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[54] **COMBINATION OF ACTIVE INGREDIENTS FOR INHIBITING OR CONTROLLING NITRIFICATION**

[75] Inventors: **Margrit Grabarse**, Seelingstädt; **Sieghard Lang**, Cunnersdorf; **Hans-Jürgen Michel**, Machem; **Hartmut Wozniak**, Cunnersdorf, all of Germany

[73] Assignee: **SKW Stickstoffwerke**, Lutherstadt Wittenberg, Germany

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[52] **U.S. Cl.** **71/27**; 71/902

[58] **Field of Search** 71/1, 11, 27, 902, 71/903, 904

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Primary Examiner—Wayne Langel
Attorney, Agent, or Firm—Henry M. Feiereisen

[57] **ABSTRACT**

This patent describes nitrification inhibitors characterized by the fact that they contain as their active ingredients 1-hydro-1,2,4-triazole, a substituted 1-hydro-1,2,4-triazole, or their salts or metallic complexes, plus at least one other chemical compound, such as a substituted pyrazole, or its salts or metallic complexes, dicyanodiamide, guanyl thiocarbamide, thiocarbamide, ammonium rhodanide, or ammonium thiosulfate, where said combination exhibit readily recognizable synergetic effects compared to the case where said chemical compounds are employed alone, and thus provide benefits in terms of better efficacies, reduced dosages, and/or cost savings.

3 Claims, No Drawings

COMBINATION OF ACTIVE INGREDIENTS FOR INHIBITING OR CONTROLLING NITRIFICATION

This is a continuation of U.S. patent application Ser. No. 08/693,141, filed Aug. 13, 1996, U.S. Pat. No. 5,951,736, which is a continuation of PCT/DE95/00248, Feb. 20, 1995.

The present invention concerns combinations of two or more active ingredients for inhibiting or controlling nitrification of ammonia in arable topsoil and subsoil.

Reduced nitrogen, such as that contained in ammonia, ammonium compounds, or nitramide, present in arable soil is rapidly transformed into nitrates via intermediate nitrite stages by bacterial action. The rates at which nitrification proceeds are largely determined by the temperatures, moisture contents, pH, and bacterial activities of the soils involved. A counteracting effect here is that, unlike the nitrogen of ammonia or ammonium compounds, that of nitrates will not be sorbed by the sorbing agents present in arable soil, and will thus either precipitate out and be washed away by surface runoff, or will end up being deposited in deep-lying strata extending down to the water table and below levels accessible to plants. Under adverse weather or soil conditions, runoff losses may exceed 20% of total available reduced nitrogen. To be added to these losses are denitrification losses due to reduction of nitrates formed by nitrification processes to gaseous compounds under anaerobic conditions, losses that may reach comparable levels.

Employing suitable chemicals to inhibit or control nitrification can promote utilization of nitrogen fertilizers by plants. Moreover, this approach provides further benefits in that it reduces nitrate concentrations in ground water and surface runoff, and counteracts nitrate enrichment in cultivated plants, particularly forage crops.

In addition to substituted pyrazoles (U.S. Pat. No. 3,494,757, DD 133088), other known solutions to these problems involve employing dicyanodiamide (DCD) (DE 2702284, DE 2714601), guanyl thiocarbamide (JP 7301138), thiocarbamide (DE 2051935), 1,2,4-triazole, 4-amino-1,2,4-triazole (JP 7104135), or other triazole derivatives (U.S. Pat. Nos. 3,697,244, 3,701,645).

Combinations of active ingredients supposedly superior to the above-mentioned compounds when employed alone have also been recommended. Among those combinations worth noting here are admixtures of pyrazoles and DCD (DD 222471) or guanyl thiocarbamide (DD 247894), admixtures of 4-amino-1,2,4-triazole (ATC) and DCD (SU 1137096), and amalgams of, e.g., ATC in carbamide/thiocarbamide or carbamide/DCD-mixtures (DD 227957). Employing admixtures of dicyanodiamide and ammonium thiosulfate has also bee recommended (DE 3714729).

The disadvantages of these known nitrification inhibitors are their low efficacies, which implies that large dosages will be required, volatilities or instabilities that are too high to allow them to be of much benefit in practical applications, or decomposition rates that are too rapid for the types of applications involved. Moreover, although some of these inhibitors retard nitrification to acceptable degrees, their efficacies are severely reduced by "incompatibility reactions" with several types of fertilizers.

The object of the present invention is identifying combinations of active ingredients suitable for employment in mineral and organic nitrogen fertilizers that will have synergetic effects on inhibition of nitrification, and will thus be more beneficial than either employing the compounds involved alone, or employing any of those combinations mentioned above.

Surprisingly, it has been found that when employed for inhibiting or controlling nitrification in arable topsoil and subsoil, combinations of active ingredients containing 1-hydro-1,2,4-triazole, a substituted 1-hydro-1,2,4-triazole, or their salts or metallic complexes, plus at least one other chemical compound, such as a substituted pyrazole, or its salts or coordination compounds, dicyanodiamide, guanyl thiocarbamide, thiocarbamide, ammonium rhodanide, or ammonium thiosulfate, exhibit marked synergetic effects, and are thus are more effective than any of these compounds when employed alone.

The ingredients of the combinations of the present invention may be admixed in proportions ranging from 0.5:99.5 to 99.5:0.5. Where combinations contain more than two ingredients, mixing ratios may be arbitrarily adjusted for each ingredient involved.

