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Ionic Effect of Salts on Mineral Nitrogen Release in an Allophanic Soil[1]

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ABSTRACT

A comparison of the effects of sulfate and chloride salts on N release and microbial activity in Akaka soil showed that only sulfate salts at low concentrations increased CO_2 evolution. The chlorides were more effective than sulfates in effecting NH_4-N release in the soil. The addition of $CaCl_2 \cdot 2H_2O$ resulted in the greatest NH_4-N release, followed by that of KCl and NaCl. Among sulfates, K_2SO_4 ranked first, followed by Na_2SO_4 and $CaSO_4 \cdot 2H_2O$. The idea that certain chemical reactions and/or processes are involved in splitting NH_4-N from organo-inorganic complexes of a soil and that NH_4^+ ions are subsequently exchanged with cations in the surrounding soil solution was further substantiated by results of this investigation. The exchange reaction was noted to depend on the nature and valence of the cation, concentration in the soil solution, length of reaction, and the anionic species associated with the cation. The capacity of the cations for releasing NH_4-N decreased in the order Ca > K > Na for the chloride series.

Unlike the NH_4-N release pattern, sulfates were more effective than chlorides in promoting nitrification. In general, all salts, excepting $CaSO_4 \cdot 2H_2O$, at higher concentrations curtailed nitrification. The results indicated a real participation of anions in soil N release. Two salts containing the same cation but different anions released different magnitudes of N at an equivalent concentration. Thus, the results of this investigation provide further support for the role of cations in soil N release and, in addition, furnish reasonable evidence of the participation of anionic species. A consideration of the overall values of NH_4- and NO_3-N at various salt concentrations led to the series, $CaCl_2 \cdot 2H_2O$ > KCl > NaCl > K_2SO_4 > Na_2SO_4 > $CaSO_4 \cdot 2H_2O$, in order of decreasing N release power.

Additional Key Words for Indexing: **allophane, electrolyte, organo-inorganic complex, nitrification, soil respiration.**

IN A PREVIOUS paper, Singh et al. (14) reported the results on the effect of chloride salts on the release of mineral N in two Hawaiian soils, viz. Akaka silty clay and Wahiawa silty clay. They included chloride salts of Na, K, Ca, Mg, Al, and Fe in concentrations ranging from 0 to 1*M*. The magnitude of NH_4-N release depended on the nature and valence of the cation and was a direct function of salt concentration and length of incubation. They speculated that NH_4-N comes from the breaking down of microbial cells and/or from chemical processes. Once NH_4^+ ions are released from soil organo-inorganic complexes, the cation has a second but large effect on exchange reactions in transferring the NH_4^+ ions from surface sites to soil solution. Considering the overall effect of the cations on NH_4-N release, they formulated the series, Al > Fe > Ca > Mg > K > Na, in order of decreasing NH_4^+ replacing power. It is pertinent to mention that the anion, viz. chloride, was kept constant to get a clear insight of the cationic effect on NH_4^+ release. There was little or no change in the NO_3-N content of the soil. The investigation reported herein was undertaken to study the effect of salts containing different anions on N release in the allophanic Akaka soil. The influence of salts on CO_2 evolution was also measured.

MATERIALS AND METHODS

The Akaka silty clay (Typic Hydrandept) was collected from the Hilo Coast on the Island of Hawaii. The soil is derived from volcanic ash and, although comparatively young in age, it is highly weathered. It has developed under an annual rainfall of over 5 m (200 inches) with no pronounced dry season during the year. The moisture equivalent value (determined by the centrifuge method) of this soil is 165%, at which moisture level the soil was incubated in subsequent treatments. The clay fraction contains large amounts of allophane and hydrated iron-aluminum oxides. In the hydrated state, the soil

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has a cation exchange capacity of 80 meq/100 g and a base saturation of 2%. The soil possesses a very high buffering capacity. It contains 14.6% organic C and 0.8% total N (all values expressed on oven-dry weight basis) and has a pH of 4.4. The soil was prepared by passing it through a 6-mesh sieve.

The soil was treated with NaCl, Na_2SO_4, KCl, K_2SO_4, $CaCl_2 \cdot 2H_2O$, and $CaSO_4 \cdot 2H_2O$ in concentrations ranging from 0 to 0.56*M*. The osmotic pressure in the soil solution due to these salts was calculated by the van't Hoff equation for strong electrolytes (12) and is explained in more detail in an earlier paper (14).

