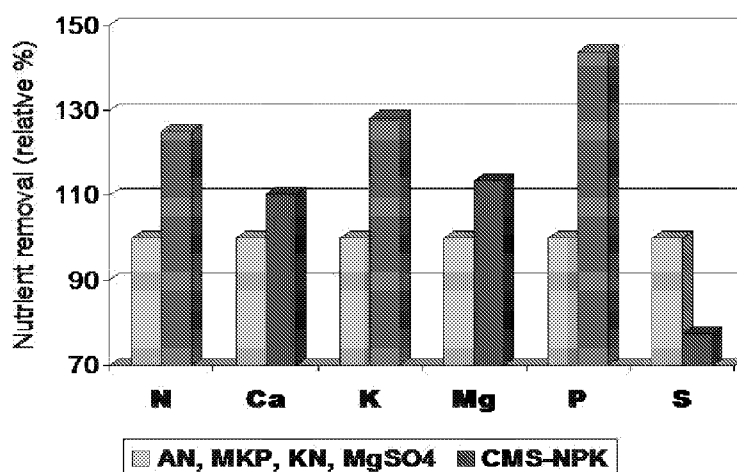


FIG. 1

(57) Abstract: A composition containing an aqueous solution of primary and secondary macronutrients, and an aqueous solution of micronutrients, wherein the primary and secondary macronutrients, and micronutrients contain divalent metallic salts of sulfamic acid.

TITLE OF THE INVENTION

NON-CHELATED DIVALENT METALLIC SULFUR-NITROGEN COMPOSITIONS

Field of the Invention

[0001] The present invention relates to non-chelating divalent metallic sulfamic acid salts and their stabilization with phosphoric acid, and to their use in plant nutrition compositions and systems containing the same, which exhibit storage stability.

Description of the Background

[0002] In agriculture, divalent metal cations, Ca, Mg, Fe, Mn, Zn, Cu and Ni, are currently considered essential nutrients for plant growth, development, and disease resistance. Plants can develop metal deficiency, because of the unavailability, loss or exhaustion and are often the cause of poor plant growth and development. Metals can be determinant factors of growth and crop deficiencies may occur even at extremely low levels of metal deficiency, at levels of parts per million in the plant tissue.

[0003] Secondary macro (Ca and Mg) and micro (Fe, Mn, Zn, Cu, Ni) nutrients - must be presented to plants in a form suitable for plant uptake, translocation and

assimilation. Divalent metals and many nutrient ingredients, such as sulfates, ammonium and phosphates, are chemically incompatible and have a tendency to precipitate in soil, in solution and/or within the plant tissue, forming, for instance, calcium sulfate or gypsum, or in other instances, highly insoluble metallic ammonium phosphates and metallic phosphates. To compensate for such precipitation loss, recommended dosage rates for metallic nutrients that are based on sulfates, oxides, chlorides, nitrates, and other similar inorganic metallic salts are often excessively high, resulting in phytotoxicity and early senescence, higher costs and environmental damage.

[0004] To counter divalent metallic precipitation, one way in which certain metals have been successfully applied to and utilized by plants is by application of metal chelate solutions. The term chelate is from the Greek for claw, and describes a "complex" in which organic molecules form ring-like structures through coordinate bonds with metal ions. The metal chelate structure loosely ties up the constituent metal ion(s) in a form in which the metal component is less likely to dissociate or precipitate in chemical reactions when the chelate is in the soil or in solution with other fertilizers, especially derivatives of sulfuric and phosphoric acids. The use of chelate, in theory, allows the metal from the chelate metal complex to remain available until after the product penetrates and translocates within plant.

[0005] Both root and foliar application of chelated metal ions may prevent, correct or minimize crop mineral deficiencies. Chelated complexes have been favored because the chelated metal ions remain soluble in different or changing environments, such as

alkaline soil. Conventional products have used synthetic chelates. However, administration of metal ions, synthetic chelates may contaminate the environment.

[0006] The use of naturally occurring organic acids, and their derivatives, as chelating agents to provide an inexpensive and biodegradable alternative has been proposed. However metal chelates of citric acid were reported as unstable at a pH above 7 and as having low stability constant compared to the synthetic chelating agents. See, Cline, et al, Soil Sci. Soc. Am. J., vol. 46, pp. 1158-1164 (1982) and U.S. Pat. No. 5,372,626.

[0007] Because some synthetic chelates are not biodegradable, the uses of such compounds are being regulated in many parts of the world. See, Tiedje, "Microbial Degradation of Ethylenediaminetetraacetate in Soils and Sediments," Applied Microbiology, August 1975, pp. 327-329. Often the use of naturally occurring organic acids and organic bases that readily degrade are not always efficacious. The use of a synthetic chelate that biodegrades may substitute for the synthetic compound with environmental persistence and still may be ineffective.

[0008] In particular, ethylenediaminetetraacetic acid (EDTA) is a compound that forms strong and very stable complexes with many metal cations (divalent and trivalent ions), increasing the metal ion solubility in aqueous solution as water-soluble complexes. It is one of the cheapest and most suitable multipurpose chelating agents. Besides acids, EDTA, may degrade by absorption of oxygen and Fe(II), which is the most active form of iron, is usually available as Fe (III). Further, formaldehyde is

produced from EDTA when it is oxidized by the photochemical reduction of ferric iron and it can accumulate to inhibitory levels. Replacing EDTA with other chelators, such as tartaric or citric acid, is not likely to eliminate the loss of available metals because several di- and tricarboxylic acid chelators have also been shown to be photo-oxidized.

[0009] Chelated metals are currently available in the fertilizer industry in powder and liquid forms. Both forms tend to be more expensive than inorganic metal compounds. For example, aqueous metal chelate formulations typically are supplied in 2.5 or five gallon plastic jugs containing from 5% to 11% by weight of the chelated metal. Cost of shipping these products is high, primarily because of the relatively low weight percent of the chelated metal in the product as compared to the volume of water in which the metal chelate is dissolved. In addition, if temperatures drop below point some metal chelates crystallize out of liquid formulations and concentrate at the bottom of the container. Naturally this creates problems when subsequently applying the metal chelate solution to crops.

[0010] While powder metal chelates are available and solve some of the stability, storage and disposal problems associated with metal chelate solutions, others remain unaddressed. For example, to produce certain powdered metal chelates, constituents are reacted in an aqueous solution and then dried, a process requiring substantial time, energy and expense. Powdered metal chelates produced in this manner include ethylene diamine tetraacetic acid (EDTA) chelates and lignin sulfonate-based metal chelates. While these powdered metal chelates can provide the

constituent metal in greater concentration than metal chelate solutions, (e.g., 6% to 15% weight percent), powdered metal chelates are substantially more expensive, e.g., \$1.50 to \$8.00 per pound. The high cost of these products tends to limit their use to the horticulture industry. See, Barak and Chen, *Soil Sci. Soc. Am. J.*, vol. 51, pp. 893-896 (1987).

[0011] Furthermore, some metal chelates solutions are decomposed by acid. The constituent metals may then exhibit reduced agronomic effectiveness. Thus, mixing some metal chelate solutions, including reconstituted powdered metal chelates, with certain acidic fertilizers must be avoided prior to application of the metal chelate solution to plants. Yet application of metals with macronutrient fertilizers is typically preferred, because it provides all the essential nutrients at the same time, minimizing growth constraints. In alkaline soil and/or in plants applied previously with glyphosate – herbicides that sequesters and precipitates metals, plants can be fed top down by way of foliar application and should, in theory, be more economically viable.

[0012] One important method in correcting metallic deficiency of agricultural crops, especially in alkaline soil, is the application of foliar metallic nutrient spray. However, variable plant responses to metallic sprays, ranging from defoliation and leaf burns to no effect, have been often described in fertilization literature. Studies show the choice of an adequate electrolyte carrier compound is the one strategy to favor the penetration of ions through plant leaves. Suitable element carriers for foliar

fertilization should preferentially have a high solubility and a low molecular weight. Another factor to penetration is the waxy cuticle that covers upper and lower leaves and even the walls of stomata. This layer has a negative charge. Positively charged particles will be stopped at this point from further progress into the plant. Nutrients that accumulate at the leaf surface may become toxic to the plant. See Schönherr, J., 2001, Cuticular penetration of calcium salts: effects of humidity, anions and adjuvants. *Journal of Plant Nutrition and Soil Science* 164:225-231 and Schönherr, J, and R. Hüber, 1977, Plant cuticles are polyelectrolytes with isoelectric points around three. *Plant Physiology* 59: 145-150.