The combinations of the present invention are beneficial in the sense that they provide enhanced long-term effects, i.e., nitrification is inhibited over extended periods, and they thus contribute to providing that nitrogen released by nitrogen fertilizers will be better utilized, and that these fertilizers will therefore be more effective, even where lower dosages are employed. A related effect of employing such combinations is that cultivated plants have been observed to yield more biomass.

The combinations of active ingredients of the present invention may be employed admixed with liquid or solid mineral or organic fertilizers containing nitramide or ammonium compounds, in which case they should be applied in dosages ranging from 0.5 kg/ha to 20 kg/ha.

The following examples will serve to clarify the present invention, but shall not be construed as imposing any restrictions on same. Table 1 lists a selection of those triazoles and their salts and metallic complexes employed as basic ingredients of those combinations studied, while Table 2 lists several of the other ingredients that were admixed with said triazoles.

TABLE 1

Symbol	Designation/Chemical Formula
Tr	1-hydro-1,2,4-triazole
Tr × HCl	1-hydro-1,2,4-triazole × HCl
HMT	1-hydroxy-methyl-1,2,4-triazole × HCl
Na—Tr	1-sodium-1,2,4-triazolate
Fe—Tr	$[Fe(Tr)_6]Cl_3$
GTr	1-guanyl-1,2,4-triazole × HCl
CTS	$[Cu(Tr)_2]SO_4 \times 2H_2O$
MT	$[Mn(Tr)_4]Cl_2$

TABLE 2

Symbol	Designation/Chemical Formula
GTH	guanyl thiocarbamide
TH	thiocarbamide
AR	ammonium rhodanide
DCD	dicyanodiamide
ATS	ammonium thiosulfate
MP	3-methylpyrazole
CMP	1-carbamyl-3-methylpyrazole
GMP	1-guanyl-3-methylpyrazole × HCl
Mg—MP	Mg-3-methylpyrazolate
Zn—MP	$[Zn(MP)_2]SO_4$
GZC	$(GMPH)_2ZnCl_4$
GM	$Mg(GMP)_2Cl_2 \times H_2O$

The results of employing such combinations in the examples presented below were all obtained using the same methodology.

EXAMPLES

The combinations of the present invention, along with carbamide (urea), which served as a source of nitrogen, were admixed with a sandy loam similar to humus in the concentrations listed in the following tables (all concentrations stated in ppm are by weight, referred to the total weight of soil involved), brought up to 50% of their maximum moisture-retention capacities, and then vigorously mixed. The concentration of elemental nitrogen employed was 10 mg/100 g of soil. Soil samples prepared in this fashion were placed in plastic bottles, the bottles sealed, incubated at 20° C., and the resultant rates of nitrate formation and declines in ammonia concentrations monitored.

Percentage nitrification inhibitions were computed from the relation

$$\text{percentage nitrification inhibition} = \frac{K - A}{K - B} \times 100,$$

where

K is the nitrate concentration in soil samples that were admixed with nitrogen fertilizer, but had no active ingredients added,

A is the nitrate concentration in soil samples that were admixed with both nitrogen fertilizer and active ingredients, and

B is the nitrate concentration in soil samples that were admixed with neither nitrogen fertilizer nor active ingredients.

Values of t_{50}, which are efficacy factors representing those time periods, expressed in days, that had elapsed until nitrification inhibitions had declined to 50% of their initial levels, were determined from nonlinear regressions applied to the temporal degradation data.

Values of t_{50} obtained in this fashion were subjected to Logit-Probit transforms (which linearize effect-dosage curves) in order to assess the effects of the combinations involved based on the independence model of Groeger, et al, [*Pharmazie* 36 (1981), pp. 81–87], which incorporates a generalization of the theories of Gowing [*Weeds* 8 (1960), pp. 379–391] and of Colby [*Weeds* 15 (1967), pp. 20–22], according to which the effects of such combinations were regarded as synergetic if they were better than those of the ingredients involved when employed alone, or if the dosages required to yield given effects were less than those predicted by the independence model.

Example 1

Combinations of 1-hydro-1,2,4-triazole (Tr) and Dicyanodiamide (DCD)

Values of t_{50} were computed and compared for cases where Tr alone, DCD alone, and admixtures of the two were employed, following the methodology referred to above.

TABLE 3a

Values of t_{50} for Tr alone, DCD alone, and admixtures of the two.

1-Hydro-1,2,4-Triazole Concentration [ppm]	Dicyanodiamide Concentration [ppm]	Tr:DCD Mixing Ratio	t_{50} [days]
0.096			5.3
0.227			14.0
0.545			30.0
0.909			41.5

TABLE 3a-continued

Values of t_{50} for Tr alone, DCD alone, and admixtures of the two.

1-Hydro-1,2,4-Triazole Concentration [ppm]	Dicyanodiamide Concentration [ppm]	Tr:DCD Mixing Ratio	t_{50} [days]
1.25			46.0
2.0			50.0
3.0			52.3
5.0			57.0
	1.25		10.0
	2.0		14.3
	3.0		17.6
	3.846		19.7
	5.0		22.0
	5.882		23.6
	8.333		27.3
	9.091		28.4
	10.0		29.6
5.0	5.0	50:50	73.8
3.0	3.0		58.2
2.0	2.0		57.1
1.25	1.25		52.5
1.667	8.333	17:83	106.6
1.0	5.0		71.5
0.667	3.333		53.7
0.417	2.083		37.1
0.909	9.091	9:91	111.8
0.545	5.445		69.4
0.364	3.636		45.5
0.227	2.273		28.7
0.25	3.75	6:94	37.3
0.156	2.344		23.9
0.19	3.81	5:95	32.1
0.119	2.38		22.2
0.385	9.615	4:96	73.5
0.231	5.769		41.5
0.154	3.846		29.6
0.096	2.404		21.3
0.196	9.804	2:98	48.1
0.118	5.882		31.2

TABLE 3b

Percentage savings of active ingredients and incremental improvements in efficacies, relative to those predicted by the independence model (IM).