The incubation procedure was essentially the same as described by Singh et al. (14). Soil samples of 25 g each (on oven-dry basis) were placed in 500-ml Erlenmeyer flasks. The calculated amount of the respective salt was added to the soil in the flask and mixed well. The mouth of the flask was tightly capped with polyethylene film. Samples were incubated for periods of 7, 14, and 23 days. At the end of each period, samples were analyzed for NH_4- and NO_3-N by the micro-Kjeldahl distillation procedure of Bremner (2). Aeration in incubating samples was provided by removing the stoppers for 1 minute, first at 48-hour intervals and subsequently every 72 hours.

The CO_2 evolved was measured in another set of flasks receiving a similar treatment as above. The CO_2 was determined at frequent intervals up to 23 days. The procedure was essentially the same as described by Agarwal and Kanehiro (1). It consisted of trapping evolved CO_2 in 5 ml of standard 1*N* NaOH solution placed in a glass vial which was suspended from a cork stopper in a 500-ml Erlenmeyer flask containing 50 g soil. The excess alkali was titrated against standard 0.5*N* HCl. Further details of this procedure are also found in Singh et al. (14).

RESULTS AND DISCUSSION

Effect on Carbon Dioxide Production

Data on the influence of salts on CO_2 production are shown in Table 1 for Na-, K-, and Ca- chlorides and sulfates. The amounts of CO_2 evolved from the samples treated with chloride salts of Na, K, and Ca were generally lower than the control. The CO_2 production initially declined sharply at low osmotic pressures (OP) caused by the addition of chloride salts, but increased a little later on. In any event, the magnitude remained lower than the control. Singh et al. (14) similarly found lowered CO_2 production with chloride salts. Among the sulfates, Na_2SO_4 and K_2SO_4 resulted in higher CO_2 production at lower OP and lower production at higher OP as compared to the control. This indicates that sulfates acted as a stimulus to at least some organisms at low concentrations. With $CaSO_4 \cdot 2H_2O$, the CO_2 values generally showed no difference from those of the control irrespective of the increase in OP, possibly due to the low solubility of this salt which failed to create the desired OP in the soil system. Only at the two lowest salt concentrations at 23 days was there any significant increase in CO_2 production over that of the control. Therefore, it can be concluded that the addition of salts had little or no stimulative effect on the microbial activity in the Akaka soil except the sulfates at low concentrations.

Table 1—Effect of chloride and sulfate salts on the production of carbon dioxide (cumulative) in the Akaka silty clay

Salt	Molar conc	Osmotic pressure	Days 7	14	23
	M	atm	mg C/50g soil		
NaCl	0.00	0.00	20	33	52
	0.011	0.55	17	30	48
	0.028	1.39	15	27	40
	0.056	2.78	18	28	44
	0.28	13.90	16	29	43
	0.56	27.80	19	30	42
Na_2SO_4	0.00	0.00	20	33	52
	0.011	0.83	22	40	64
	0.028	2.08	28	43	66
	0.056	4.16	22	37	57
	0.28	20.80	18	31	44
	0.56	41.60	18	28	39
KCl	0.00	0.00	19	36	51
	0.011	0.55	16	28	42
	0.028	1.39	16	28	41
	0.056	2.78	17	30	44
	0.28	13.90	19	32	44
	0.56	27.80	20	39	52
K_2SO_4	0.00	0.00	19	36	51
	0.011	0.83	25	46	66
	0.028	2.08	22	39	58
	0.056	4.16	21	37	54
	0.28	20.80	19	33	48
	0.56	41.60	19	32	46
$CaCl_2 \cdot 2H_2O$	0.00	0.00	23	42	72
	0.011	0.83	18	31	49
	0.028	2.08	20	33	51
	0.056	4.16	23	36	50
	0.28	20.80	22	40	54
	0.56	41.60	20	39	55
$CaSO_4 \cdot 2H_2O$	0.00	0.00	19	36	51
	0.011	0.55	21	38	57
	0.028	1.39	21	38	56
	0.056	2.78	21	37	53
	0.28	13.90	20	36	53
	0.56	27.80	21	38	54