[0013] In practice, the uptake and utilization of metallic nutrients involves a tradeoff between stability and uptake. For instance, chelating based metals have large molecular size and large molecular size has a highly detrimental effect on fast uptake of metals into plants. For foliar applications, the pore size in the leaf is one of the main factors affecting nutrients uptake. The smaller ionic molecular size has the advantage allowing easier passage through the pores in leaves, while a larger molecule is normally too large to fit into such pore and therefore has their access slowed or blocked. On the other hand, soil is generally negative in charge, especially clay soils. Pores on the leaves of plants are also negatively charged. Positive charged metals trying to penetrate the plant get tied up thus slowing nutrient uptake. The neutral charge of minerals allows them to enter the pores unimpeded. Stability constant, which is an equilibrium constant for the formation of a complex in solution and is a measure of the strength of the interaction between the reagents that come together to form the complex, shows that metallic chelates such as EDTA and EDDHA

have the highest constants and sulfuric acid salts based in citric acid the lowest. This tradeoff is also seen in the solubility of the metals. High stability constant metallic chelates derived from EDTA show relatively low solubility, i.e. less than 100 g/l at 20°C. Sulfuric acid salts with chelation have higher solubility, less than 300 g/l, but those are still low compared with chlorides and nitrates based metals, over 600 g/l.

[0014] In foliar applications, chelates and metals with organic chelating agents are often used with phytotoxic results. The commonly used Iron (III) EDTA must always hold on to a metal. For example, iron EDTA will correct iron deficiency in plants, but in order for the EDTA to release the iron it must hold onto some other metal. Often EDTA will take up manganese in order to release the iron, thus causing a manganese deficiency. Furthermore, EDTA is known to take calcium from cell walls in both plants and animals. Once plants have absorbed the minerals, the EDTA that may reach the plasmalemma can scavenge calcium from the cell walls, thus causing leakage, cell damage and disease. On the other hand, foliar application of metallic sulfate requires substantially higher dosage rates due to their lower efficacy and compatibility, which may burn the leaves or cause other phytotoxic results.

[0015] Last but not least important, while much of the development of secondary macro and micro nutrients is focused on stability and compatibility issues there is a need for metals to be binded with much higher proportion of sulfur. For instance, in the essential clusters of iron-sulfur proteins in ferredoxin molecules, which mediate electron transfer for a number of essential plant reactions, e.g., NADP+ in photosyn-

thesis, nitrite reductase, sulfite reductase, N₂ reduction, GOGAT, each iron is linked by several atoms of sulfur, usually at the molar ratio of Fe:S is 1:4. Similarly, metals can also be linked with sulfur and other micronutrients, such as Fe-Mo cofactor in nitrogenase and its clusters of Fe:S:Mo is 7:9:1. Existing metallic products either lack metallic sulfur altogether or have insufficient levels of sulfur combined with metals. In chelates, such as EDTA, DTPA and EDDHA, and in metallic chloride and nitrates, metals are not bonded by any sulfur. High redox potential divalent metals based in sulfate, such as Fe (II), Mn (II), Zn (II), Cu (II) and Ni (II) sulfate, have a molar ratio of metal:sulfur at 1:1 and is substantially less than the optimal ratio required by ferredoxin and other metallic sulfur protein, cofactors and others. Although calcium and magnesium thiosulfates have metal to sulfur molar ratio at 1:2, thiosulfates are generally unavailable for plant uptake until it is converted from thiosulfate to tetrathionate and then to sulfate, reactions in soil that may take weeks. Thiosulfates also lacks stability in strong acids as thiosulfates degrade into harmful sulfur dioxide gas.

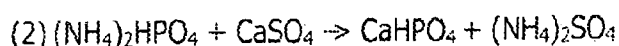
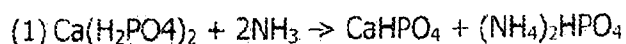
[0016] There are several important production and logistic considerations for the utilization of metallic nutrients that have low dosage rates and higher compatibility among essential nutrients. For instance, in foliar applications, where the nutrients and other chemicals are dispersed by airplane, solubility of metals in water is critical. In airplane spraying, water dilution ranges from 5 to 10 gal. per acre, dissolving micronutrients, pesticides and fungicides into a limited volume of water can easily over saturate the solution. A product with a higher solubility than chelate based metals is highly desirable in reducing application costs. Complete fertilizer with all macro and

micro nutrients are more efficient and economic. But, it is known that divalent metals, such as calcium, magnesium, iron, manganese, zinc, copper, cobalt and nickel, may precipitate out phosphorus compounds commonly available in fertilizer, such as monopotassium phosphate (MKP) and monoammonium phosphate (MAP), in mixing tanks or within plant. Ammonium and phosphate can react with metals and precipitate out either as metallic phosphate or as metallic ammonium phosphate. Calcium and sulfate can form calcium sulfate or gypsum. Incompatibility between phosphate/sulfates and metals and metals themselves has required multiple tanks of fertilizer instead of a single system. Usually two tanks with fertilizer mixtures are required: tank A for materials compatible with calcium and tank B for those compatible with sulfur. In reality, all nutrients should be mixed and stored in one single tank prior to plant application, foliar or root feeding. The one tank approach would simplify production and increase yield. Also, the lack of compatibility between metals may restrict their use in complete metallic mixtures with long shelf life, especially in water based solution. In dry mixtures, inert materials are often added to prevent metals from precipitating among themselves but these add to cost and add little to plant nutrition.

[0017] US 2,237,826 to Woodhouse teaches use of sulfamic acid and salts of sulfamic acid in the preparation of ammonium sulfamate and such nitrifying liquor is applied as an ammoniating reagent in the neutralization of acid components in the superphosphate, specifically phosphoric acid. According to Moose (US 2,033,389), in the reaction of ammonia and phosphoric acid for the production of ammonium phos-

phate, pH affects the size of the crystals of ammonium phosphate and the tendency to adhere to metallic surfaces. At low pH, the crystals are small and irregular and adhere firmly to metallic surfaces of the saturator. At a pH of between 7-7.4, the crystals have a tendency to crystallize with a minimum amount of occluded impurity giving a very pure product.

[0018] Two fundamental distinctions must be emphasized. First, Woodhouse does not assert that divalent metallic sulfamates can be used to react with superphosphate with the product thereof being mixed with other fertilizers. Rather, this assertion is made only for ammonium sulfamate, a well known herbicide. That is, divalent metallic sulfamates, individually and/or combined with sulfamic acid, cannot neutralize the excess acidity of the superphosphate. On the contrary, it would further lower the pH of the superphosphate. Woodhouse effectively equates sulfamic acid and its salts with ammonium sulfamate or that ammonium sulfamate can be substituted by any other related ammonium salt, and that ammonium from the ammonium sulfamate is supposed to react with acidic compounds of superphosphate in a neutralization reaction. Second, regardless of whether Woodhouse employs divalent metallic sulfamates or not, the neutralization and displacement reactions produce neither divalent metallic nor ammonium sulfamates. During the neutralization reaction, ammonium and other cations would turn into ammonium or other cationic sulfates:



and during the displacement reaction, either metallic ammonium phosphate or metallic phosphate would be made resulting in highly insoluble products, unavailable for plant nutrition. According to Casimer et al (US 3,416,910), in an ammonium/phosphatic slurry, Cu^{+2} from chelated EDTA reacts with Ca^{+2} , releasing Cu from the chelate, which Cu^{+2} would react with NH_4^+ and PO_4^{-3} . In contrast with highly soluble copper sulfamate, the resulting copper ammonium phosphate has low solubility and would not leach out of the soil as readily. Further, at a pH of 6-8 of the superphosphate, copper ammonium would precipitate out of solution. No metallic sulfamate would be available in the Woodhouse fertilizer. Similarly, according to Brown et al (US 6,322,607), insoluble zinc ammonium phosphate (ZnNH_4PO_4) may be formed in the presence of ammonium ion and phosphate ion in the granulator which is not available for crops, and particularly in sandy neutral or alkaline soils under dry conditions. Further, Brown et al discloses that when a synthetic chelate such as ZnEDTA is mixed with phosphoric acid before ammoniation, acid decomposition of the chelate molecule results in decreased availability of some Zn fertilizers. At pH 2, the K_{sp} for ferrous ammonium phosphate is 1.8×10^{-11} , and for magnesium ammonium phosphate is 3×10^{-13} , both at 25°C . Thus, no metallic sulfamate would be available from the Woodhouse fertilizer. Hence, the final mixture with other fertilizers cannot hold either divalent metallic or ammonium sulfamates.

