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AMMONIUM, PHOSPHATE AND POTASSIUM SORPTION STUDIES ON PEAT AND MINERAL SOILS

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ABSTRACT

The previous field trials on Sago palm cultivation in Malaysian peat under Nitrogen (N), Phosphorus (P) and Potassium (K) fertilizers application failed to produce positive growth response. Consequently, the comparative studies reported herein were carried out on peat and mineral soils, both strongly acidic (pH <5), to elucidate on the problems encountered and proffer suitable fertilizer management option for Sago palms in peat soil. To achieve this, physico-chemical characterization and ammonium (NH⁺₄), phosphate (H₂PO₄⁻) and potassium (K⁺) sorption were carried out on both soils at their initial pH levels. The results of the nutrient sorption studies established that both soils, at comparable degrees, poorly sorbed the added NH₄⁺ and K⁺ ions at all levels of application. The quantity-intensity (Q-I) plots characteristics are: ammonium sorption (mineral soil: Ceo = 27.2 mg N/dm³ and \Box Qo = -42.8 mg N/dm³ soil; peat: Ceo = 35.7 mg N/dm³ and \Box Qo = -0.21 cmol(+) K/dm³ soil and potassium sorption (mineral soil). Ceo implies solution concentration when neither sorption nor

the equilibrium solution concentration of the nutrient is zero. However, phosphate sorption plots showed both soils have very dissimilar P sorption properties. While the mineral soil sorbed very high \bar{a} mount at all levels of P addition (Pmax = 1434 mg P/dm³ soil), peat sorbed none at all. With His hydromorphic induce, this hon sorption of the added http://www.sorption.com/dissimilar hon sorption of the added NH₄⁺ and K⁺ will have far reaching implications as regards mineral fertilizers use, the mobility of released NH₄⁺, H₂PO₄⁻ and K⁺ ions in soil and their utilization by Sago palms.

Key words: Peat, ammonium sorption, phosphate sorption, potassium sorption, Malaysia

INTRODUCTION The estimated total peatland areas in Malaysia is 2.4 million ha out of which about 60 percent are said to be located in state of Sarawak in East Malaysia (Hashim, 1984). Their formation resulted from the accumulation and anaerobic decomposition of organic remains (Rowell, 1981). However, the thickness of

peat layer so formed varies widely. Thus, peatland is classified "shallow" if the organic layer is less than 100 cm in depth and "deep" if greater than 100 cm. In Malaysia, the local classification is based on both the depth of organic layer and on the mineral soils on which the peats overlie. Igan series overlie quartzatic sandy soil with less than 15% clay while Mukah series and Anderson series overlie heavy clay or silty clay loam. Thus, Igan and Mukah series are classified "shallow" because the organic depths are in the range of 25 - 100 cm while the Anderson series are "deep" because the organic depth is greater than 100 cm (Tie et al., 1991; Lim et al., 1991; Hassan, 1994).

The peat soil formations are found in wetland ecosystems along coasts, rivers and stream banks in Malaysia. The topography description of such areas of formation is always low-lying (Tie et al., 1991) and hence explains their poor drainage conditions and the usually high water table found at or nearer soil surface. In addition to their poor drainage conditions, the peat soils have poor load bearing capacity for heavy equipments and for heavy structure and are difficult to work (Kueh et al., 1991; Hashim, 1984; Ismail, 1984). Chemically, the peat soils are high in acidity and are reportedly low in plant nutrients (Lim et al., 1991; Yim et 1984). Despite limitations. al.. these considerable portion of peat swamp forest areas across Malaysia are being converted, over the years, for production of some crops in plantation scale. One of such crops is Sago palm of Genus: Metroxylon and family: Palmaceae.

Research findings have proved Sago growth performance and starch yield in organic soils as satisfactory (Tie et al., 1991). However, they are found to be thinner and take longer time to attain maturity compared to their counterparts growing in mineral soils. In order Physical characterization to sustain Sago production and also to reduce the times taken to attain maturity in peat soil, Flasch and Schuiling (1991) had suggested the

use of fertilizer or appropriate nutrient cycling methods. In this regard, the previous fertilizer trials have been reported unsuccessful.