Effect on NH_4-N Release

The NH_4-N release data for Akaka soil treated with chloride and sulfate salts are given in Table 2. (Minus figures in this table indicate lower values than initial NH_4- and NO_3-N in the soil). The chlorides were very effective in causing NH_4-N release in the soil. Calcium chloride additions resulted in the greatest release of NH_4-N among the salts tested. The effect of KCl was next to that of $CaCl_2 \cdot 2H_2O$ and was followed by NaCl in the order of

Table 2—Effect of chloride and sulfate salts on NH_4 and NO_3-N release in the Akaka silty clay (ppm N represents change in NH_4- and NO_3-N status, before and after treatment)

Salt	Molar conc	Osmotic pressure	NH_4 N Days 7	14	23	NO_3 N Days 7	14	23
	M	atm	ppm N*					
NaCl	0.00	0.00	6	4	-5	11	24	45
	0.011	0.55	1	4	3	8	32	-7
	0.028	1.39	4	16	24	7	18	35
	0.056	2.78	20	29	67	0	10	5
	0.28	13.90	50	58	114	0	15	1
	0.56	27.80	60	111	142	5	2	3
Na_2SO_4	0.00	0.00	6	4	-5	11	24	45
	0.011	0.83	6	5	3	1	22	42
	0.028	2.08	5	3	3	8	31	51
	0.056	4.16	2	3	19	4	28	37
	0.28	20.80	19	46	86	6	8	2
	0.56	41.60	28	55	98	5	6	2
KCl	0.00	0.00	5	7	5	13	29	44
	0.011	0.55	2	7	6	23	34	71
	0.028	1.39	25	25	33	6	18	35
	0.056	2.78	42	61	93	6	-3	6
	0.28	13.90	84	100	136	7	5	5
	0.56	27.80	112	140	182	5	5	-7
K_2SO_4	0.00	0.00	-5	7	5	13	29	44
	0.011	0.83	5	5	4	20	31	45
	0.028	2.08	2	7	7	26	41	59
	0.056	4.16	12	7	7	20	53	75
	0.28	20.80	69	79	109	8	-5	-8
	0.56	41.60	71	94	122	7	-5	7
$CaCl_2 \cdot 2H_2O$	0.00	0.00	2	2	1	2	3	33
	0.011	0.83	32	54	57	0	2	50
	0.028	2.08	50	79	92	1	4	2
	0.056	4.16	72	99	120	1	4	1
	0.28	20.80	144	186	218	1	4	1
	0.56	41.60	136	209	248	1	4	2
$CaSO_4 \cdot 2H_2O$	0.00	0.00†	5	7	5	13	29	44
	0.011	0.55	5	7	7	18	35	48
	0.028	1.39	4	7	6	25	46	64
	0.056	2.78	5	7	7	26	49	72
	0.28	13.90	-5	7	7	26	45	71
	0.56	27.80	0	5	0	27	47	68

* Minus figures indicate lower values than initial NH_4 and NO_3 N in the soil

† Osmotic pressures for $CaSO_4 \cdot 2H_2O$ are calculated values; actual values are presumed to be lower because of the low solubility of this compound

decreasing magnitude of inducing NH_4-N release. Sulfates were less effective than chlorides. Among the sulfates, K_2SO_4 ranked first in effecting NH_4-N release, followed by Na_2SO_4 and lastly by $CaSO_4 \cdot 2H_2O$. The failure of $CaSO_4 \cdot 2H_2O$ to rank first among sulfates when $CaCl_2 \cdot 2H_2O$ did so among chlorides can be explained on the basis of the low solubility of the former compound. Because of this low solubility, $CaSO_4 \cdot 2H_2O$ resulted in a low activity of cations in the soil solution and also failed to produce the desired OP in the system. The same cation associated with different anions had a varying effect on N release in the soil even at the same concentration. This leads us to conclude that both cation as well as anion species are involved in effecting N release from the organo-inorganic complex or in exchange reactions involving adsorbed or fixed ions in the soil.

The magnitude of NH_4-N release, except with $CaSO_4 \cdot 2H_2O$, generally increased with successive increments in salt concentration. The negative values for NH_4-N (Table 2) at lower concentrations of all salts and at all concentrations of $CaSO_4 \cdot 2H_2O$ are due to nitrification of released NH_4-N, as will be discussed later on. The NH_4-N release increased with time, although the magnitude of release was related to the kind and amount of the salt.