[0019] Further, there are least two more reasons why Woodhouse and/or an expert in the art cannot possibly predict the usefulness of divalent metallic sulfamates as plant

nutrients without extensive greenhouse and/or field testing, and at sharply lower recommended dosage rates. Firstly, in Woodhouse, the role of sulfamate is strictly one of an ammonium carrier, effectively to neutralize acidic components of superphosphate, rather than as a nutrient. There are many examples of chemical compounds with one or more of the individual essential chemical elements that cannot be used as a nutrient. For instance, some chemicals with wrong isomeric position, such as in o-p in Fe EDDHA, or byproducts, such as biuret, or even ammonium sulfamate, a registered herbicide, can be by varying degrees turn from inefficient to phytotoxic. Woodhouse does not recommend or claim the use of sulfamate as plant nutrient. Secondly, application of divalent metallic sulfamate at the recommended dosage rate of equivalent metallic nutrients, such as sulfates, nitrates, chlorides, oxides, chelates, etc, should show that these divalent metallic sulfamate salts are highly phytotoxic and can teach away by assuming these sulfamate salts are generally unsuitable for plant nutrition. When a nutrient concentration increases from deficient to optimal and then to excess levels, the latter can rapidly alter the adequate balance of all other nutrients, e.g., bivalent metals calcium and magnesium competing against potassium, slowing growth and even shrinking the size of leaves. Contrary to Woodhouse's invention, recommended dosage rates for divalent metallic sulfamates must be reduced to a much safer range, three to fifteen times, compared to those from equivalent products, before it can be rendered effective and non-phytotoxic. For instance, ferrous sulfamate in foliar application should be used at the rate of 0.25 to 0.5 lb/acre in corn while comparable FeEDTA and ferrous sulfate must be used at a recommended rate between 1 lb to 5 lb per acre. While the reaction of divalent metallic sulfamates is known, the dual combination of lack of understanding of their

bio-availability and its low level dosage requirement may help explain why divalent metallic sulfamates have not been used as plant nutrient and why some of these salts of sulfamic acid were neither registered in the TSCA Inventory at U.S. Environmental Protection Agency (EPA) nor were commercially available.

[0020] US 4,383,846 to Newsom teaches use of N-substituted sulfamic acids to flocculate magnesium salts from fertilizers derived from the ammoniation of phosphoric acids. The metallic carbonaceous particles are flocculated and float to the surface, leaving a clarified liquid below, free of metals, after treatment with surfactants based on N-substituted sulfamic acids. No metallic salts of sulfamic acid are formed or intended as fertilizer.

[0021] US 6,353,1347 to Von Locquenghien et al discloses use of malonic acid diureid bis (potassium sulfonate). It discloses imido and nitride derivatives of sulfuric acid instead of amides derivatives of sulfuric acid, the latter being derivatives of sulfamic acid. In contrast to divalent metallic sulfamate salts, the compound described therein is highly insoluble in water and require a "mineralization" by chemical hydrolysis, enzymatic cleavage and/or microbial conversion prior to plant uptake. Further, the preferred use of alkali metals such as cesium and lithium discloses no use of metals as fertilizer from the sulfonate in diureid compound and/or the displacement reaction. No divalent metallic sulfamate salts are formed or intended as fertilizer.

SUMMARY OF THE INVENTION

[0022] Accordingly, there has been a long felt, but unfulfilled need for a new and complete family of non-chelating metallic-sulfur-nitrogen ionic nutrients, which are more efficient, economical and easier to use. The combination effect of more efficient metal to sulfur ratio, small molecule size, non-chelating divalent metallic cations, higher stability constant, higher phosphate and ammonium compatibility can yield higher productivity and create greater demand for NPK and high solubility in plants. More efficiency and higher uptake can translate into lower dosage rates. Having a significant reduction in dosage rate has obvious additional beneficial effects, including reduction in foliar burning, delayed senescence and lesser discharge of metals into the environment. In addition, lower dosage rates may cut the need for multiple applications and lower its application costs. Further, lower recommended dosage rates results in reduction of other costs, such as packaging and transportation. It is highly desirable to have products with greater solubility in water, higher chemically stable and compatible with other fertilizers and with other metals, greater shelf life and photo resistance, faster uptake of non-chelating divalent metals, nitrogen and sulfur to plants, and for methods of producing such fertilizers with the readily available essential metal, sulfur and nitrogen nutrients necessary for plant growth. The present invention solves those needs.

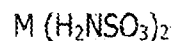
[0023] It is an object of the present invention to provide chemical compounds which may be used in mixtures with phosphates and ammonium and which are superior to the known substances with regard to their compatibility with water and superior plant

uptake. Furthermore, divalent metallic salts with or without phosphoric acid contain a multitude of plant nutrients, which may be applied without the need of organic chelating agents.

[0024] It is also an object of the present invention to provide chemical divalent metallic sulfur compounds which provides higher ratio of sulfur to metal.

[0025] It is also an object of the present invention to provide chemical divalent metallic sulfur-nitrogen compounds which provides an alternative source of inorganic nitrogen, other than, for example, nitrate, ammonia and urea. Similar to urea, sulfamates provide $-NH_2$, the nitrogen found in amino acids and proteins.

[0026] The above objects and others are provided by plant nutrient compositions containing divalent metallic sulfamate salts of the formula:



in which:

M is divalent metal which may be any of calcium, magnesium, iron, manganese, zinc, copper, cobalt, or nickel or a combination thereof. Specifically, macronutrient compositions are described below containing sulfamic acid salts of calcium and magnesium, and micronutrient compositions are described below containing other divalent metallic salts of sulfamic acid.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 illustrates the effect of nutrient removal in petunias grown in hydroponic solution.

Figure 2 illustrates dry weight matter of root and shoot of maize and tomato grown in rockwool blocks, and collected after four (4) weeks.

Figure 3 illustrates the effect of iron (II) sulfamate with and without calcium and magnesium sulfamates compared against iron DTPA and equivalent fertilizers on dry weight matter in maize.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0027] The divalent metallic sulfamate salts of the present invention can be prepared using well known chemical reactions. For example, sulfamic acid readily forms various metal sulfamates by reaction with a metal or with the respective carbonates, oxides or hydroxides. See Kirk-Othmer Encyclopedia of Chemical technology, "Sulfamic Acid and Sulfamates" (John Wiley & Sons). Plant nutrient compositions containing these salts may be prepared, and are advantageously used to remedy either or both micronutrient and/or macronutrient soil deficiencies to, thereby, promote plant growth. In accordance with another aspect of the present invention, the plant nutrient compositions also contain phosphoric acid, as it has been discovered that phosphoric

acid affords a long shelf life with resistance against phosphate and ammonium precipitation while other acids, such as citric acid, sulfuric acid and nitric acid may react with sulfamic acid and its divalent metallic salts and forming precipitates. Generally, concentrated phosphoric acid, i.e., at least 50% by mass, is used. Preferably, phosphoric acid of about 75% by mass is used. For convenience, technical grade phosphoric acid of 85% by mass may be used directly or may be diluted with water to a lesser concentration by mass prior to use. Such compositions may be prepared as follows, for example.

[0028] Concentrated phosphoric acid, e.g. 75%, is added to one or more divalent metallic sulfamate salts in water at a temperature of about 0 to 80°C, preferably about 10 to 30°C, to increase chemical compatibility with salts of ammonium and phosphate.

[0029] The preparation may be continuous or batchwise.

[0030] The compounds are highly soluble in water and are therefore suitable as a source for foliar and fertigation application in plants. What makes these compounds particularly interesting is their potential use as a combined nutrient source of primary macro nutrients (N, P, K), secondary macro nutrients (Ca, Mg, S), and micronutrients (Fe, Mn, Zn, Cu, B, Mo, Ni) in one tank instead of the customary tanks A and B, where tank A contains compounds based in calcium salts and tank B contains compounds that might react with the nutrients in tank A, such as sulfur and phosphate salts.

