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Behavior of "Organic" and "Synthetic" Fertilizer Nutrients When Applied to Irrigated, Unsaturated Soil

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It is well known that agrochemical nutrients are rapidly transported through soils (Bergstrom & Jarvis, 1993, Quisenberry et al., 1994; Roth et al., 1991). The movement of agrochemicals through soil to groundwater or their discharge to surface waters represents an ecological risk and financial loss to the farmers applying the chemicals. Research has shown that the impacts of organic farming practices are less of a hazard to many forms of wildlife, agricultural workers and local communities (Lieberg and Doran 1999). Organic farming systems are those that rely on crop rotation, use of animal or green manure, use biological pest control and exclude the use of synthetic fertilizers and pesticides. Consumer demand for food produced without the use of synthetic fertilizers or pesticides has increased dramatically over the last decade. Such food has developed into a more than US$3 billion a year industry in the USA (Lieberg and Doran 1999).

The perceived benefits of organically grown food have now caused a dramatic increase in the promotion of 'organic fertilizers ' in the Australian media, many implicitly promoting the message that these fertilizers are more environmentally friendly than their synthetic counterparts. Farmers are now under pressure to choose their fertilizers based on non-scientific factors, such as their being 'organic,' despite this term being rather vaguely defined when applied to commercial fertiliser formulations. As little as 1% natural organic material appears to be, enough for some companies to brand their otherwise synthetic material as such. A better knowledge of the behaviour of nutrients in such 'organic' fertilizers when directly compared to synthetic fertilizers in field soils is required by society, including farmers and agrochemical companies, for the sustainable ecological management of agricultural soils. Herein, we present the results of one such study.

MATERIALS AND METHODS

When assessing the fate of agrochemical nutrients in soil, undisturbed soil columns spiked with granular fertilizers offer a better means of studying mobility than standard leaching tests **using** sterile, homogeneous soils with standard nutrient solutions because they preserve the natural structure of both the soil (Stagnitti et al., 1998) and the physico-chemical behaviour of the granules.

This study was conducted on soil cores extracted from a farm near Overland Comer in the South Australian Riverland (-250 km E of Adelaide in the Murray River Valley). Small, undisturbed soil cores were extracted in late November 1998, from the surface soil between a rows of vines and a row of lemon trees in the following manner : Soil columns were carefully carved out of the soil structure between two trenches using hand-trowels and encased in PVC sewage pipe. A lid was screwed firmly to the top of the core. The soil beneath the base was then carefully removed by hand trowelling, and the core extracted by slicing and tipping the core. The base was trimmed

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so that it was the same level as the piping. Thereafter, a lid was screwed firmly onto the base. Undisturbed cores collected in this manner were transported to Warrambool and placed in a controlled environment laboratory (20 ± 2 °C). Twelve undisturbed soil cores (diameter, 200 mm; length, 200 mm) were extracted in this manner.

The cores were attached to lysimeters. Each lysimeter consisted of a 12.5 cm diameter glass fibre filter paper pressed between the Centre of he core and a single 40 cm glass fibre wick, the top 15 cm of which was spread out evenly underneath the filter paper (Ueoka et al., 1998). The wick passed through a porous mesh taped between the core and the shelving supporting the soil core encased in the PVC pipe. This enabled the leachate to flow undisturbed down the wick without concomitant transport of eroded soil particles. The location on the shelf of each core was randomly selected to ensure statistical validity.

The twelve undisturbed soil cores were irrigated by gravity-feed at a rate comparable to that received by the vineyard (approximately 12.5 mm per day by spray irrigation) for one month to flush the cores of gross levels of soluble nutrients and to allow the establishment of a baseline nutrient level in the leachates. On 5 January 1998 (Day 0) chemical analysis of the leachate was initiated. On the 12 January 1998 (Day 7) the cores were divided into three groups, each of four cores. One group of cores (0) was dosed with 1.77 g of the ‘organic’ fertiliser, and a second group of cores (I) dosed with 1.77 g of the synthetic (or inorganic) fertiliser. A further group (SNS) was dosed with 10 mL of a standard nutrient solution. This latter treatment was used to examine the affect of granule dissolution on nutrient dynamics. All groups were dosed with nutrients at a rate equivalent to 1000 kg/ha fertiliser [equivalent to 80 kg/ha P, 40 kg/ha P, 80 kg/ha K]. Thereafter, the cores were irrigated at a rate equivalent to normal vineyard irrigation for another four weeks. Again, samples were taken every two to three days and the irrigation volume, leachate volume, pH and nutrient (soluble N (NO_3^--N), Total N, soluble P (PO_4^{3-}-P), Total P), chlorine (as chloride ion (Cl^-), sulphur (as sulphate ion (SO_4^{2-}) and major cations (Na^+, K^+, Ca^{2+}, Mg^{2+}) concentrations determined. At the end of the irrigation period, the soil cores were dissected into three layers : the top 2 cm of the core, the layer approximately 2 to 6 cm beneath the surface, and the remaining, deeper soil.