Tr:DCD Mixing Ratio	Concentration in Host Soil [ppm]	Empirically Determined Efficacy	Efficacy Predicted by the IM	Efficacy Increment	Dosage Savings [%]
50:50	10	74	82	−8	−53
	6	58	72	−14	−68
	4	57	61	−4	−17
	2.5	52	48	4	14
17:83	10	100	64	36	—
	6	71	50	21	55
	4	54	39	14	42
	2.5	37	29	8	31
9:91	10	100	53	47	—
	6	69	40	29	69
	4	45	31	14	47
	2.5	29	23	6	29
6:94	4	47	37	10	36
	2.5	30	28	2	12
5:95	4	40	34	6	25
	2.5	28	26	2	11
4:96	10	92	52	40	—
	6	52	61	9	40
	4	37	33	4	21
	2.5	27	25	2	11
2:98	10	60	46	14	48
	6	39	36	3	17

Example 2

Combination of 1-hydro-1,2,4-triazole (Tr) and Guanyl Thiocarbamide (GTH)

The experimental methodology and computerized data analyses employed here were similar to those employed in the case of Example 1, above.

TABLE 4a

Values of t_{50} for Tr alone, GTH alone, and admixtures of the two.

1-Hydro-1,2,4-Triazole Concentration [ppm]	Guanyl Thiocarbamide Concentration [ppm]	Tr:GTH Mixing Ratio	t_{50} [days]
0.096			5.5
0.227			14.0
0.545			30.0
0.909			41.5
1.25			46.0
2.0			50.0
3.0			52.3
5.0			57.0
	2.0		1.0
	4.0		9.3
	6.0		18.4
	8.0		28.0
	10.0		37.4
	12.0		47.2
5.0	5.0	50:50	63.4
2.5	2.5		53.8
1.25	1.25		40.3
0.909	9.091	9:91	81.8
0.545	5.445		70.3
0.227	2.273		19.2
0.385	9.615	4:96	60.5
0.231	5.769		35.4
0.154	3.846		25.1
0.196	9.804	2:98	49.4
0.118	5.882		28.9

TABLE 4b

Percentage savings of active ingredients and incremental improvements in efficacies, relative to those predicted by the independence model (IM).

Tr:GTH Mixing Ratio	Concentration in Host Soil [ppm]	Empirically Determined Efficacy	Efficacy Predicted by the IM	Efficacy Increment	Dosage Savings [%]
50:50	10	95	95	0	−4
	5	81	86	−6	−29
	2.5	68	68	0	1
9:91	10	100	74	26	89
	6	100	53	47	93
	2.5	29	21	8	23
4:96	10	91	59	32	62
	6	54	38	16	32
	4	38	24	14	34
2:98	10	74	51	23	44
	6	43	32	11	27

Example 3

Combinations of 1-hydro-1,2,4-triazole (Tr) and Thiocarbamide (TH)

The experimental methodology and computerized data analyses employed here were similar to those employed in the case of Example 1, above.

TABLE 5a

Values of t_{50} for Tr alone, TH alone, and admixtures of the two.

1-Hydro-1,2,4-Triazole Concentration [ppm]	Thiocarbamide Concentration [ppm]	Tr:TH Mixing Ratio	t_{50} [days]
0.1			5.8
0.25			14.3
0.5			29.0
1.0			42.1
2.0			49.1
3.0			51.9
5.0			56.2
	2.0		6.5
	4.0		8.5
	8.0		10.5
	10.0		12.6
	16.0		17.3
3.0	3.0	50:50	58.2
2.0	2.0		54.8
0.909	9.091	9:91	49.9
0.545	5.445		42.2
0.227	2.273		27.1
0.385	9.615	4:96	37.1
0.154	3.846		24.7
0.096	2.404		14.9
0.196	9.804	2:98	26.4
0.118	5.882		18.0

TABLE 5b

Percentage savings of active ingredients and incremental improvements in efficacies, relative to those predicted by the independence model (IM).

Tr:TH Mixing Ratio	Concentration in Host Soil [ppm]	Empirically Determined Efficacy	Efficacy Predicted by the IM	Efficacy Increment	Dosage Savings [%]
50:50	6	87	80	7	40
	4	82	72	10	42
9:91	10	75	63	12	39
	6	63	49	14	41
	2.5	40	28	12	42
4:96	10	55	48	8	24
	4	37	26	11	40
	2.5	22	18	5	25
2:98	10	40	38	1	5
	6	27	27	0	2

Example 4

Combination of 1-hydro-1,2,4-triazole (Tr) and Ammonium Rhodanide (AR)

The experimental methodology and computerized data analyses employed here were similar to those employed in the case of Example 1, above.

TABLE 6a

Values of t_{50} for Tr alone, AR alone, and admixtures of the two.

1-Hydro-1,2,4-Triazole Concentration [ppm]	Ammonium Rhodanide Concentration [ppm]	Tr:AR Mixing Ratio	t_{50} [days]
0.096			5.5
0.227			14.0
0.545			30.0
0.909			41.5
1.25			46.0

TABLE 6a-continued

Values of t_{50} for Tr alone, AR alone, and admixtures of the two.