[0031] The compounds are highly resistant for a period of days to months and years to metallic ammonium phosphate precipitation without the use of an organic chelating agent. For example, the present inventor has observed that in the absence of phosphoric acid, divalent metallic sulfamates will precipitate in the presence of ammonium and phosphates. However, in addition to shelf life, there are other advantages in using an inorganic divalent metallic sulfamate as in the present invention.

[0032] The size of the cuticle pores of the leaves is one of the limiting factors for nutrient uptake; it is known that ionic molecules, having a small molecular size, has higher permeation than those with organic molecules. See Marschner, Mineral Nutrition of Higher Plants, pp. 120-121, 2nd edition.

[0033] A divalent metallic sulfamate has roughly half the molecular weight of an equivalent EDTA metal. Further, as an organic chelating agent may not be absorbed if its molecular size exceeds the plant pore aperture size, metallic nutrients are exposed to metallic phosphate precipitation within the plant. In tissue analysis of the leaves, it is often difficult to distinguish and quantify what proportion of metal uptake is useable and what is precipitated out.

[0034] For instance, metals such as ferrous iron will oxidize in a few hours. As for ferredoxin type of molecules, there is an improvement in the supply of nutrient, the molar ratio metal to sulfur increases from 2:3 in ferric sulfate to 1:2 in ferrous

sulfamate and 1:3 in ferric sulfamate. In the present invention, recommended dosages of metallic sulfamate are lower than those for chelated formulations. Thus, in accordance with the present invention, a metal:sulfur (Me:S) molar ratio of equal or greater than 1:2 is used. Further, divalent metallic sulfamate salts are used advantageously as the S source as opposed to other sources of S which might otherwise be used. For example, thiosulfate is not used in accordance with the present invention because thiosulfate is only stable in neutral and alkaline solution. Under acidic conditions, thiosulfate degrades to release sulfur dioxide. This can happen when vacuoles or other parts of plants are acidic, and must be avoided. However, in the present invention, sulfur sources, such as sulfuric acid or ferrous sulfate or both, for example, may be added to either macronutrient or micronutrient solutions to increase the sulfur content of those solutions.

[0035] The compounds of the present invention can be employed alone or as mixtures or in combination with other customary fertilizers or additions. For example, they can be formulated together with customary potash fertilizers (K fertilizers) such as potassium nitrate, nitrogen fertilizers (N fertilizers) such as ammonium nitrate, urea, nitrogen/phosphorus fertilizers (NP fertilizers) such as ammonium phosphates, potassium/phosphorus (PK fertilizers) such as monopotassium phosphate, nitrogen/potassium/phosphorus (NPK fertilizers) such as potassium ammonium phosphate, all of which are compatible in a water solution for extended periods of weeks and months.

[0036] For use, they can be brought to a desired particle size in the known manner, for example by granulation or compacting. They can also be brought to water solutions with contents of metal exceeding 10% in weight.

[0037] The present invention will now be further described by certain examples which are provided solely for purposes of illustration and are not intended to be limitative. All reference below to metal/sulfur ratios for molar ratios.

Example 1

[0038] Preparation of manganese (II) sulfamate solution: 237 g of manganese (II) oxide is added to 523 g of sulfamic acid in water to make a 1 liter solution. Final formulation has 10% Mn and 11% S in weight and with the molar ratio of Mn to S at 1:2 and pH of solution in water is below 2. Phosphoric acid is added to increase compatibility with phosphate, ammonium and other salts.

Example 2

[0039] Preparation of calcium and magnesium sulfamate solution 222g of dolomite (calcium and magnesium carbonate) and 530 g of sulfamic acid are stirred for 6 hours in water to form a 1 liter solution. Formulation provides 3.6% Ca, 2% Mn, 5% N and 11% S and pH below 2. Phosphoric acid is added to increase compatibility with phosphate, ammonium and other salts.

Example 3

[0040] Preparation of 190 g of zinc oxide and 451 g of sulfamic acid in one liter of water solution. Final formulation provides 10% Zn and 11% S in weight and a molar ratio Zn:S at 1:2 and pH below 2. Phosphoric acid is added to increase with phosphate, ammonium and other salts.

Example 4

[0041] Preparation of mixture with all the essential micronutrients: 2.8 lb of ferrous carbonate, 0.44 lb of manganese carbonate, 0.6 lb of zinc carbonate, 0.07 lb of copper carbonate are added to 6.7 lb of sulfamic acid in water, resulting in 4 liters of solution with 5% iron, 1.% manganese, 0.5% zinc, 8% sulfur and 0.02% copper. One can also add 60 g of boric acid and 0.8g of ammonium molybdate to make it complete of boron and molybdenum as micronutrients in this micronutrient solution. It is also acceptable to add other metals such as cobalt and nickel to augment the micronutrients in the mixture. This micronutrient solution is stable for a period of at least one or more years. The final solution has a pH below 2. Quantities of different micronutrients can be varied according to plants and growing conditions as needed. Mixtures can be made with one or more micronutrients without limitation. Phosphoric acid is added to increase compatibility with phosphate, ammonium and other salts. This concentrated micronutrient fertilizer solution must be diluted before application to plants. Recommended foliar or fertigation varies with plants and growing factors, e.g.

3-6 oz of concentrated micronutrient fertilizer diluted in 10-100 gal of water per acre for foliar, and 1,000 or more gal of water per acre for fertigation. Preferred sources of metals are hydroxides, oxides or carbonates, but are not restricted thereto.

Example 5

[0042] Preparation of complete primary (N-P-K) and secondary (Ca-Mg-S) macronutrients solution with 80 ml of solution Ca/Mg sulfamate (from Example 2) and 15 ml phosphoric acid 75% are diluted in water and then 120 g of ammonium nitrate, 120 g of calcium nitrate, 80 g of potassium nitrate, 50 g of magnesium nitrate and 110 g of monopotassium phosphate are diluted into this solution to form 1 liter solution. Final concentrated solution is complete with all macro, primary and secondary, nutrients and has 6% nitrogen (total nitrogen includes nitrogen from sulfamate), 6% phosphate (calculated as P_2O_5), 6% K (calculated as K_2O), 2% calcium, 1% sulfur (sulfur comes from sulfamate) and 0.5% magnesium (or respectively in fertilizer notation 6-6-6-2Ca-1S-0.5Mg). This concentrated fertilizer is complete with all primary and secondary macro nutrients and is stable for three years at 20°C. This concentrated fertilizer must be diluted before application to plants. Recommended foliar or fertigation varies with plants and growing factors, e.g., 1 to 3 qt of concentrated fertilizer diluted in 10 to 100 gal of water per acre for foliar and 1,000 or more gal per acre for fertigation. Mixtures can vary the composition of any and/or all macronutrients without limitation. Preferred sources of nitrogen are, but not restricted to, salts of nitric acid and urea. Preferred sources of phosphate are, but not

restricted to, salts of phosphoric acid and phosphoric acid. Preferred sources of potassium are, but not restricted to, salts of nitric and phosphoric acids.

[0043] Preparation of a complete formulation with all essential macro and micro nutrients in one tank solution may consist of mixtures of micronutrients described in example 4 at the preferred dosage rate of 6 oz./acre and example 5 at dosages of 1 qt/acre in diluted in water for foliar feeding. Dosage rates and individual formulations may vary according to method of feeding, crop, weather conditions, age of crop, soil, pH of soil, etc. Individual nutrient deficiency can be corrected by adding the nutrient as a supplement or in complete mixtures. For instance, in crops requiring more zinc, one would add more zinc sulfamate described in example 3 individually or in combination with example 4 and 5, and so on.

[0044] To demonstrate the compatibility of the compounds and their stability with fertilizer based salts of phosphates and nitrates, the following studies were carried out. For most applications, except for commercial shelf life and packaging, a few weeks of compatibility between common fertilizer based in nitrate and phosphate and metal-sulfur will result in satisfactory growth and blooming of plants. For instance, most crops, such as corn, wheat, cotton, soybean, etc., have a short growth period of 1-6 months. Multiple applications, by either foliar or root feeding, during the season is done to insure metal-sulfur-nitrogen nutrients are sufficient and to avoid any deficiency during the growing season.

Example 6

[0045] Mixing of final product, such as the product in example 2, with salts of nitric and phosphoric acid and other nutrients, through a software and hardware system, on internet or other devices, resulting in a complete mixture with all essential macro and micronutrients such as the example 5. System could also provide information on density of mixture, percentage of individual nutrient, parts per million, dilution, etc.