Hence, the comparative studies reported herein were carried out with the aims to elucidate on the likely problem or problems associated with the fertilizers used for Sago production in peat soil and to advice on their management. To accomplish these, physico-chemical characterization and nutrient sorption studies were carried out on two soil types (mineral and peat soils) to compare their ammonium-, phosphate- and potassium-sorption properties at their natural pH levels.

MATERIALS AND METHODS

Soils collection and preparation

Two soils of interest, mineral and peat, were collected for a comparative investigation on their sorption characteristics with different levels of addition of ammonium, phosphate and potassium ions at their natural pH levels. The mineral soil was collected from a location prone to occasional flooding within Universiti Putra Malaysia (UPM) premises in Serdang while the peat soil was collected from Golden Hope Estate oil palm plantation at Kampung Kundang, Banting, Selangor State.

The peat soil collected was sieved while still wet through a large mesh sieve (1.2 cm by 2.4 cm) to remove dead woods, stumps and roots and the mineral soil collected was first airdried and then passed through 2 mm mesh cylindrical sieve with the aid of an electrically powered rolling mill. Sub sample of both soils were taken, air dried and passed through 2 mm screen, bagged and stored for both physico-chemical characterization and nutrient sorption studies.

Textural analysis was carried out on the mineral soil only using pipette method after initial oxidation of organic matter present with 81 30% hydrogen peroxide solution as described

in ISRIC laboratory manual (ISRIC, 1993). Water holding was determined for both soils using "soak and drain" method (Parent and Caron, 1993) while organic matter and ash contents of the peat were determined gravimetrically after dry combustion according to Richards, 1993.

Chemical characterization

Soil pH in both water and 0.1 M CaCl₂ was measured for both soils after the method of Hendershot et al., (1993). In either case, the soil-to-solution ratio used for the mineral soil was 1:2.5 while the ratio used for the peat was 1:10. Total N was determined by micro-Kjedhal hot acid digestion of the soils followed by steam distillation of known volume of soil digests and acid titration of distillates as described by Bremner and Mulvaney (1982). Total carbon was determined by combustion method using Carbon Analyzer (LECO CR-412). Available and water extractable ammonium- and nitrate-N were determined by initial extractions of known weight of the soils (1 g for peat, 3 g for mineral soil) with 30 cm³ of either 2 M KCl solution or distilled water followed by steam distillation of a known volume of extracts and acid titration of distillates after the methods described by Maynard and Kalra (1993) and Keeney and Nelson (1982). Available and water extractable P were determined by initial extractions of known weight of the soils (1 g for peat, 3 g for mineral) with 30 cm^3 of either Bray and Kurtz no. 1 solution or distilled water followed by color development of known volume of extract and absorbance measurements on a colorimeter after Murphey and Riley method (ISRIC, 1993; Olsen and Sommers, 1982). Extraction of the soils for cation exchange capacity (CEC), exchangeable bases and base saturation determinations was by sequential leaching of known weight of the soils (3 g for peat; 10 g for mineral) with 100

 cm^3 of 1 N ammonium acetate solution, 100 cm^3 of 95% ethanol and 100 cm^3 of 0.1 N K₂SO₄ solution after the method of ISRIC (1993). Determinations were carried out as described in the manual.

Each determination was carried out on triplicate samples of each soil and the result is expressed as the average of the triplicate values obtained. As soil dry weight per volume for peat is different from that of mineral soil, most of the results were expressed in volume basis for ease of comparison between the two soils.

Nutrients sorption technique and measurements

Equal volume (3 cm^3) of the two air-dried soils was used for the nutrient sorption experiments described here. The equivalent dry weight of soil sample is 1 g for peat and 3 g for mineral soil.

Similar to the method described for P sorption by Fox and Kamprath (1970), samples of the test soils placed in 100 cm³ extraction cups were mixed with 30 cm³ of 0.01 M CaCl₂ solutions containing different concentrations of NH_4^+ , $H_2PO_4^-$ or K^+ as given in Table 1 and two drops of toluene were added to each soilsolution mixture to inhibit microbial activity. Shaking was done for 30 minutes two times daily on a reciprocal shaker. Samples for ammonium sorption were equilibrated for one day while those for phosphate and potassium sorption were equilibrated for eight days under room conditions. At the end of equilibration, clear supernatant solutions of the equilibrated samples were obtained for chemical analysis. In the case of potassium sorption, the supernatant solutions were filtered prior to determinations potassium on flame photometer. All treatments were in triplicate.