For reasons of commercial sensitivity, we will not mention the names of the selected fertilizers However, the typical composition of the N:P:K blends was :

- ‘Organic’ 8:4:8 N:P:K Fertiliser : N, 8.0% (as ammonium, 5.0%; as urea, 2.0%; as natural organic compounds, 1.0%); P, 4% (water soluble, 2.5%; citrate (soluble), 1.0%; citrate (insoluble), 0.5%); K, 8% (as sulphate); S, 10% (as sulphate); Ca, 5% (as sulphate); Cu, 0.04% (as sulphate); Zn, 0.04% (as sulphate); Mn, 0.1% (as sulphate); Fe, 0.3% (as sulphate); Mo, 0.003% (as molybdate); B, 0.02% (as boric acid).
- ‘Synthetic’ 8:4:8 N:P:K Fertiliser : N, 8.0% (as ammonium); P, 3.6% (as water soluble, 3.3%; citrate (soluble) 0.3%); K, 7.9% (as sulphate); S, 17% (as sulphate); Ca, 8.0% (as sulphate, 5.8%; as phosphate, 2.2%).
- The standard nutrient solution was prepared from a mixture of 1.01 M ammonium chloride, 0.18M potassium sulphate, 0.229 M sodium phosphate, and sodium 0.18M sulphate.

All pH measurements were undertaken using a Hannah Instruments Mode1 HI 8519 pH meter. All chemicals used were reagent grade. Deionised water of resistivity > 18 MΩ cm^{-1} was produced by passing distilled water through an ion exchange - activated carbon filter system (MilliQ, Millipore Corp., USA). Leachate concentrations of sodium, potassium, calcium, and magnesium ions were determined spectra-photometrically using a Perkin Elmer 305B Atomic Absorption Spectrophotometer, and an Hitachi 6000 Polarised Zeeman Atomic Absorption

Spectrophotometer. Chloride and sulphate ion were determined by ion chromatography using Waters IC-Pak Anion HC column (i.d. 4.6 x 150 mm) and borate-gluconate mobile phase.

Nitrate nitrogen (NO_3^--N) in the leachate was determined by flow injection analysis The method of Hosomi and Sudo with modifications described in Stagnitti et al. (1998) was adopted. The concentration of total nitrogen (Total N), defined as being the sum of nitrite nitrogen (NO_2^--N), nitrate nitrogen (NO_3^--N), ammonia (NH_3-N), and. dissolved or < 45 µm particulate organic and inorganic material containing nitrogen, was also determined by flow injection analysis after oxidation of nitrogen species in the leachate to nitrate by an alkaline solution of potassium persulphate. The resulting nitrate in the sample was then determined in the manner described above.

Phosphate phosphorus (PO_4^{3-}-P) in the aqueous samples was also determined by flow injection. The method of Benson with modifications described in Stagnitti et al. (1998) was adopted. The concentration of total phosphorus (Total P), defined as being the sum of phosphate phosphorus and dissolved or < 45 µm particulate organic and inorganic material containing phosphorus, was also determined by flow injection analysis after oxidation of phosphorous species to phosphate phosphorus by alkaline potassium persulphate.