1-Hydro-1,2,4-Triazole Concentration [ppm]	Ammonium Rhodanide Concentration [ppm]	Tr:AR Mixing Ratio	t_{50} [days]
2.0			50.0
3.0			52.3
5.0			57.0
	2.0		3.1
	4.0		6.3
	8.0		8.5
	10.0		9.3
	16.0		11.9
3.0	3.0	50:50	56.9
2.0	2.0		52.5
1.25	1.25		46.3
0.545	5.445	9:91	61.6
0.364	3.636		40.8
0.227	2.273		35.1
0.19	3.81	5:95	33.7
0.119	2.38		25.7
0.196	9.804	2:98	29.1
0.118	5.882		22.4

TABLE 6b

Percentage savings of active ingredients and incremental improvements in efficacies, relative to those predicted by the independence model (IM).

Tr:AR Mixing Ratio	Concentration in Host Soil [ppm]	Empirically Determined Efficacy	Efficacy Predicted by the IM	Efficacy Increment	Dosage Savings [%]
50:50	6	57	57	0	−2
	4	52	49	3	15
	2.5	46	39	7	29
9:91	6	62	30	32	79
	4	41	24	17	62
	2.5	35	17	18	68
5:95	4	34	18	16	66
	2.5	26	12	14	66
2:98	10	29	22	7	36
	6	22	16	6	41

Example 5

Combinations of 1-hydroxy-methyl-1,2,4-triazole× HCl (HMT) and Guanyl Thiocarbamide (GTH)

The experimental methodology and computerized data analyses employed here were similar to those employed in the case of Example 1, above.

TABLE 7a

Values of t_{50} for HMT alone, GTH alone, and admixtures of the two.

1-Hydroxy-Methyl-1,2,4-Triazole × HCl Concentration [ppm]	Guanyl Thiocarbamide Concentration [ppm]	HMT:GTH Mixing Ratio	t_{50} [days]
0.25			14.8
0.5			22.9
0.75			29.7
1.0			37.4
2.0			44.1
5.0			50.0
7.5			57.1
	1.0		1.1

TABLE 7a-continued

Values of t_{50} for HMT alone, GTH alone, and admixtures of the two.

1-Hydroxy-Methyl-1,2,4-Triazole × HCl Concentration [ppm]	Guanyl Thiocarbamide Concentration [ppm]	HMT:GTH Mixing Ratio	t_{50} [days]
	2.0		3.4
	4.0		10.2
	8.0		29.1
	10.0		38.2
5.0	1.0	83:17	53.1
2.5	0.5		44.2
1.25	0.25		38.7
3.0	3.0	50:50	52.1
1.5	1.5		43.1
1.0	5.0	17:83	56.9
0.5	2.5		29.1
0.545	5.445	9:91	64.9
0.273	2.727		28.3
0.286	5.714	5:95	61.7
0.143	2.857		23.9
0.118	5.882	2:98	39.4

TABLE 7b

Percentage savings of active ingredients and incremental improvements in efficacies, relative to them predicted by the independence model (IM).

HMT:GTH Mixing Ratio	Concentration in Host Soil [ppm]	Empirically Determined Efficacy	Efficacy Predicted by the IM	Efficacy Increment	Dosage Savings [%]
83:17	6	80	87	−7	−50
	3	66	73	−7	−32
	2.5	58	54	4	11
50:50	6	78	80	−2	−10
	3	65	62	3	8
17:83	6	85	59	26	59
	3	44	36	8	21
9:91	6	97	47	50	88
	3	42	26	16	42
5:95	6	92	38	56	85
	3	36	20	16	47
2:98	6	59	31	28	59

Example 6

Combinations of 1-sodium-1,2,4-triazolate (Na—Tr) and Dicyanodiamide (DCD)

The experimental methodology and computerized data analyses employed here were similar to those employed in the case of Example 1, above.

TABLE 8a

Values of t_{50} for Na—Tr alone, DCD alone, and admixtures of the two.

1-Sodium-1,2,4-Triazolate Concentration [ppm]	Dicyanodiamide Concentration [ppm]	Na—Tr:DCD Mixing Ratio	t_{50} [days]
0.25			9.7
0.5			21.4
0.75			26.1
1.0			31.9
1.5			33.7
2.0			38.4
5.0			41.8
	1.0		12.4

TABLE 8a-continued

Values of t_{50} for Na—Tr alone, DCD alone, and admixtures of the two.

1-Sodium-1,2,4-Triazolate Concentration [ppm]	Dicyanodiamide Concentration [ppm]	Na—Tr:DCD Mixing Ratio	t_{50} [days]
	2.0		22.1
	4.0		26.1
	6.0		29.6
	10.0		38.1
5.0	1.0	83:17	52.1
2.5	0.5		46.7
3.0	3.0	50:50	60.1
1.5	1.5		51.9
1.0	5.0	17:83	73.2
0.5	2.5		51.4
0.545	5.445	9:91	64.2
0.273	2.727		42.9
0.231	5.769	4:96	47.9
0.115	2.885		35.1

TABLE 8b

Percentage savings of active ingredients and incremental improvements in efficacies, relative to those predicted by the independence model (IM).