Soil type	Test nutrient	Compound used	Initial concentrations (Ci) of test nutrients placed in 0.01 M CaCl ₂ equilibrating solutions used
Peat	Ammonium Phosphate Potassium	$\begin{array}{l} (NH_4)_2SO_4\\ KH_2PO_4\\ KH_2PO_4\end{array}$	0, 1.25, 2.5, 5, 10, 20, 30, 50 mgNdm ⁻³ solution 0, 1.25, 2.5, 5, 10, 20 mgPdm ⁻³ solution 0, 1.6, 3.2, 6.3, 12.6, 25.3 mgKdm ⁻³ solution
Mineral	Ammonium Phosphate <u>Potassium</u>	(NH ₄) ₂ SO ₄ KH ₂ PO ₄ KH ₂ PO ₄	0, 1.25, 2.5, 5, 10, 20, 30, 50 mgNdm ⁻³ solution 60, 80, 100, 120, 140, 160, 180, 200 mgPdm ⁻³ solution 0, 1.6, 3.2, 6.3, 12.6, 25.3 mgKdm ⁻³ solution

Table 1: Initial concentrations of the test nutrients in the equilibrating solutions used

For each of the nutrients in consideration, the nutrient concentration initial in the equilibrating solution added (Ci) and its concentration in the supernatant equilibrated solutions obtained (Cei) were determined for each sample as appropriate. For ammonium sorption, NH_4^+ -N was determined by steam distilling 10 cm³ of each solution in the presence of magnesium oxide (MgO) and the distillate collected in indicator-boric acid solution (indicators: methyl red and o-phenanthroline). Distillates collected were titrated with standardized 0.002 M HCl solution. The initial and equilibrium solution concentrations of NH_4^+ -N for each treatment were then calculated from the titre values obtained. For the phosphate sorption, PO_4^{3-} - P concentration was determined with one-cm³ of each sample after Murphey and Riley method (ISRIC, 1993). Finally for the potassium sorption, solution K^+ concentration of each sample was measured with Flame Photometer.

Nutrient sorption calculations and sorption plots

The average of the triplicate values of equilibrium concentration (Cei) obtained at each level of nutrient addition was computed for each treatment. The amount of nutrient (Q_{Ai}) in the volume of equilibrating solution added to soil at each level of initial concentration (Ci) is estimated using Eq. 1 while the amount of each nutrient sorbed or desorbed (Qs-di) by the solid soil phase at each level "i" of addition is estimated as the difference between its initial amount in the equilibrating solution added and the amount

remaining in solution after equilibration as given by Eq. 2.

1.
$$Q_{Ai}$$
 (mgdm⁻³ soil) = Ci x V x R / W

2. Qs-di (mgdm⁻³ soil) = (Ci – Cei) x V x R / W

where C*i* is the initial solution concentration of each nutrient in the equilibrating solution used while Ce*i* is its corresponding soil equilibrium solution concentration, both are expressed in mgdm⁻³, *i* is the level of nutrient addition, V is the volume of the equilibrating solution used in cm³, W is the weight of the soil used in grams (g), and R is the soil weight per unit volume in g.cm⁻³. For peat, R is taken to be 0.333 gcm⁻³ and for the mineral soil, it is 1 gcm⁻³.

Amounts of each nutrient added to soil (Q_{Ai}) and the amounts sorbed or desorbed (Qs-di)were both expressed per volume of soil used (dm^3) .

For each nutrient under study, the equilibrium solution concentration (Ce) was plotted as a function of the amount of the nutrient in equilibrating solution added to soil (Q_A). Also, the amount of nutrient sorbed or desorbed (Ns-d) was plotted as a function of its equilibrium solution concentration (Ce).