Several investigators (6, 7, 10) reported that salts stimulate ammonifiers. Increased NH_4-N release (Table 2) in this experiment might lead one to support this view. But as pointed out earlier, CO_2 production remained lower in chloride-treated samples and was slightly higher at lower OP and lower at higher OP in sulfate-treated samples, (except for $CaSO_4 \cdot 2H_2O$) than the control (Table 1). The data in Table 2 show that the NO_3-N content of salt-treated samples was higher at lower concentrations of chlorides (which resulted in lesser CO_2 evolution), as well as at lower concentrations of sulfates (which resulted in higher CO_2 evolution), as compared to the controls. Thus, the salts seemed to have no stimulative effect on microorganisms, and even if they did, it may just have been limited to nitrifiers, depending of course upon the salt and its concentration. Therefore, whatever the stimulative effect of salts on microorganisms, it cannot account for the NH_4-N release. Another explanation for NH_4-N release could be on the basis of "osmotic effect" as was advanced by Broadbent (3). He believed that NH_4-N comes from microbial cell breakdown due to increased OP and subsequent cell lysis. However, OP is not the sole factor contributing to NH_4-N release, because different salts at equivalent OP or concentration resulted in different magnitudes of NH_4-N release in the experimental soil. Singh et al. (14) postulated that in addition to the "osmotic effect," certain chemical reactions and/or processes are also involved in splitting off NH_4-N from organo-inorganic complexes of a soil, and NH_4^+ ions are subsequently exchanged with cations in the surrounding soil solution. The exchange reaction depends on the nature and valence of cations, concentration in the soil solution, and period of reaction. The data in Table 2 indicate that NH_4-N release is also dependent on the anionic species associated with a particular cation. The results on NH_4-N reported herein further support the above view of Singh et al. (14). Replacing power of different cations based on hydrated ionic size and valence is of considerable significance. Replacing power is fairly well known to decrease in the order: Ca > K > Na. The capacity of these cations in releasing NH_4-N from organo-inorganic complexes also followed this same order in this investigation.

Effect on Nitrification

The data on the nitrification of released NH_4-N due to the chloride and sulfate salts are also included in Table 2. Unlike the NH_4-N release pattern, sulfates were more effective than chlorides in promoting nitrification. Sodium sulfate and potassium sulfate additions promoted nitrification but only at the two and three lower concentrations, respectively; the two higher rates were detrimental. However, appreciable nitrification occurred with calcium sulfate at all rates, with the magnitude being greater at higher than at lower concentrations. In the case of KCl and NaCl treatments, nitrification was stimulated at the lowest concentration (0.011N), slightly depressed at the next higher concentration (0.028N), and greatly depressed at the three highest concentrations. It was curtailed with $CaCl_2 \cdot 2H_2O$, except for the appearance of some nitrate at the lowest concentration at the end of 23 days. Apparently, chlorides are more toxic to nitrifiers than sulfates. The data (Table 2) further indicate that $CaCl_2 \cdot 2H_2O$ at all concentrations and the other salts (except for $CaSO_4 \cdot 2H_2O$) at higher concentrations curtailed nitrification; this is consistent with the earlier reports (4, 8, 9, 11, 13). The observation that nitrification was affected less by Na_2SO_4 than by NaCl is in agreement with that of Johnson and Guenzi (9). The promotion of nitrification by $CaSO_4 \cdot 2H_2O$ is in line with the data of Pathak and Jain (13) who reported that nitrification was stimulated by $CaSO_4$ and $MgSO_4$ up to certain concentrations. That anions may have been active in retarding nitrification is suggested by the reports of Butovski (5). He considered chloride ion to be active when nitrification was decreased by NaCl. In this experiment higher concentrations of sulfates apparently played a role similar to that of chlorides, although to a lesser extent.