[0046] The present invention is practiced so that agronomists and farmers using a dedicated software program running on a mobile device, such as a telephone or portable computer, or on the Internet, can rapidly, yet economically, formulate a multitude of plant nutrient compositions by combining one or more prepared concentrated plant nutrient solutions of the present invention with a small number of single chemical compounds, i.e., mainly salts of nitric and phosphoric acid, such as calcium nitrate and monopotassium phosphate and phosphoric acid. A computer software program is especially useful to agronomists for mixing highly complex plant nutrient compositions containing up to all 16 essential nutrients in a solution stable state. This reduces or eliminates the need for agronomists to stock a larger number of specialty fertilizer formulas and to avoid having incompatible fertilizers in different mixing tanks. Instead, any desired formula can be rapidly formulated and mixed from a small number of raw materials. Typically, an infinite number of macronutrient formulations can be mixed using no more than seven compounds. Generally, the precise final and complete formulation for any particular application will depend upon a preliminary soil or hydroponic analysis using any conventional testing or assay kits

or tests to determine soil deficiencies. A suitable computer program for determining amounts of micronutrients and macronutrients to be added for any particular type of plant can be prepared by one of ordinary skill in the art, once input values (baseline soil concentrations of macronutrients and micronutrients) have been determined, and the desired final values of micronutrient and macronutrients are ascertained. As mentioned above, desired macronutrient and micronutrient levels are known for different types of plants, and are, thus, well known to those skilled in the art. Alternatively, the amounts of macronutrients and micronutrients to be added may be determined by manual calculation without the aid of a computer.

[0047] Standard commercially-available soil test kits may be used to determine whether any soil deficiencies exist, or a commercial firm may be used to conduct the soil testing. In addition tissue analysis of the plants is also tested. Many such firms exist, such as, for example, Logan Labs, LLC of Lakeview, Ohio and Timberleaf Soil Testing of Murrieta, California. In either case, soil and tissue results are obtained and any deficiencies determined, e.g. Table 4.12. Sufficiency levels of plant nutrients for several crops at recommended stages of growth, e.g., Soil Fertility Handbook, Oklahoma State University. The macronutrient and micronutrient solutions are then formulated to rectify the soil deficiencies. Alternatively, such tests may be by-passed complete macro- and micronutrient formulations in accordance with the present invention are used, if deemed suitable.

[0048] Preparation of complete macronutrient formulations is effected with a

multitude of combinations of NPK and Ca/Mg/S, e.g., a formulation with 5N-7P-5K-2Ca-1S-0.5Mg, and preparation of a complete micronutrient formulation, with a multitude combinations of Fe-Mn-Zn-Cu-B-Mo-Ni, e.g. 5Fe-2Mn-1Zn-0.001Cu-0.2B-0.001Mo. Concentrated solutions of macronutrients and micronutrients are diluted in water applied in fertigation and foliar application and other feeding techniques.

[0049] Preparation of complete macronutrient formulations with a commercially available formulation NPK, e.g., 20-20-20, from a third party manufacturer and Ca/Mg/S from Example 2, e.g., a formulation with 5N-7P-5K-2Ca-1S-0.5Mg, and preparation of a complete micronutrient formulation, with a multitude of combinations of Fe-Mn-Zn-Cu-B-Mo-Ni, e.g. 5Fe-2Mn-1Zn-0.001cu-0.2B-0.001Mo. Concentrated solutions of macronutrients and micronutrients are diluted in water and applied in fertigation and foliar application and other feeding techniques.

[0050] Thus, complete (i.e., as required from soil or hydroponic analysis) macronutrient and complete (i.e., as required from soil or hydroponic analysis) micronutrient solutions are prepared and maintained in separate (first and second) containing means. Prior to use, the separate contents of the separate containing means are mixed, and then applied as needed.

[0051] The compatibility results are shown in Table 1-5. In Tables 3, 4 and 5 below, low pH values were obtained by addition of phosphoric acid. For divalent metallic salts of sulfamic acid to be stable against phosphate- and ammonium-induced precipitation, phosphoric acid must be added to the mixture. Thus, phosphoric acid functions as a

solution stabilizer to prevent and avoid precipitation greatly increase storage stability.

Table 1

Solubility of 10 g/l of metal 9% in 100 g of monopotassium phosphate
plus water is added to make 1 liter solution with pH 3

	5 minutes	1 month	12 month
Calcium sulfamate	Clear	Clear	Clear
Magnesium sulfamate	Clear	Clear	Clear
Iron (II) sulfamate	Clear	Clear	Precipitate
Manganese (II) sulfamate	Clear	Clear	Precipitate
Zinc (II) sulfamate	Clear	Clear	Precipitate

Table 2

Solubility of 1 ml of phosphoric acid in 100 ml of metal 9%

	5 minutes	1 month	12 month
Calcium sulfamate	Clear	Clear	Clear
Magnesium sulfamate	Clear	Clear	Clear
Iron (II) sulfamate	Clear	Clear	Clear
Manganese (II) sulfamate	Clear	Clear	Clear
Zinc (II) sulfamate	Clear	Clear	Clear

Table 3

Solubility of 10 ml of metal 9% in 100 ml of calcium nitrate (0-0-8-11Ca)

plus water is added to make 1 liter solution with pH 3

	5 minutes	1 month	12 month
Calcium sulfamate	Clear	Clear	Clear
Magnesium sulfamate	Clear	Clear	Clear
Iron (II) sulfamate	Clear	Clear	Precipitate
Manganese (II) sulfamate	Clear	Clear	Precipitate
Zinc (II) sulfamate	Clear	Clear	Precipitate

Table 4

Solubility of 10 ml of metal 9% in 100 g of ammonium nitrate
plus water is added to make 1 liter solution with pH 3

	5 minutes	1 month	12 month
Calcium sulfamate	Clear	Clear	Clear
Magnesium sulfamate	Clear	Clear	Clear
Iron (II) sulfamate	Clear	Clear	Precipitate
Manganese (II) sulfamate	Clear	Clear	Precipitate
Zinc (II) sulfamate	Clear	Clear	Precipitate

Table 5

Solubility of Ca/Mg sulfamate (5-0-0-4Ca-12S-2Mg) in nitrate or phosphate to make 1 liter solution with pH 2.5

	5 minutes	1 month	24 month
100 g Ammonium Nitrate	Clear	Clear	Clear
100 ml Calcium nitrate	Clear	Clear	Clear
100 g Potassium nitrate	Clear	Clear	Clear
100 g Magnesium nitrate	Clear	Clear	Clear
100 g Monopotassium nitrate	Clear	Clear	Clear
Complete macro formulation (6-6-6-2Ca-1S-0.5Mg)*	Clear	Clear	Clear

* 120 g of ammonium nitrate, 130 ml of calcium nitrate (11-0-0-8Ca), 80 g of potassium nitrate, 45 g of magnesium nitrate, 115 g of monopotassium phosphate. Sulfamate from calcium/magnesium sulfamates also contributes to total nitrogen and sulfur content in a typical NPK-2Ca-1S-0.5Mg formulation.

[0052] To demonstrate the efficacy of the present compounds against conventional compounds, the following studies were carried out in Tables 6 and 7.

Table 6. Foliar application of ferrous sulfamate 9% in three sorghum fields in Kansas. Soil pH is 8. According to the Soil Fertility Handbook, Oklahoma State University, the sufficiency levels of iron for sorghum varies between 65-100 ppm. At a dosage of 6

oz/acre, tissue analyzes show Fe at a minimum of 154 ppm and a maximum of 1130 ppm, depending on the availability of other macro and micronutrients. Recommended foliar dosage for ferrous sulfate monohydrate and iron (III) EDTA is respectively 3-6 lb/acre and 1 lb/acre.