RESULTS

The soils physico-chemical properties

The results of the chemical analyses of the two soils were presented in Table 2. Both soils are

strongly acidic with pH in water less than 5.0. However, the peat is more acidic (pH 3.72) than the mineral soil (pH 4.94). The mineral soil has high clay content (71.4%) but the peat is mainly organic with high organic matter

Fable 2: Physical and chemi	cal properties of pea	t and mineral soils
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Soil property	Peat soil	Mineral soil
pH (water)	3.72	4.94
pH (0.1 M CaCl ₂)	2.81	4.21
% clay	-	71.4
%WHC	75.3	35.2
Ash content (%)	7.2	-
Organic matter (%)	92.8	-
Total N (%)	1.11	0.21
Total C (%)	57.1	3.85
C/N	51.3	18.1
Exch. K (cmol(+)dm ^{-3} soil)	0.53	0.16
Exch. Na (cmol(+) dm^{-3} soil)	0.43	0.20
Exch. Ca (cmol(+)dm ^{-3} soil)	3.50	2.51
Exch. Mg (cmol(+)dm ^{-3} soil)	1.43	0.11
Exch. Bases (cmol(+) dm^{-3} soil)	5.89	3.00
CEC (cmol(+)dm ^{-3} soil)	49.9	15.5
Base saturation (%)	11.8	19.4
Available NH_4^+ -N (mgdm ⁻³ soil)	66.8	45.5
Water extractable NH_4^+ -N (mgdm ⁻³ soil)	33.2	28.3
Water extractable NO_3 -N (mgdm ⁻³ soil)	16.0	22.0
Available P (mgdm ⁻³ soil)	17.0	5.6
Water extractable P (mgdm ⁻³ soil)	12.9	1.7
P-sorption index (PSI)*	-	1442.2

*PSI of the mineral soil determined by the method according to Pote et al., (1999).

content (92.8%). The peat has higher water holding capacity (75.3%) than the mineral soil (35.2%). The exchangeable cations are comparatively higher in the peat than in the mineral soil. The level of exchangeable potassium of the mineral soil is medium (0.16 $cmol(+)dm^{-3}$) while that of the peat is high (0.53 $cmol(+)dm^{-3}$). The cation exchange capacity (CEC) for the peat (49.9 $cmol(+)dm^{-3}$) is higher than that for the mineral soil (15.5 $cmol(+)dm^{-3}$) The peat has base saturation of 11.8% while that of the mineral soil is19.4%. The available P contents for the two soils are

low (<30 mgPdm⁻³). The mineral soil has high P-sorption index (PSI 1442.2) determined according to Pote et al. (1999).

Ammonium sorption

The plots of equilibrium solution concentration (Ce-N) as a function of amount of N added were linear for both soils (Figure 1) and the slopes were 0.08 and 0.07 for the mineral and peat respectively. The y-intercept for the mineral soil is 3.54 mgNdm⁻³ while that for peat is 4.14 $mgNdm^{-3}$.



Figure 1: Soil equilibrium solution concentration of ammonium-N (Ce-N) versus amount of N added as ammonium ions

Quantity (Q)-Intensity (I) plots for both soils are linear (Figure 2) with positive slopes. With increasing equilibrium solution concentration of ammonium ions, negative sorption by the solid soil phase changes gradually to positive especially for the mineral soil. From the Q-I plots, the equilibrium solution concentration when neither sorption nor desorption occurs (Ceo) is 27.2 mgNdm⁻³ for the mineral soil and 35.7 mgNdm⁻³ for peat. The amount that will be desorbed from the solid soil phase (\Box Qo) when the equilibrium solution concentration of NH₄⁺ ions is zero is 42.8 mgNdm⁻³ soil for the mineral soil and is 66.0 mgNdm⁻³ for peat.



Figure 2: Ammonium-N sorption isotherms: Amount of ammonium- N sorbed or desorbed (QNs-d) against soil equilibrium concentration of ammonium ions (Ce-N)

Phosphate sorption The plots of equilibrium solution concentration (Ce-P) as a function of amount of P added, Figure 3, show that for mineral soil increases curvilinearly with increasing rate of addition while that for peat increases

linearly. In the case of mineral soil, P was first detected in equilibrium solution after addition of 600 mgPdm⁻³ soil. For peat soil, y-intercept

is 0.86 mgPdm⁻³ and the slope of the curve is 0.09.



Figure 3: Soil equilibrium solution concentration of phosphate-P (Ce-P) versus amount of P added as phosphate ions

The Q-I plots for phosphate- P sorption, Figure 4, show there is curvilinear increase in the amount of P sorbed which tends toward maximum with increasing equilibrium solution concentration P while on the other hand for peat soil, there is curvilinear increase in the amount of P desorbed. When the sorption data for the mineral soil was fitted into Langmuir's

equation according to Syers et al. (1973), the sorption characteristics are: adsorption maximum = $1434.3 \text{ mgPdm}^{-3}$ soil and binding energy constant = $5.34 \text{ dm}^3 \text{mg}^{-1}\text{P}$. Conversely for peat, there is no indication of P sorption tendency. The characteristic of the Q-I plot for peat is: $\Box Q \Box = -16.6 \text{ mgPdm}^{-3}$ soil.