CONCLUSIONS

Evidence presented herein indicates that the nature and extent of participation of anions in soil N release may be somewhat diffuse; nevertheless, there is a real participation and a difference in behavior of the anions studied. Two salts containing the same cation but different anions, e.g. NaCl and Na_2SO_4 or KCl and K_2SO_4 at equivalent concentrations, produced different magnitudes of N release, thus suggesting the role of anions in this phenomenon. If only cations were responsible for the observed release of soil N, then KCl and K_2SO_4 or NaCl and Na_2SO_4 should have effected N release of similar magnitude. Differences in behavior of anions in N release is amply evidenced by comparing values of NH_4^+ and NO_3^- associated with chlorides and sulfates of common cations in the salts studied. Thus, $CaCl_2 \cdot 2H_2O$, KCl, and NaCl *enbloc* proved more effective in N release than K_2SO_4, Na_2SO_4,

and $CaSO_4 \cdot 2H_2O$. The results of this experiment provide further support for the role of cations and, in addition, furnish reasonable evidence of the participation of anionic species in N release. The nature and extent of the contribution by individual cations and anions may be rather difficult to comprehend fully at this stage.

Taking into consideration the overall values of nitrogen ($NH_4^+ + NO_3^-$) release at various concentrations of added salts, the following series in decreasing order was obtained:

$$CaCl_2 \cdot 2H_2O > KCl > NaCl > K_2SO_4 > Na_2SO_4 > CaSO_4 \cdot 2H_2O .$$

Although this study was conducted in the laboratory, it has field implications. The additions of nonnitrogen fertilizers, such as potassium chloride [which is commonly applied at the rate of 280–336 kg K_2O/ha (250–300 lb/acre) for a sugar cane crop (*Saccharum officinarum* L.) grown in the Akaka and related soils], may trigger the release of N from soil organo-inorganic complex with a resultant increased N uptake by crops. A crop like the sugar cane could suffer detrimental effects on yield if this release unexpectedly occurs at a time when it is imperative that the N supply be kept low. Thus, it is important to consider the effects of nonnitrogen fertilizer applications in the overall nitrogen program of crops, especially those grown in high organic matter soils in wet regions.

LITERATURE CITED

1. Agarwal, A. S., and Y. Kanehiro. 1966. Measurement of nitrogen and carbon release under drying and rewetting conditions. Soil Biol. Int. News Bull., Paris, no. 6, p. 44–45.
2. Bremner, J. M. 1965. Inorganic forms of nitrogen. *In* C. A. Black (ed.). Methods of soil analysis, Part 2. Agronomy 9:1179–1237.
3. Broadbent, F. E. 1965. Effect of fertilizer nitrogen on the release of soil nitrogen. Soil Sci. Soc. Amer. Proc. 29: 692–696.
4. Brown, P. E., and E. D. Hitchcock. 1917. The effect of alkali salts on nitrification. Soil Sci. 4:207–229.
5. Butovskii, V. 1950. Pocvovedenie (Pedology, Moscow): 492. (Citation in G. W. Skyring and J. C. Barbara. 1962. *In* A review of nitrogen in the tropics with particular reference to pastures. C.S.I.R.O. Bull. 46, p. 56–71).
6. Greaves, T. H. 1916. The influence of salts on bacterial activities of the soil. Soil Sci. 2:443–480.
7. Greaves, T. H., and Y. Lund. 1921. The role of osmotic pressure in the toxicity of soluble salts. Soil Sci. 12:163–181.
8. Greaves, T. H., E. G. Crater, and H. C. Goldthorpe. 1919. Influence of salts on the nitric-nitrogen accumulation in the soil. J. Agr. Res. 16:107–135.
9. Johnson, D. D., and W. D. Guenzi. 1963. Influence of salts on ammonium oxidation and carbon dioxide evolution from soils. Soil Sci. Soc. Amer. Proc. 27:663–666.
10. Lipman, C. B. 1909. Toxic and antagonistic effects of salts as related to ammonification by *Bacillus subtilis*. Bot. Gaz. 48:105–125.
11. Martin, A. E., and J. F. Cox. 1956. Nitrogen studies in black soils from the Darling Downs, Queensland. II. The nitrification activity of subsurface horizons. Austr. J. Agr. Res. 7:184–193.
12. Moore, W. J. 1962. Physical chemistry. 3rd ed. Prentice Hall, Inc., Englewood Cliffs, N.J.
13. Pathak, A. N., and S. L. Jain. 1965. Effect of alkali salts: II. On nitrification. J. Soil Water Conserv. India. 13:30–32. *In* Soils and Fert. 29(2530).
14. Singh, B. R., A. S. Agarwal, and Y. Kanehiro. 1969. Effect of chloride salts on ammonium nitrogen release in two Hawaiian soils. Soil Sci. Soc. Amer. Proc. 33:557–560.