RESULTS AND DISCUSSION

The cores were taken exclusively from the topsoil. The average soil pH (1:5 water) was 6.0 ± 0.1 (surface), 6.7 ± 0.1 (2 to 6 cm depth), 7.3 ± 0.1 (> 6 cm depth). There were no statistically significant differences in pH with depth between the cores. The average organic carbon content was 2.0% (surface) and 1% (below 6 cm). The average soil moisture ranged from 8.5 to 10.5% (surface), 8.0 to 11.9% (2 to 6 cm depth), and 9.5 to 11.4 % (> 6 cm depth). Dry soil colour was determined from Munsell Colour charts. There was some variation with depth : surface, 5YR 3.5/4; 2-6 cm 7.5 YR 4/6; below 6 cm, 5YR 3/3 . Particle size analysis indicated that this sandy loam at the surface was 9% clay (particles less than 2 µm), 12% silt (2 to 5 µm), 58% fine sand (5 to 200 µm) and 21% coarse sand (0.2 to 2 mm); at 2 to 6 cm, 9% clay, 10% silt, 58% tine sand and 23% coarse sand; and below 6 cm 3% clay, 10% silt, 59% tine sand and 28% coarse sand.

All cores received similar volumes of irrigation water over the entire experiment (approximately 170 mL/day). All cores leached similar volumes of irrigation water over the time period of the experiment (approximately 110 mL/day). Comparisons between the rate of irrigation and collected leachate indicated that approximately 65% of the applied water leached into the lysimeters. The lysimeter units were not designed to collect water from the extreme edges of the soil cores, and there were no obvious losses of irrigation water from under the edges of the core casings. It can therefore be assumed that there were no significant edge effects and the remaining irrigation water, approximately 35% of applied, was lost from the soil surface by evaporation. This latter assumption is consistent with observed rates of evaporation from open containers (aquaria, approximately 4 mm/day) previously housed in the constant temperature room.

The average pH in the leachate was 8.1 ± 0.1. There were no large differences in the average pH of the leachate from any core on a day-to-day basis, as evidenced by small coefficients of variation for individual cores and within treatments. The leachate was more alkaline than the soil, although there was also no trend toward acidification of the leachate with time. There was a general trend towards higher pH with increasing depth in the soil profile. In general, the top two centimetres of the soil profile were always more acidic than the four centimetres of underlying soil, which in turn were more acidic than the soil greater than six centimetres from the soil surface. Presumably this is a result of increased organic material, including humic acids, in the surface soils.

Tables 1 and 2 present the results for the comparisons between the three treatments, organic fertilizer (O), synthethic or inorganic fertilizer (I) and standard nutrient solution (SNS) for each of the major leached analytes : nitrate, total nitrogen, phosphate, total phosphorus, chloride, sulphur, calcium, magnesium, potassium and Sodium. The variables considered are average concentration, average mass and average time-to-peak concentration. The latter variable, the time-to-peak concentration, is not often reported in solute transport studies. However in comparative studies, such as this one, it provides important information on chemical retardation in the soil and hence nutrient bioavailability to plant materials.

Table 1. Comparisons of leachate concentrations for cores applied with standard nutrient solution (SNS), organic (0) and inorganic (I) fertilizers, for nitrate, total nitrogen, phosphate and total phosphorus.

Analyte	Treatment	Leachate										
		Average Daily Mass (mg/day)	c.v.	Average Concentration (mg / L)	c.v.	Average Peak Concentration (mg / L)	c.v.	Ave Time to Peak Conc (h)	c.v.	Leached Mass (mg)	Applied Mass (mg)	Ratio LM : AM
Nitrate	SNS	0.3	42	3.9	74	7.7	43	214	0	10	142	0.07
	O	0.5	81	3.9	53	7.4	36	256	22	16	142	0.11
	I	0.3	17	8.4	9	6.4	17	226	11	10	142	0.07
Total N	SNS	0.9	57	8.5	16	17.4	21	311	19	29	142	0.2
	O	0.7	62	5.6	36	9.2	35	293	21	22	142	0.15
	I	0.6	27	10.2	9	10.0	14	281	13	19	142	0.13
Phosphate	SNS	0.2	46	2.1	13	3.0	10	166	0	6	71	0.08
	O	0.3	20	2.5	21	3.8	18	251	55	9	71	0.13
	I	0.2	30	7.9	4	3.3	20	166	0	6	71	0.08
Total P	SNS	1.7	44	17.1	15	26.8	11	155	44	54	71	0.76
	O	2.4	28	20.4	26	29.7	23	239	28	77	71	1.08
	I	1.8	24	19.4	7	26.8	20	95	24	58	71	0.82