Na—Tr:DCD Mixing Ratio	Concentration in Host Soil [ppm]	Empirically Determined Efficacy	Efficacy Predicted by the IM	Efficacy Increment	Dosage Savings [%]
83:17	6	78	79	−1	−5
	3	70	65	5	20
50:50	6	90	77	13	55
	3	78	61	17	51
17:83	6	100	68	32	—
	3	77	50	27	66
9:91	6	96	63	33	—
	3	64	45	19	53
4:96	6	72	57	15	47
	3	53	40	13	41

Example 7

Combinations of 1-hydro-1,2,4-triazole (Tr) and 3-methylpyrazole (MP)

The experimental methodology and computerized data analyses employed here were similar to those employed in the case of Example 1, above.

TABLE 9a

Values of t_{50} for Tr alone, MP alone, and admixtures of the two.

1-Hydro-1,2,4-Triazole Concentration [ppm]	3-Methylpyrazole Concentration [ppm]	Tr:MP Mixing Ratio	t_{50} [days]
0.1			5.3
0.25			14.9
0.5			27.8
0.75			36.8
1.0			41.9
1.5			48.7
3.0			56.9
	0.1		9.1
	0.25		24.5
	0.5		43.6
	0.656		46.3
	1.0		48.7
	2.0		52.3
1.0	1.0	50:50	95.6
0.5	0.5		72.7
1.818	1.182	91:9	69.8
0.909	0.091		51.7
1.923	0.077	96:4	59.8
0.962	0.038		42.8
0.077	1.923	4:96	61.0
0.038	0.962		52.4

TABLE 9b

Percentage savings of active ingredients and incremental improvements in efficacies, relative to those predicted by the independence model (IM).

Tr:MP Mixing Ratio	Concentration in Host Soil [ppm]	Empirically Determined Efficacy	Efficacy Predicted by the IM	Efficacy Increment	Dosage Savings [%]
50:50	2	100	90	10	86
	1	100	74	26	93
91:9	2	100	83	17	88
	1	77	64	13	36
96:4	2	90	81	9	40
	1	64	63	1	5
4:96	2	91	88	3	27
	1	79	74	5	18

Example 8

Combination of $[Cu(Tr)_2]SO_4 \times 2\ H_2O$ Hydrated Cuprotriazole-Sulfate Complex (CTS) and $(GMPH)_2ZnCl_4$ 1-guanyl-3-methylpyrazoline-chlorozineate Complex (GZC)

The experimental methodology and computerized data analyses employed here were similar to those employed in the case of Example 1, above.

TABLE 10a

Values of t_{50} for CTS alone, GZC alone, and admixtures of the two.

CTS-Concentration [ppm]	GZC-Concentration [ppm]	CTS:GZC Mixing Ratio	t_{50} [days]
0.1			1.9
0.25			4.9
0.5			11.6
1.2			27.0
1.8			36.1
2.5			43.1
	0.25		9.5
	0.5		19.1
	0.75		26.8
	1.5		43.3
	3.0		59.1
1.0	1.0	50:50	77.2
0.5	0.5		53.6
0.25	0.25		21.9
1.818	0.182	91:9	45.9
0.909	0.091		27.8
0.182	1.818	9:91	53.6
0.091	0.909		30.0

TABLE 10b

Percentage savings of active ingredients and incremental improvements in efficacies, relative to those predicted by the independence model (IM).

CTS:GZC Mixing Ratio	Concentration in Host Soil [ppm]	Empirically Determined Efficacy	Efficacy Predicted by the IM	Efficacy Increment	Dosage Savings [%]
50:50	2	100	72	28	84
	1	80	42	38	61
	0.5	33	19	14	37
91:9	2	69	64	5	14
	1	42	36	6	13
9:91	2	80	74	5	16
	1	45	51	−5	−15

Example 9

Combinations of 1-hydro-1,2,4-triazole (Tr), Dicyanodiamide (DCD), and Ammonium Rhodanide (AR)

The experimental methodology and computerized data analyses employed here were similar to those employed in the case of Example 1, above.

TABLE 11a

Values of t_{50} for Tr alone, DCD alone, AR alone, and admixtures of all three.

Tr-Concentration [ppm]	DCD-Concentration [ppm]	AR-Concentration [ppm]	Tr:DCD:AR Mixing Ratio	t_{50} [days]
0.096				5.5
0.227				13.8
0.545				30.2
0.909				41.5
1.25				46.0
2.0				50.1
3.0				52.3
5.0				57.0
	1.25			10.1
	2.0			14.3
	3.0			17.6
	3.846			19.7
	5.0			22.1
	5.882			23.6
	8.333			27.4
	10.0			29.6
		2.0		2.8
		4.0		6.3
		8.0		8.5
		10.0		9.3
		16.0		11.9
0.833	4.167	0.833	14.3:71.4:14.3	67.1
0.5	2.5	0.5		52.4
0.385	3.846	0.769	7.7:76.9:15.4	58.9
0.231	2.308	0.462		37.7
0.192	3.846	0.962	3.8:77:19.2	45.7
0.115	2.308	0.575		34.7

TABLE 11b

Percentage savings of active ingredients and incremental improvements in efficacies, relative to those predicted by the independence model (IM).

Tr:DCD:AR Mixing Ratio	Concentration in Host Soil [ppm]	Empirically Determined Efficacy	Efficacy Predicted by the IM	Efficacy Increment	Dosage Savings [%]
14.3:71.4:14.3	5.83	100	67	33	—
	3.5	79	53	26	61
7.7:76.9:15.4	5.0	89	53	36	75
	3.0	57	39	18	46
3.8:77:19.2	5.0	69	44	25	56
	3.0	52	31	21	54

Example 10

Combinations of 1-hydro-1,2,4-triazole Hydrochloride (Tr×HCl), Guanyl Thiocarbamide (GTH), and Thiocarbamide (TH)

The experimental methodology and computerized data analyses employed here were similar to those employed in the case of Example 1, above.