Tissue Analysis	N	P	K	Ca	Mg	S	Fe	Mn	Zn	Cu	B	N:S ratio
NW of 4	4.18	0.42	2.78	2.19	0.61	0.28	1130	276	58	18	51	14.9
NW of 4 RE	5.12	0.31	1.52	1.78	0.35	0.29	154	133	46	14	35	17.7
Cemetery	3.84	0.39	2.92	0.7	0.29	0.22	347	112	45	18	16	17.5
Soil Analysis	Nitrate	P	K	Ca	Mg	S	Fe	Mn	Zn	Cu	B	Organic Matter
NW of 4	11	26	373	5555	544	20	4	3	0.6	0.7	NA	1.1
NW of 4 RE	4	32	227	5540	554	21	4	3	0.5	0.7	NA	0.8
Cemetery	10	14	318	5758	589	10	3	2	0.7	0.8	NA	0.8

Table 7. Effect of Metals on Chlorophyll Content (corn test after 2 applications - measured by Minolta chlorophyll meter SPAD 502)

	Application	Chlorophyll percentage change
Ca and Mg sulfamates	foliar	8.2
Ca and Mg and Fe sulfamates	foliar	43.2
Fe (III) EDDHA	fertigation	12.0

[0053] Corn plants without application were used as controls, and chlorophyll was measured one (1) week after applications. Percentage change of chlorophyll reported represents the difference between the two groups (test and control) as a function of composition applied and means of application as shown. Note the significant improvement caused by application of both macro- and micronutrients, as compared to application of macronutrients alone, or application of Fe (III) EDDHA alone.

[0054] Thus, aqueous solutions of secondary macronutrients (CMS) in combination with one or more micronutrients as described herein, may be used advantageously to increase chlorophyll content of growing plants.

[0055] Additional results are shown in Figures 1, 2 and 3, which are described in more detail below.

[0056] Figure 1 illustrates the effect of nutrient removal in petunia grown in hydroponic solution. Calcium and magnesium sulfamate was formulated into a 5-7-5-2Ca-1S-05Mg formulation and compared with an equivalent formulation based on ammonium nitrate, monopotassium phosphate, calcium carbonate, potassium phosphate and magnesium sulfate. Trial period was 4 weeks. Sulfur content from sulfamate cannot be directly measured as sulfur is traditionally measured by barium sulfate precipitation.

[0057] Figure 2 illustrates dry weight matter of root and shoot of maize and tomato grown in rockwool blocks and was collected after 4 weeks. Weekly foliar application

of Fe sulfamate ("Fe- Sulf") vs. Fe DTPA at the rate of 100 ppm Fe dilution.

[0058] Figure 3 illustrates the effect of iron (II) sulfamate with and without calcium and magnesium sulfamates (CMS) compared against iron DTPA and equivalent fertilizers on dry weight matter in maize. Maize was grown in hydroponic solution. Calcium and magnesium sulfamate was formulated into a 5-7-5-2Ca-1S-05Mg formulation and compared with an equivalent formulation based on ammonium nitrate (AN), monopotassium phosphate (MKP), potassium phosphate (KNO₃) and magnesium sulfate (MgSO₄). Trial period was 4 weeks.

[0059] Generally, the plant nutrient solutions of the present invention have a pH of less than 3.0, and preferably 2.5. Further, the use of concentrated phosphoric acid in the present plant nutrient solutions affords a stabilizing, i.e., precipitation-retarding, effect beyond simply reducing pH. This may be readily appreciated by the fact that when other acids, including citric acid and nitric acid, are used in place of phosphoric acid for purposes of comparison, the present inventors observed the formation of a precipitate in as little as 1-2 days.

[0060] Generally, all cultivated plants may be treated in accordance with the present invention, which includes ornamental, herbs and crop plants. For example, ornamentals include, for example, roses, geraniums, hibiscus, hollyhocks, and daisies. Herbs may include, for example, rosemary, thyme, sage or oregano. Crops may include corn, wheat, rye, tomatoes, lettuce and carrots, for example. Of course, the

above are only examples and are not intended to be limitative. Notably, an excess of macro- or micronutrients may cause phytotoxicity, and a deficiency of either may cause under development. Thus, a balance must be struck between these two extremes. However, what constitutes such a balance varies from one type of plant to another, and dosage recommendations are determined based upon type of crop or ornamental plant, temperature, soil and humidity, for example. Yet, such balanced levels of both macro- and micronutrients are known for each type of crop and ornamental plant, hence, these values may be used in formulating macro- and micronutrient compositions for use in accordance with the present invention.

[0061] Additionally, while the present macro- and micronutrient formulations are stored and used in a form of aqueous solutions, these formulations may also be stored and used in a dry powder or pellet form, or as a controlled-release solid form. Controlled-release formulations for fertilizers are described in U.S. 6,540,808 and 7,267,707, both of which are incorporated herein in their entirety.

[0062] The macro- and micronutrient formulations of the present invention may be applied as aqueous solutions, powders or pellets by ground-based fertilization systems or by airplane in diluted form. If a pellet form for the macro- and/or micronutrient formulation is used, the pellets may be formed using conventional pelletizing or prill forming methodologies. These are formed from dilute solutions, and most commonly composite pellets of both macronutrient and micronutrient compositions are used. For example, see U.S. patents 5,851,261, and 5,030,267 (specifically for controlled release pellets and prills). Both of these patents are incorporated herein in

their entirety. Generally, it is advantageous to use both complete macronutrient and micronutrient compositions, and most commonly in aqueous solution form. As noted above, macronutrient and micronutrient compositions are obtained in stock or concentrated solution, and then diluted as indicated above, or as conditions warrant, for use in diluted form. The aqueous solutions may be applied to soil separately or in combination. Further, it is generally advantageous to use macronutrient and micronutrient solutions as described above when treating hydroponic solutions containing plants therein in dilute form. It is preferred, in accordance with the present invention to use aqueous solutions, but the present invention is not restricted to water solutions.

[0063] The present invention provides different compositions which may be used for different specific purposes. For example, an aqueous solution of primary and secondary macronutrients containing calcium sulfamate, magnesium sulfamate or a mixture thereof is provided. In such a solution, the primary macronutrients may further contain salts of nitric acid or urea or both for nitrogen, salts of phosphoric acid or phosphoric acid or both for phosphorus, and salts of nitric or phosphoric acids or both for potassium. These aqueous solutions generally have a pH of 2.5 or more. However, to prevent and avoid precipitation and increase storage stability, the pH may be reduced to 2.5 or less by addition of phosphoric acid.

[0064] The present invention also provides an aqueous solution containing zinc sulfamate, copper sulfamate, manganese sulfamate, iron sulfamate, cobalt sulfamate

or nickel sulfamate or a mixture thereof. This aqueous solution may also contain salts of boric and/or molybdic acids, and generally has a pH of 2 or more. However, to prevent and avoid precipitation and increase storage stability, a pH of 2 or less may be effected by addition of phosphoric acid.

[0065] Advantageously, divalent metallic salts of sulfamic acid compatibility with salts of ammonium and phosphate shows "storage stability" by the addition of phosphoric acid and all of the aqueous solutions of the present invention contain no chelating compound as none is necessary. Further, all of the aqueous solutions of the present invention generally have a metal:sulfur molar ratio of equal or greater than 1:2.

[0066] The present invention further provides a plant nutrition system which entails a first aqueous solution containing primary and secondary macronutrients, wherein the macronutrients contain calcium sulfamate, magnesium sulfamate or a mixture thereof, the solution having a pH of 2.0 or less; in a first containing means; and a second aqueous solution containing micronutrients containing zinc sulfamate, copper sulfamate, manganese sulfamate, iron sulfamate, cobalt sulfamate or nickel sulfamate, the aqueous solution having a pH of 2.0 or less; in a second containing means. As noted above, the first aqueous solution may further contain as primary macronutrients salts of nitric acid or urea or both for nitrogen, salts of phosphoric acid or phosphoric acid or both for phosphorus, and salts of nitric or phosphoric acids or both for potassium. These aqueous solutions generally have a pH of 2.5 or more, but the pH may be reduced to 2.5 or less by addition of phosphoric acid. Further, the second aqueous solution may further contain salts of boric and molybdic acids or a mixture

thereof, the second aqueous solution having a pH of 2.0 or more. Generally, addition of boric or molybdic acids or a mixture thereof causes pH to increase, but the pH may be reduced to 2.0 or less by addition of phosphoric acid.

[0067] The present invention also provides a method of providing nutrition for plants which entails diluting the first and second aqueous solutions, which are stock or concentrated solutions, then mixing the diluted first and second solutions, and finally applying the mixture directly to plants or soil adjacent to the plants. The application may be foliar or fertigation or other forms of delivery.

[0068] The present invention also provides a method of providing nutrition for hydroponic plants which entails a step of diluting the first and second aqueous solutions as described above, mixing the solutions and adding the mixture into a hydroponic basin containing the plants.