Figure 4: Phosphate- P sorption isotherms: Amount of phosphate- P sorbed or desorbed (QPs-d) against soil equilibrium concentration of phosphate ions (Ce-P)

Potassium sorption

The plots of equilibrium solution concentration (Ce-K) as a function of amount of K added were linear for both soils (Figure 5) and the slopes of the curves were 0.06 and 0.04 for the mineral and peat respectively. The y-intercept for the mineral soil is 4.85 mgKdm⁻³ and that for peat is 8.81 mgKdm⁻³.



Figure 5: Soil equilibrium solution concentration of potassium (Ce-K) versus amount of K added as potassium ions

The Q-I plots for both soils are linear (Figure 6) with positive trend in slopes. With increasing equilibrium solution concentration of K ions, negative sorption by the solid soil phase changes gradually to positive especially for the mineral soil. From the Q-I plots, Ceo

for mineral soil is 13.0 mgKdm⁻³ and that for peat soil 19.2 mgKdm⁻³. The \Box Q α for the mineral soil is -81.3 mgKdm⁻³ soil (-0.21 cmol(+)dm⁻³ soil) and that for peat is -217.8 mgKdm⁻³ soil (-0.56 cmol(+)dm⁻³ soil).



Figure 6: Potassium sorption isotherms: Amount of potassium sorbed or desorbed (QKs-d) against soil equilibrium concentration of potassium ions (Ce-K)

DISCUSSION

Table 2, the results of soil In pН measurements show the peat and mineral soils investigated are both strongly acidic (pH <5.0) and with further indication that the peat has greater acidity potential than the mineral soil. Furthermore, the peat has higher amounts of negative charge in its exchange complex as indicated by its high CEC value (49.9 $cmol(+)dm^{-3}$ soil) than the mineral soil (CEC = $15.5 \text{ cmol}(+)\text{dm}^{-3}$ soil). However at their present pH levels, the basic cations (Ca^{2+} , Mg^{2+} , K^+ and Na^+) saturation of the cation exchange sites will be relatively low. The estimated base saturation for the peat is 11.8% while it is 19.4% for the mineral soil. In both cases, the low base saturation level indicates that the substantial portion of the cations exchange sites is occupied by the acidic cations: Al³⁺ and H⁺. This is characteristic of variable charge soils, which quantities of surface charges are pH dependent.

The variable charge surfaces in soils are reportedly resulted from the amphoteric nature of humus, free oxides and hydrated oxides of iron, aluminum and manganese and the broken edges of layer silicate clay minerals and such charges are influenced by the environmental conditions such as pH, concentration and kind of electrolyte, and the specific adsorption of ions (Zhang and Zhao, 1997; Ji and Li, 1997; Ji, 1997; Ross, 1989; Nommik and Vahtras, 1982). Zhang and Zhao (1997) reported that the surface negative charges of four variable charge soils they investigated decreased with decreasing pH of the systems and they concluded that pН is important an environmental factor affecting the surface charges of variable charge soils or their components.

Thus, both the mineral and the peat soils being assessed are characteristically variable charge soils with low base saturation and relatively fewer surface negative charges at their present pH levels. The implications of the resulting few surface negative charges for both soils

when cations are applied to soil are demonstrated in the results obtained from the nutrient sorption experiments with NH_4^+ and K^+ ions in Figures 2 and 6. While the plots showed clearly that the mineral soil sorbed the added NH_4^+ and K^+ ions to some degrees, the same cannot be said of the peat within the equilibrium concentration range observed.

The sorption results indicated both soils have comparably weak affinities for the added NH_4^+ and K^+ ions at their present pH levels and hence, the amounts of both NH_4^+ and K^+ ions that are adsorb by them are low. Ji and Li (1997) have shown that the sorptions of NH_4^+ and K^+ ions by variable charge soils decrease with increasing acidities of soil.