TABLE 12a

Values of t_{50} for Tr × HCl alone, GTH alone, TH alone, and admixtures of all three.

Tr × HCl-Concentration [ppm]	GTH-Concentration [ppm]	TH-Concentration [ppm]	Tr × HCl: GTH:TH Mixing Ratio	t_{50} [days]
0.15				5.0
0.3				11.5
0.75				28.4
1.5				41.3
3.0				48.9
4.5				52.1
	2.0			1.9
	4.0			9.5
	8.0			28.1
	10.0			37.0
	16.0			60.1
		2.0		6.3
		4.0		8.7
		8.0		10.9
		10.0		13.0
		16.0		18.1
0.115	2.308	0.577	3.8:77:19.2	17.9
0.231	4.615	1.155		44.8
0.115	1.422	1.422	3.8:48.1:48.1	11.9
0.231	2.885	2.885		37.9
0.231	1.155	4.615	3.8:19.2:77	27.8
0.5	2.0	0.5	17:66:17	53.1
0.5	1.25	1.25	16.6:41.7:41.7	39.9
0.188	1.875	0.937	6.3:62.5:31.2	21.3
0.375	3.75	1.875		47.1

TABLE 12b

Percentage savings of active ingredients and incremental improvements in efficacies, relative to them predicted by the independence model (IM).

Tr × HCl: GTH:TH Mixing Ratio	Concentration in Host Soil [ppm]	Empirically Determined Efficacy	Efficacy Predicted by the IM	Efficacy Increment	Dosage Savings [%]
3.8:77:19.2	3.0	27	16	11	36
	6.0	67	35	32	57
3.8:48.1:48.1	3.0	19	12	7	28
	6.0	57	30	27	51
3.8:19.2:77	6.0	42	25	17	40
17:66:17	3.0	81	33	48	74
16.6:41.7:41.7	3.0	60	30	30	55
6.3:62.5:31.2	3.0	33	17	16	43
	6.0	71	38	33	56

Example 11

Combinations of 1-guanyl-1,2,4-triazole Hydrochloride (GTr), Dicyanodiamide (CDC), and Thiocarbamide (TH)

The experimental methodology and computerized data analyses employed here were similar to those employed in the case of Example 1, above.

TABLE 13a

Values of t_{50} for GTr alone, DCD alone, TH alone, and admixtures of all three.

GTr-Concentration [ppm]	DCD-Concentration [ppm]	TH-Concentration [ppm]	GTr:DCD:TH Mixing Ratio	t_{50} [days]
1.4				27.5
2.14				37.5
4.3				47.3
8.5				49.2
10.0				55.2
	1.0			8.9
	2.0			14.2
	3.0			17.1
	5.0			22.3
	8.0			26.8
	10.0			30.1
		2.0		6.3
		4.0		8.7
		8.0		10.9
		10.0		13.0
		16.0		18.1
0.192	3.840	0.968	3.8:76.8:19.4	43.8
0.308	6.160	1.54		61.7
0.192	2.404	2.404	3.8:48.1:48.1	37.4
0.308	3.846	3.846		57.8
0.192	0.968	3.840	3.8:19.4:76.8	27.9
0.308	1.540	6.160		32.7

TABLE 13b

Percentage savings of active ingredients and incremental improvements in efficacies, relative to those predicted by the independence model (IM).

GTr:DCD:TH Mixing Ratio	Concentration in Host Soil [ppm]	Empirically Determined Efficacy	Efficacy Predicted by the IM	Efficacy Increment	Dosage Savings [%]
3.8:76.8:19.4	5.0	66	48	18	60
	8.0	93	32	61	98
3.8:48.1:48.1	5.0	56	46	10	40
	8.0	87	55	31	84
3.8:19.4:76.8	5.0	42	42	0	−1
	8.0	49	51	−2	−10

Example 12

Combinations of 1-hydro-1,2,4-triazole (Tr), Dicyanodiamide (CDC), and Ammonium Thiosulfate (ATS)

The experimental methodology and computerized data analyses employed here were similar to those employed in the case of Example 1, above.

TABLE 14a

Values of t_{50} for Tr alone, DCD alone, ATS alone, and admixtures of all three.

Tr-Concentration [ppm]	DCD-Concentration [ppm]	ATS-Concentration [ppm]	Tr:DCD:ATS Mixing Ratio	t_{50} [days]
0.096				5.5
0.227				14.0
0.545				30.0
0.909				41.5
1.25				46.0
2.0				50.0
3.0				52.3
5.0				57.0
	1.25			10.0
	2.0			14.3
	3.0			17.6
	3.846			19.7
	5.0			22.0
	5.882			23.6
	8.333			27.3
	9.091			28.4
	10.0			29.6
		2.0		0
		4.0		0
		8.0		0
		10.0		0
		16.0		0
0.115	2.308	0.577	4:77:19	35.7
0.115	1.422	1.422	4:48:48	27.8
0.115	0.577	2.308	4:19:77	14.1

TABLE 14b

Percentage savings of active ingredients and incremental improvements in efficacies, relative to those predicted by the independence model (IM).