[0069] The present invention also provides a method of increasing chlorophyll production in plants, which entails a step of applying an aqueous solution containing at least secondary calcium sulfamate and magnesium sulfamate, and at least one micronutrient selected from the group consisting of zinc sulfamate, copper sulfamate, manganese sulfamate, iron sulfamate, cobalt sulfamate or nickel sulfamate, to the plant or soil adjacent to the plant. The application may be foliar or fertigation or other forms of delivery.

[0070] The present invention also provides a method of increasing available sulfur and nitrogen content for a growing plant, which entails a step of applying to a plant, or soil adjacent to the plant, an amount of a divalent metallic salt of sulfamic acid to the plant or soil either in aqueous solution, in powder or pellet or controllable release form.

[0071] Thus, in accordance with the present invention, sulfamic acid is not merely a carrier molecule for divalent metallic cations, but also a source of both sulfur and nitrogen, the latter of which are both important, in and of themselves for promoting plant growth and health.

[0072] Additionally, while it is unnecessary to use chelates with the disclosed compositions and formulations, in another embodiment chelates may be included. For example, NPK may be formulated with secondary macronutrients based upon divalent metallic sulfamic acid salts and micronutrients containing metallic chelates, e.g., macronutrients from example 5 are combined with 0.1% iron EDTA or DTPA and 0.05% Mn EDTA 0.03%, Zn EDTA and 0.001% Cu EDTA. As another example, a mixture of NPK and chelated secondary macronutrients and divalent metallic sulfamic acid may also be mentioned.

[0073] Terms used in this application are defined as follows:

DM = Dry weight matter

Fe - DTPA = Fe (III) diethylenetriaminepentaacetic acid

Fe EDDHA = Fe (III) ethylenediamine-N,N'-bis (2-hydroxyphenylacetic acid)

AN = Ammonium nitrate

KN = Potassium nitrate

MKP = monopotassium phosphate

CMS-NPK = calcium - magnesium sulfamate/nitrogen/phosphorus/potassium

NPK = nitrogen, phosphorus, potassium sources in a mixture

EDTA = ethylenediaminetetraacetate

Storage-stable = means an aqueous solution that can be stored without visible precipitation occurring therefrom. Generally, the duration of storage-stability is at least 90 days, and more preferably at least 12 months.

Primary macronutrients = N-P-K (nitrogen/phosphorus/potassium)

Secondary macronutrients = Ca-Mg-S (calcium/magnesium/sulfur)

Concentrated = means an as-prepared macronutrient and/or micronutrient solution that must be diluted prior to use in fertilizing plants. It also means solutions that contain macro and micro nutrients that may approach saturation point while maintaining a shelf life of a commercial product and/or may satisfy government labeling regulations and/or have amounts considered unsafe to apply directly through foliar or fertigation into plants without phytotoxicity.

Diluted = means a macronutrient and/or micronutrient solution that has been diluted with water and the solution may be applied directly to plants or soil or hydroponic basin in which they grow. It also means an amount of applied macro and/or micro nutrients that may be applied to plants that may be safely and properly absorbed through foliar or fertigation into plants without phototoxicity.

Containing means = means any container, vessel, bottle, tank or even paper or plastic/aluminum foil bag or cardboard box, for example, that is used to hold, contain or envelope the first and second aqueous solutions, which are macronutrient and micronutrient solutions, respectively.

Fertigation = means the application of fertilizer, soil amendment or other water-soluble products through an irrigation system.

Available = means a plant nutrient, either macro- or micro-, that may be taken up by plant roots, and not precluded from such availability by being binded or compounded with other elements or substances in soil.

[0073] Generally, aqueous solutions of calcium- and/or magnesium sulfamate (CMS) have a pH of 2.0 or less, usually less than 2.0; and aqueous solutions of micronutrient, based upon salts of sulfamic acid, as described above have a pH of 2.0 or less, usually less than 2.0.

[0074] Generally, aqueous solutions of NPK have a pH greater than 6. A mixture of NPK and CMS may result in a solution with pH greater than 2. Aqueous solutions of boron and molybdenum have pH greater than 4. A mixture of metallic micronutrient salts of sulfamic acid and boron and molybdenum may result in a solution with pH greater than 2. The boron and molybdenum are added, for example, as boric acid and ammonium molybdate. The particular pH value of the latter depends upon the amount of boron and molybdenum added, since the pH of the added boric acid, for example, in aqueous solution is from 4 to 7.

[0075] As used herein, the term "system" means a combination of both primary and secondary macronutrients, and micronutrients, with the former (primary and secondary macronutrients) and the latter (micronutrients) in separate (first and

second) aqueous solutions in a kit or package. However, the combination of these first and second solutions in a single, mixed solution may also be described as a system both in concentrated form and in diluted form for use.

[0076] Having described the present invention, it will be clear to one skilled in the art that many changes and modifications may be made to the above-described embodiments, without departing from either the spirit or the scope of the claimed invention.

WHAT IS CLAIMED IS:

1. An aqueous solution of primary and secondary macronutrients for plant nutrition, which comprise calcium sulfamate, magnesium sulfamate or a mixture thereof.

2. The aqueous solution of claim 1, wherein the primary macronutrients further comprise salts of nitric acid or urea or both for nitrogen, salts of phosphoric acid for phosphorus, and salts of nitric or phosphoric acids or both for potassium, said aqueous solution having a pH of 2.5 or more.

3. The aqueous solution of claim 1, wherein the primary macronutrients further comprise salts of nitric acid or urea for nitrogen, salts of phosphoric acid or phosphoric acid or both for phosphorus, and salts of nitric acid or phosphoric acid or both for potassium, said aqueous solution having a pH of 2.5 or less effected by addition of an amount of phosphoric acid sufficient to attain said pH; said phosphoric acid being added to the aqueous solution prior to addition of the salts of nitric acid or urea for nitrogen, the salts of phosphoric acid for phosphorus, and the salts of nitric acid or phosphoric acid or both for potassium thereto.

4. The aqueous solution of claim 1, having a metal/sulfur molar ratio by weight of equal or greater than 1:2.

5. The aqueous solution of claim 1, containing no chelating compound.

6. An aqueous solution of micronutrients for plant nutrition, which comprises sulfamic acid salts of divalent metals comprising zinc, copper, manganese, iron, cobalt or nickel or a mixture thereof.

7. The aqueous solution of claim 6, which further comprises salts of boric and molybdic acids and its acids or a combination thereof, said aqueous solution having a pH of 2.0 or more.

8. The aqueous solution of claim 7, which further comprises phosphoric acid, which is added to the aqueous solution prior to addition of the salts of boric acid and molybdic acid or a combination thereof, whereby after adding said phosphoric acid said aqueous solution has a pH or 2.0 or less.

9. The aqueous solution of claim 6, having a metal/sulfur molar ratio by weight of equal or greater than 1:2.

10. The aqueous solution of claim 6, containing no chelating compound.

11. A plant nutrition system, comprising:

a) a first aqueous solution comprising primary and secondary macronutrients for plants, wherein the macronutrients comprises calcium sulfamate, magnesium sulfamate or a mixture thereof, the solution having a pH of 2.0 or less; in a first containing means; and

b) a second aqueous solution comprising micronutrients for plants comprising sulfamic acid salts of divalent metals comprising zinc, copper, manganese, iron, cobalt or nickel, the aqueous solution having a pH of 2.0 or less; in a second containing means.

12. The plant nutrition system of claim 11, wherein the macronutrients of the first aqueous solution further comprises primary macronutrients in the form of salts of nitric acid or urea or both for nitrogen, salts of phosphoric acid for phosphorus, and

salts of nitric acid or phosphoric acid or both for potassium, said first aqueous solution having a pH of 2.5 or more.

13. The plant nutrition system of claim 11, wherein the micronutrients of the second aqueous solution further comprises of salts of boric and molybdic acids and its acids or a combination thereof, said second aqueous solution having a pH of 2.5 or more.

14. The plant nutrition system of claim 11, said first aqueous solution having a pH of 2.5 or less by addition of phosphoric acid.

15. The plant nutrition system of claim 11, said second aqueous solution having a pH of 2.0 or less by addition of phosphoric acid.

16. The plant nutrition system of claim 11, wherein both the first and second solutions have a metal/sulfur molar ratio by weight of equal or greater than 1:2.