The results of a one-way ANOVA suggest that there was no statistical difference in the average daily concentration between treatments for leached nitrate ions ($p > 0.05$, Table 1). Neither was there a difference between the time-to-peak concentration of nitrate in the leachate ($p > 0.05$). There was also no difference in the average daily concentration of Total N in the leachates, nor a difference in the time-to-peak concentration of Total N ($p > 0.05$). Finally, there was no difference in the ratio of nitrate : Total N in the leachates. The appearance of nitrate ions in the leachates is perhaps a predictable observation, since ammonium from fertilizers can be transformed into nitrate by soil bacteria, and then readily leached through soil (McLaren and Cameron 1997). In all cases, the leached mass : applied mass ratio (LM:AM; Table 1) of nitrate and Total N is less than I, suggesting that a substantial proportion of the applied nitrogen is being bound up in the soil.

There was no statistical difference between the treatments in the average daily concentration of phosphate ions in the leachates or the time-to-peak concentration (one way ANOVAs, $p > 0.05$). There was also no difference in the average daily concentration of Total P ($p > 0.1$), nor a difference between the timeto-peak concentration of Total P in the leachates ($p > 0.1$). Finally, there was no difference in the ratio of phosphate : Total P in the leachates. In all cases, the phosphate LM:AM is less than one, suggesting that much of the applied phosphate was readily incorporated in the soil. This in itself is not surprising since others have found that phosphates are sorbed strongly by soil particles, particularly in the top few centimetres of the soil profile (McLaren and Cameron 1997). The Total P LM:AM ratio of cores O and I was approximately 1. Given that other studies have found that phosphorus - or at least phosphates - are strongly sorbed by soil particles, particularly in the top few centimetres of the soil profile (McLaren and Cameron 1997), our results suggest that a phosphorus saturation level for this soil was reached, after which any additional phosphorus was readily leached.

Table 2. Comparisons of leachate concentrations for cores applied with standard nutrient solution (SNS), organic (0) and inorganic (I) fertilizers, for other major analytes.

Analyte	Treatment	Leachate										
		Average Daily Mass (mg/day)	c.v.	Average Concentration (mg / L)	c.v.	Average Peak Concentration (mg / L)	c.v.	Ave Time to Peak Conc (h)	c.v.	Leached Mass (mg)	Applied Mass (mg)	Ratio LM : AM
Chloride	SNS	10.3	37	112.4	47	369.8	18	336	35	329	388	0.85
	O	1.1	48	9.2	36	35.8	92	300	24	35	0	N/A
	I	3.2	91	28.5	72	180.5	92	252	64	103	0	N/A
Sulphur	SNS	2.7	29	30.6	53	333.0	42	360	86	86	94	0.91
	O	6.3	21	55.2	37	564.5	42	282	202	202	177	1.14
	I	9.5	6	76.7	21	1051.0	13	288	304	304	301	1.01
Calcium	SNS	3.5	43	41.8	80	149.6	66	558	35	112	0	N/A
	O	4.2	44	34.3	24	101.0	25	480	10	134	89	1.51
	I	5.3	25	47.2	40	188.4	24	431	7	170	142	1.20
Magnesium	SNS	2.3	44	24.0	48	69.1	23	570	35	74	0	N/A
	O	2.7	21	22.8	26	61.1	35	456	9	86	8.9	9.66
	I	3.3	16	30.5	30	94.2	10	443	11	106	3.5	30.29
Potassium	SNS	0.8	69	7.3	28	13.7	20	341	32	26	142	0.18
	O	1.1	28	8.8	15	14.1	17	462	27	35	142	0.25
	I	0.9	24	12.4	20	19.0	42	348	53	29	142	0.20
Sodium	SNS	2.9	45	29.0	19	53.8	24	528	22	93	602	0.15
	O	2	36	18.1	54	43.8	60	252	83	64	22	2.91
	I	2	32	19.9	30	40.0	29	293	54	64	16	4.00