Tr:DCD:ATS Mixing Ratio	Concentration in Host Soil [ppm]	Empirically Determined Efficacy	Efficacy Predicted by the IM	Efficacy Increment	Dosage Savings [%]
4:77:19	3.0	53	35	18	55
4:48:48	3.0	42	30	12	42
4:19:77	3.0	21	24	−3	−20

Example 13

Combinations of $[Fe(Tr)_4]Cl_3$ Ferrochlorotriazole Complex (Fe—Tr), Dicyanodiamide (DCD), and Ammonium Thiosulfate (ATS)

The experimental methodology and computerized data analyses employed here were similar to those employed in the case of Example 1, above.

TABLE 15a

Values of t_{50} for Fe—Tr alone, DCD alone, ATS alone, and admixtures of all three.

Fe—Tr-Concentration [ppm]	DCD-Concentration [ppm]	ATS-Concentration [ppm]	Fe—Tr:DCD:ATS Mixing Ratio	t_{50} [days]
0.072				3.9
0.163				10.3
0.39				21.2
0.65				29.4
0.9				33.3
1.44				35.7
2.15				39.4
4.0				42.9
6.0				49.9
	0.5			4.8
	1.0			9.3
	2.5			15.4
	5.0			22.6
	7.5			27.3
	10.0			32.8
		2.0		0.09
		4.0		0.09
		6.0		0.1
		8.0		0.1
		10.0		0.1
2.0	2.0	2.0	33.3:33.3:33.3	54.6
1.0	1.0	1.0		45.8
0.231	4.615	1.154	3.8:77:19.2	51.2
0.115	2.308	0.577		35.8
0.231	2.885	2.885	3.8:48.1:48.1	44.9
0.115	1.422	1.422		28.8
0.231	1.154	4.615	3.8:19.2:77	29.5
0.115	0.577	2.308		16.7
0.545	4.364	1.091	9.1:72.7:18.2	57.9
0.273	2.182	0.545		39.7

TABLE 15b

Percentage savings of active ingredients and incremental improvements in efficacies, relative to those predicted by the independence model (IM).

Fe—Tr:DCD:ATS Mixing Ratio	Concentration in Host Soil [ppm]	Empirically Determined Efficacy	Efficacy Predicted by the IM	Efficacy Increment	Dosage Savings [%]
33.3:33.3:33.3	6.0	82	66	16	58
	3.0	68	52	16	55
3.8:77:19.2	6.0	77	46	29	76
	3.0	53	32	21	63
3.8:48.1:48.1	6.0	67	40	27	69
	3.0	43	27	16	56
3.8:19.2:77	6.0	44	32	12	44
	3.0	25	21	4	26
9.1:72.7:18.2	6.0	87	55	32	81
	3.0	60	39	21	60

Example 14

Combinations of $[Mn(Tr)_4]Cl_2$ Manganochlorotriazole Complex (MT), $Mg(GMP)_2Cl_2 \times H_2O$ Hydrated 1-guanyl-3-methyl Pyrazole Magnesium-Chloride Complex (GM), and Dicyanodiamide (DCD)

The experimental methodology and computerized data analyses employed here were similar to those employed in the case of Example 1, above.

TABLE 16a

Values of t_{50} for MT alone, GM alone, DCD alone, and admixtures of all three.

MT-Concentration [ppm]	GM-Concentration [ppm]	DCD-Concentration [ppm]	MT:GM:DCD Mixing Ratio	t_{50} [days]
0.2				5.6
0.5				15.5
1.0				28.4
1.5				35.4
2.0				42.1
3.0				49.7
	0.2			8.5
	0.6			25.6
	1.0			42.9
	1.5			46.8
	2.0			48.4
		2.0		20.7
		4.0		25.9
		8.0		31.5
		10.0		35.4
		16.0		52.5
1.667	1.667	1.667	33.3:33.3:33.3	106.9
1.0	1.0	1.0		85.7
0.667	0.667	0.667		61.8
0.417	0.417	4.166	8.3:8.3:83.4	64.1
0.25	0.25	2.5		44.8
0.167	0.167	1.666		34.1
0.185	0.185	4.630	3.7:3.7:92.6	60.7
0.111	0.111	2.778		40.1
0.543	0.109	4.348	10.9:2.1:87	54.6
0.109	0.543	4.348	2.1:10.9:87	61.4

TABLE 16b

Percentage savings of active ingredients and incremental improvements in efficacies, relative to those predicted by the independence model (IM).					
MT:GM:DCD Mixing Ratio	Concentration in Host Soil [ppm]	Empirically Determined Efficacy	Efficacy Predicted by the IM	Efficacy Incre-ement	Dosage Savings [%]
33.3:33.3:33.3	5.0	100	89	11	84
	3.0	100	76	24	91
	2.0	93	62	31	68
8.3:8.3:83.4	5.0	96	64	32	73
	3.0	67	45	22	44
	2.0	51	31	20	44
3.7:3.7:92.6	5.0	91	54	37	73
	3.0	60	37	23	50
10.9:2.1:87	5.0	82	59	23	52
2.1:10.9:87	5.0	92	63	29	67

Example 15

Combinations of 1-hydro-1,2,4-triazole (Tr), 3-methylpyrazole (MP), and Guanyl Thiocarbamide (GTH)

The experimental methodology and computerized data analyses employed here were similar to those employed in the case of Example 1, above.