17. The plant nutrition system of claim 11, wherein neither the first nor second aqueous solutions contain a chelating compound.

18. A method of providing nutrition for plants, comprising diluting the first and second aqueous solutions of the plant nutrition system of claim 11, mixing the solutions, and applying the mixture directly to plants or soil adjacent to the plants by foliar application or fertigation, or by adding the mixture to hydroponic media.

19. A method of increasing chlorophyll production in a growing plant, which comprises the step of applying an aqueous solution comprising at least secondary macronutrients comprising calcium sulfamate and magnesium sulfamate, and at least one micronutrient comprising at least one divalent metallic salt of sulfamic acid selected from the group consisting of zinc, copper, manganese, iron, cobalt or nickel, to the plant, said applying being by either foliar application or fertigation.

20. The method of claim 19, whereby available sulfur and nitrogen content is increased for the plants.

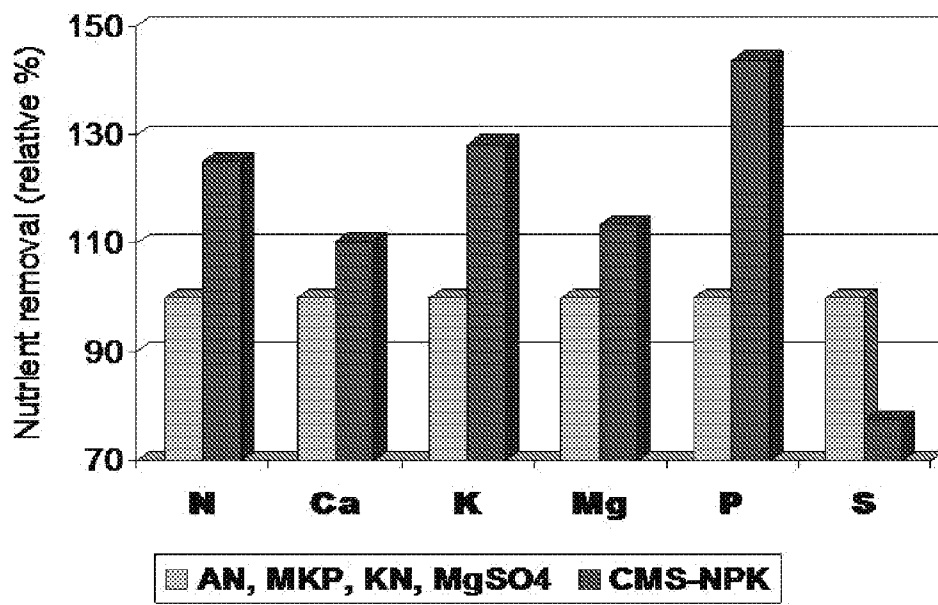


FIG. 1

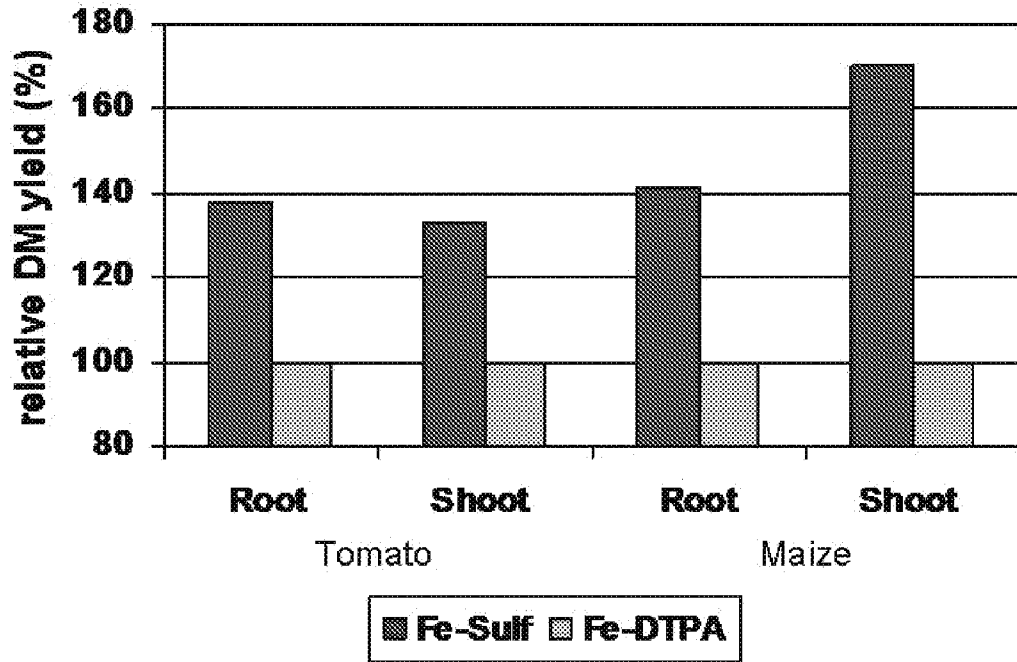


FIG. 2

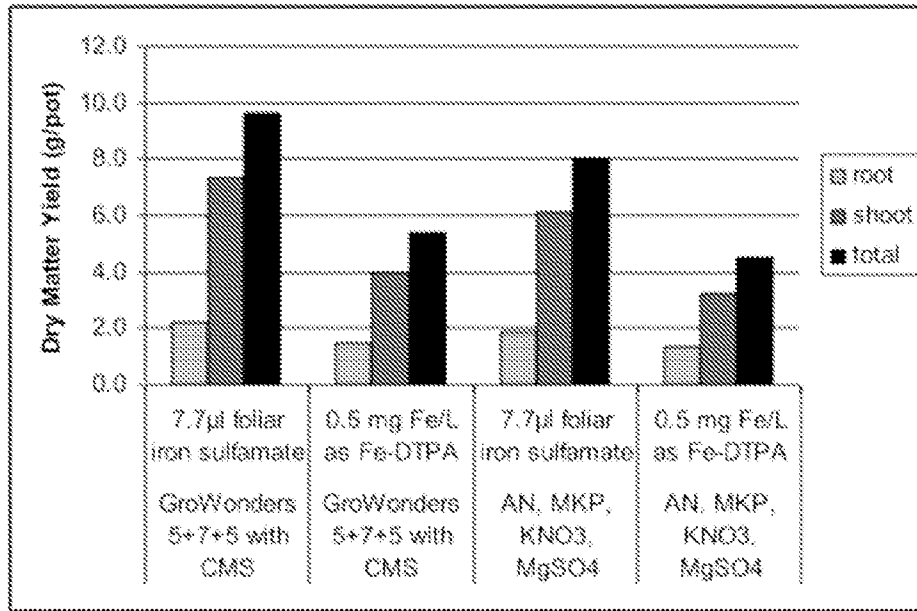


FIG. 3

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2012/045216

A. CLASSIFICATION OF SUBJECT MATTER
 IPC(8) - A01G 1/00 (2013.01)
 USPC - 71/64.1
 According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
 IPC(8) - A01G 1/00; C05B 15/00; C05C 11/00; C05G 3/00, 5/00 (2013.01)
 USPC - 71/32, 35, 41, 64.1

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
 CPC - A01G 1/00; C05B 15/00; C05C 11/00; C05G 3/00, 3/0064, 3/0076 (2013.01)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
 Orbit.com, Google Patents, Google Scholar

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X ----- Y	US 2003/0073580 A1 (RUNKIS) 17 April 2003 (17.04.2003) entire document	1, 6 ----- 2-5, 7-20
Y	IN 448/DEL/2001 A (SINGH) 05 October 2007 (05.10.2007) entire document	2, 3, 7, 8, 12, 13
Y	US 2005/0123644 A1 (REIF et al) 09 June 2005 (09.06.2005) entire document	4, 9, 16
Y	US 2003/0029211 A1 (SHEPPARDSON et al) 13 February 2003 (13.02.2003) entire document	5, 10, 17
Y	EP 0949221 A1 (BOLHUIS) 13 October 1999 (13.10.1999) entire document	3, 8, 11-20
Y	US 5,330,552 A (RIZZO) 19 July 1994 (19.07.1994) entire document	20

Further documents are listed in the continuation of Box C.

* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"E" earlier application or patent but published on or after the international filing date	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search 19 February 2013	Date of mailing of the international search report 12 MAR 2013
Name and mailing address of the ISA/US Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-3201	Authorized officer: Blaine R. Copenheaver PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774