The results of phosphate sorption study (Figure 4) showed that the soils affinities for the added $H_2PO_4^-$ ions are comparatively dissimilar. While the mineral soil showed very strong affinity for the added $H_2PO_4^-$ ions, the peat showed no detectable attraction for the ions. The reason for this disparity in their affinities for added P is because the mineral soil has high amount of clay content (71.4%) while the peat has none (Table 2). Thus, unlike with the mineral soil, there is no detectable sorption of phosphate ions at all levels of P addition to peat. The P-sorptive property of the highly weathered soils of the tropics has been attributed to the presence of clay, and the sesquioxides and hydroxides of Fe and Al (Yu, 1997; Sanyal and De Datta, 1991; Zhang and Zhao, 1997; Yu, 1997; Syers et al., 1973). Also, the study reported by Roy and De Datta (1985) showed that soil inherent physical and mineralogical properties influence P-sorption. So, it is obvious why the peat has no affinity for $H_2PO_4^-$ ions.

The implication of these findings is that while high rates of the soluble phosphate fertilizer addition will be appropriate for use on the mineral soil for crop production because of its high P sorption ability, the same will not be true with the peat because it has no detectable P sorption ability. As Fox and Kamprath (1970) employed P isotherms technique to estimate the P fertilizer requirement of soils at a standard equilibrium solution concentration of 0.2 mgPdm⁻³, so the estimated standard P requirement for the mineral soil is 828.8 $mgPdm^{-3}$ soil. However on this basis, the peat will need no further P addition as the equilibrium P concentration (0.86 mgPdm⁻³) at zero P application already exceeded the value of recommended standard solution Ρ concentration.

In conclusion, the results of the nutrient sorption studies established that the peat weakly sorbed the added NH_4^+ and K^+ ions to comparable degrees as did the mineral soil but will not sorb the added $H_2PO_4^-$ ions. The implications of this poor or no interaction of peat with added NH_4^+ , $H_2PO_4^-$ or K^+ ions will have far reaching implications as regards mineral fertilizers use, the mobility of released NH_4^+ , $H_2PO_4^-$ and K^+ ions in soil and their utilization by Sago palms.

With the poor interaction between peat soil and ammonium, potassium or phosphate ion already established, the recommended rates of fertilizers for oil palm cultivation in peat soil as reported by Yim et al. (1984) will definitely lead to much nutrients loss to the environment.

CONCLUSION

The sorption property of soils has controlling influence on the intensities of plant nutrients in soil solution after application of soluble fertilizers. This nutrient regulatory property determines rate of nutrients uptake by plant roots, nutrients accumulation in plant tissues and the subsequent physiological growth of the plants. Also, this property explains the ability or inability of soil colloids to hold the released nutrient ions from the applied source against leaching losses and it also influences nutrient movements by diffusion and mass or leaching flow mechanisms within soil systems.

With regard to these, we established from the results that peat soil in its present physicochemical and environmental conditions will poorly sorb added ammonium and potassium ions and will not sorb added phosphate ions. Peat soil, being a variable charge soil, has fewer amounts of surface negative charge at a low pH and thus possesses poor ability to sorb added ammonium and potassium ions. On the other hand, the absence of clay minerals and the oxides of aluminum and iron in peat layer is responsible for the inability of peat soil to sorb added P ions. For these reasons, when soluble sources of N, P and K were applied to peat, virtually the nutrient ions released get associated with the solution soil phase rather than the solid soil phase and hence increase in the solution concentration of NH_4^+ , NO_3^- , $H_2PO_4^+$, and K^+ will develop in proportion to the amount of application and will be weakly constrained by soil. In this regard, if high rate of the N, P or K fertilizer is applied to peat, both in potted or field situations, high solution concentrations of the nutrients will be generated that may reach phytotoxic level and impact negatively on the growing plants. Also, poor nutrients sorption will exacerbate leaching losses of applied nutrients in drained peat leading to pollution of water bodies.

With the growing awareness on the negative implications to environment of chemical fertilizers use in crop production, guarded use of soluble N, P and K fertilizers on peat soil becomes inevitable. This is in line with the International Fertilizer Industry Association (IFA) positional statements advocating responsible, effective and efficient use of mineral fertilizers in accordance with scientific recommendations (IFA, 2002a; 2002b; 2001a; 2001b).

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