TABLE 17a

Values of t_{50} for Tr alone, MP alone, GTH alone, and admixtures of all three.				
Tr-Concentration [ppm]	MP-Concentration [ppm]	GTH-Concentration [ppm]	Tr:MP:GTH Mixing Ratio	t_{50} [days]
0.1				5.8
0.25				14.3
0.5				29.0
0.75				42.1
1.0				49.1
1.5				51.9
3.0				56.2
	0.1			9.1
	0.25			24.5
	0.5			43.6
	0.656			46.3
	1.0			48.7
	2.0			52.3
		2.0		1.0
		4.0		9.3
		6.0		18.4
		8.0		28.0
		10.0		37.4
		12.0		47.2
1.667	1.667	1.667	33.3:33.3:33.3	112.1
1.0	1.0	1.0		105.7
0.227	0.227	4.546	4.5:4.5:91	73.4
0.136	0.136	2.727		47.8
0.119	0.119	4.762	2.4:2.4:95.2	44.9
0.071	0.071	2.857		29.3

TABLE 17b

Percentage savings of active ingredients and incremental improvements in efficacies, relative to those predicted by the independence model (IM).					
Tr:MP:GTH Mixing Ratio	Concentration in Host Soil [ppm]	Empirically Determined Efficacy	Efficacy Predicted by the IM	Efficacy Incre-ment	Dosage Savings [%]
33.3:33.3:33.3	5.0	100	98	2	65
	3.0	100	92	8	69
4.5:4.5:91	5.0	100	56	44	91
	3.0	72	35	37	59
2.4:2.4:95.2	5.0	67	40	27	48
	3.0	44	23	21	46

Example 16

Combinations of 1-hydro-1,2,4-triazole (Tr), 3-methylpyrazole (MP), and Dicyanodiamide (DCD)

The experimental methodology and computerized data analyses employed here were similar to those employed in the case of Example 1, above.

TABLE 18a

Values of t_{50} for Tr alone, MP alone, DCD alone, and admixtures of all three.				
Tr-Concentration [ppm]	MP-Concentration [ppm]	DCD-Concentration [ppm]	Tr:MP:DCD Mixing Ratio	t_{50} [days]
0.1				5.2
0.25				13.4
0.5				28.1
0.75				40.7
1.0				46.9
1.5				49.8
3.0				52.1
	0.1			7.6
	0.25			19.4
	0.5			35.7
	0.656			40.1
	1.0			46.1
	2.0			49.7
		0.5		4.1
		1.0		9.1
		2.5		14.2
		5.0		22.3
		10.0		30.7
		13.0		41.8
1.667	1.667	1.667	33.3:33.3:33.3	112.9
1.0	1.0	1.0		102.3
0.227	0.227	4.546	4.5:4.5:91	79.4
0.136	0.136	2.727		52.9
0.119	0.119	4.762	2.4:2.4:95.2	57.1
0.071	0.071	2.857		41.8

TABLE 18b

Percentage savings of active ingredients and incremental improvements in efficacies, relative to those predicted by the independence model (IM).					
Tr:MP:DCD Mixing Ratio	Concentration in Host Soil [ppm]	Empirically Determined Efficacy	Efficacy Predicted by the IM	Efficacy Incre-ment	Dosage Savings [%]
33.3:33.3:33.3	5.0	100	95	5	82
	3.0	100	88	12	89

TABLE 18b-continued

Percentage savings of active ingredients and incremental improvements in efficacies, relative to those predicted by the independence model (IM).

Tr:MP:DCD Mixing Ratio	Concentration in Host Soil [ppm]	Empirically Determined Efficacy	Efficacy Predicted by the IM	Efficacy Increment	Dosage Savings [%]
4.5:4.5:91	5.0	100	64	36	94
	3.0	79	47	32	63
2.4:2.4:95.2	5.0	86	54	32	66
	3.0	63	38	25	54

What is claimed is:

1. A composition for use in inhibiting an contributing the nitrification of ammonium nitrogen in arable soils and substrates, said composition comprising:

a first compound selected from the group consisting of 1H-1,2,4-triazole, substituted 1H-1,2,4-triazole and their salts, and metallic complexes thereof; and

a second compound selected from the group consisting of 3-methylpyrazole, 1-carbamoyl-3-methylpyrazole, 1-guanyl-3-methylpyrazole their salts and metallic complexes thereof,

at a mixing ratio ranging from 25:1 to 1:25 by mass of the first to the second compound and producing synergistic efficacy in inhibiting and controlling the nitrification of ammonium nitrogen.

2. A method for inhibiting and controlling the nitrification of ammonium nitrogen in arable soils and substrates, comprising the step of applying to the soil an amount effective therefor of a composition comprising

a first compound selected from the group consisting of 1H-1,2,4-triazole, substituted 1H-1,2,4-triazole and their salts, and metallic complexes thereof; and,

a second compound selected from the group consisting of dicyanodiamide, guanyl thiocarbamide, thiocarbamide, ammonium rhodanide and ammonium thiosulfate, at a mixing ratio producing synergistic efficacy in inhibiting and controlling the nitrification of ammonium nitrogen and ranging from 1:1 to 1:50 by mass of the first to the second compound and in an amount of at least 0.2 percent by weight with respect to a nitrogen content of a fertilizer containing at least one component selected from the group consisting of ammonium and amide.

3. A composition for use in inhibiting and controlling the nitrification of ammonium nitrogen in arable soils and substrates, and composition comprising:

2 to 34% by weight of a first compound selected from the group consisting of 1H-1,2,4-triazole, substituted 1H-1,2,4-triazole and their salts, and metallic complexes thereof;

2 to 34% by weight of a second compound selected from the group consisting of 3-methyl pyrazole, substituted 3-methylpyrazole and their salts and metallic complexes thereof; and

33 to 96% by weight of a third compound selected from the group consisting of dicyanodiamide, guanyl thiocarbamide, thiocarbamide, ammonium rhodanide and ammonium thiosulfate.

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