The results of a one way analysis of variance (ANOVA) indicate that cores applied with the standard nutrient solution leached a greater average mass of chloride ion than the cores applied with the organic and inorganic fertilizers ($p < 0.001$). However, there was no difference detected between the time-to-peak concentration of chloride ($p > 0.05$). Chloride ion is often considered to be an inert tracer in preferential flow studies (Stagnitti, et al., 1998), so it is perhaps not surprising that on almost all of the applied mass of chloride in the standard nutrient solution was observed in the leachate (Table 2). Compared to many other micronutrients, the amounts and forms of chloride in soils is not well understood (McLaren and Cameron 1997). In this case the chloride breakthrough curves observed in cores O and I, treated with fertiliser that did not contain chlorine, may result from anion exchange processes or its release to buffer the increased cation concentrations in the soil moisture.

The results of a one way ANOVA suggest that Cores I leached a significantly greater average mass of sulphate than Cores SNS ($p < 0.001$), and that, while not being statistically significant, the Cores O leached an average daily mass of sulphate intermediate between Cores SNS and I. The experiment failed to detect a significant difference between the time-to-peak leachate concentration of sulphate between the treatments ($p > 0.05$). There is no difference between the treatments in terms of the sulphate LM:AM ratio. It is perhaps not surprising that sulphur was detected in the leachates since all treatments contained sulphate. Sulphate ions are adsorbed to soil particles by similar processes responsible for phosphate adsorbtion, but adsorbed sulphate is held far less strongly, and therefore leach far more readily. There were no statistically significant differences between treatments in the average mass of calcium, magnesium, potassium or sodium ($p > 0.05$) ions leaching from the cores. Nor did the experiment detect any difference between the time-to-peak concentration of calcium magnesium potassium or sodium ($p > 0.05$) ions in the leachates.

The standard nutrient solution was prepared using potassium and sodium compounds, but not those containing calcium or magnesium. The organic and synthetic fertiliser labels state that they contain the macro-nutrients potassium and calcium, but chemical analysis also showed that both fertilizers also contained small amounts of magnesium (0, 0.5%; I, 0.02 %) and sodium (0, 0.1%; I, 0.1%). The appearance of potassium ions in the leachate of all the cores is, therefore, perhaps a predictable observation, However, in all cases, the potassium LM:AM ratios are less than 1, suggesting that actually a substantial proportion of the applied potassium is being adsorbed by the soil. There are differences in the behaviour of sodium, calcium and magnesium ions between the treatments. In Cores SNS, the sodium LM:AM ratios are less than 1, suggesting that a substantial proportion of the applied mass of this element is being adsorbed by the soil. However, in Cores O and I, the sodium LM:AM ratios are greater than 1, suggesting that these ions are being released from the soil through cation exchange processes. Finally, calcium and magnesium ion breakthrough curves were observed in all treatments. The standard nutrient solution was not prepared using calcium or magnesium compounds. This leaching loss is the result of the nitrification of applied ammonium nitrogen also occurring in these non-sterilised, undisturbed cores. Nitrification releases protons (H^+) into soil solution, which readily displaces calcium ions from exchange sites. In order to maintain neutrality, the calcium ions are forced to accompany nitrate ions leaching through the soil (McLaren and Cameron 1997). That Cores O and I, dosed with fertiliser containing both calcium and magnesium, had calcium and magnesium LM:AM ratios greater than 1, suggests that the applied calcium and magnesium was not adsorbed by the soil.

In conclusion, there was little difference in leaching patterns between the standard nutrient solution and the two commercial fertiliser blends studied, suggesting that both granular fertilizers were essentially totally soluble. In almost all cases, statistical differences between the treatments could not be detected for the soil types analysed. The failure to detect statistical differences in the data may result from the fact that there truly is no difference in environmental behaviour of these commercial blends in soils studied, or that the tests lacked statistical power due to a small number of replications. The former explanation is most likely, since the ‘organic’ and ‘synthetic’ fertilizers are almost identical, suggesting that at the very least incorporating ‘natural organic materials’ to the 1% level does little to ameliorate impacts of leaching through soils to groundwater or maximise benefits for crops by improving nutrient residence in soils. Indeed, in this case, the ‘organic’ fertiliser hardly justifies the description. Commercial enterprises, particularly farmers, must be aware of such issues, and that any benefits derived from truly organic fertilizers will in any event be site specific.

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