SOIL ACIDIFICATION AND LIMING INTERACTIONS WITH NUTRIENT AND HEAVY METAL TRANSFORMATION AND BIOAVAILABILITY

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"No other single chemical soil characteristic is more important in determining the chemical environment of higher plants and soil microbes than the pH. There are few reactions involving any component of the soil or of its biological inhabitants that are not sensitive to soil pH. This sensitivity must be recognized in any soil-management system."

"Lime is truly a foundation for much of modern humid-region agriculture. Knowing how pH is controlled, how it influences the supply and availability of essential plant nutrients as well as toxic elements, how it affects higher plants and human beings, and how it can be ameliorated is essential for the conservation and sustainable management of soils throughout the world."

(Brady and Weil, 1999)

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Under areas where rainfall exceeds evapotranspiration, soil acidification is an ongoing natural process, which can either be accelerated by the activity of plants, animals and humans or can be impeded by careful management practices. In areas affected by industrial activities, soil acidification is caused by acid drainage from pyrite oxidation and also from acid precipitation. In areas that remain unaffected by industrial pollution, soil acidification in managed ecosystems is mainly caused by the release of protons (H^+) during the transformation and cycling of carbon (C), nitrogen (N) and sulfur (S). Just like in managed ecosystems, soil acidification in natural ecosystems caused by acid drainage and acid precipitation can have adverse impacts where soils have low pH buffering capacity. Liming is the most common management practice aimed at neutralizing the acid produced, thereby overcoming the adverse impacts of soil acidification.

This review brings together fundamental aspects of soil acidification and recent developments on the implications of liming in relation to soil processes, particularly nutrient and heavy metal transformation and bioavailability in soils. The article first outlines the various soil, plant and microbial processes that generate acid (protons; H^+ ions) both under natural and managed ecosystems. It then discusses the effects of soil acidity on soil chemical and biological properties. The effect of liming to overcome the problems associated with soil acidity is examined in relation to the transformation of nutrient ions and heavy metals. The practical implications of liming to overcome heavy metal toxicity have been discussed in relation to the adsorption, leaching and phytoavailability of these metal ions. Future research should aim to focus on the development of methods to quantify lime-enhanced (im)mobilization of nutrient ions and heavy metals in soils and to explore further the role of liming in remediating contaminated soils.   © 2003 Academic Press.

I. INTRODUCTION

Soil acidification is a natural process, which can either be accelerated by the activity of plants, animals and humans or can be impeded by sound management practices. Industrial and mining activzities can lead to soil acidification through acid drains resulting primarily from pyrite oxidation and from acid precipitation caused by the emission of sulfur (SO_x) and nitrogen (NO_x) gases. In areas that remain unaffected by industrial pollution, soil acidification is mainly caused by the release of H^+ ions during the transformation and cycling of C, N and S in managed ecosystems. Soil acidification can exert itself in several ways: (a) increase of soil acidity or decrease of pH, (b) decrease of base saturation, (c) unbalanced availability of elements in the root environment, or (d) decrease of the acid neutralizing capacity (ANC) of the soil (van Breemen, 1991). Soil acidification caused by these processes can have adverse impacts where soils are unable to buffer against pH decrease. For example, in parts of North America and Europe, soil acidification caused by acid precipitation has resulted in forest

decline (Binns, 1988; Longhurst, 1991) and in some parts of Australia, continuous legume cultivation and inappropriate N fertilizer use have generated sufficient soil acidity that wheat cultivation has had to be abandoned due to aluminium (Al) and manganese (Mn) toxicity (Dolling and Porter, 1994; Mason *et al.*, 1994).

Soil acidity causes detrimental effects to both plants and soil organisms (Robson and Abbott, 1989; Runge and Rode, 1991). In excessively acid soils (pH < 4.0) many plants do not grow well. The activities of soil organisms generally are reduced, resulting in the inhibition of biological N fixation by legumes and decomposition of organic matter. In acid soils, the concentrations of Al and Mn become toxic to plant growth. Likewise soil acidification enhances the mobilization of metals in soils, resulting in increased uptake by plants. Some of these toxic metals subsequently reach the food chain through plant products and grazing animals. Phosphorus (P) and molybdenum (Mo) may become insoluble and unavailable, and low pH may indicate the deficiency of basic essential cations, such as calcium (Ca) and magnesium (Mg) in soils (Ritchie, 1989; Sumner *et al.*, 1991).

Historically, liming is the most common management practice used to neutralize the acid produced in the soil and to overcome the problems associated with soil acidification. Most plants grow well at a pH range of 5.5–6.5 and liming is aimed to maintain the pH at this range. Liming enhances the physical, chemical and biological properties of soil through its direct effect on the amelioration of soil acidity and its indirect effect on the mobilization of plant nutrients, immobilization of toxic heavy metals, and improvements in soil structure and hydraulic conductivity (K_s). In variable charge soils, liming can be used as a management tool to manipulate the surface charge, thereby controlling the reactions of nutrient ions and heavy metal cations. Liming has been shown to provide optimum conditions for a suite of biological activities that include N fixation and mineralization of N, P and S in soils (Haynes and Naidu, 1998; Bolan *et al.*, 1999a).

Although the effect of acidification on chemical reactions of soils in relation to plant growth has been reviewed by a number of workers (e.g., Reuss, 1986; Sumner *et al.*, 1991), no comprehensive review on the effect of soil acidification in relations to environmental contamination has been presented. Similarly, the effect of liming has often been examined in relation to overcoming nutrient deficiencies and metal toxicity (primarily Al and Mn) for optimum plant growth. For example, Ritchie (1989) reviewed the reactions of Al and Mn, which are considered to be the major growth liming factors resulting from soil acidification. Similarly, the interaction of lime and P has been reviewed by Haynes (1984). Recently liming materials and stabilized alkaline by-products are increasingly being used to immobilize heavy metals in soils receiving industrial and domestic waste sludges (Dick *et al.*, 2000; Adriano, 2001). However, no comprehensive review on liming interactions with the transformation and (im)mobilization of nutrient ions and heavy metals in

soils in relation to sustainable production and environmental protection has been published. Liming is increasingly being viewed as a management tool in enhancing the natural attenuation of nutrient and heavy metal contaminants in soils (Adriano, 2001).

The present review aims to integrate fundamental aspects of soil acidification and recent developments on the implications of liming in relation to biogeochemical processes, particularly its interactions with nutrients and heavy metals in soils. The review first discusses the various processes that generate acid (protons; H^+ ions) from acid precipitation and pyrite oxidation, resulting from industrial activities, and during the cycling of C, N and S in managed farming systems. The detrimental effects of soil acidity on plant growth and microbial functions, and the beneficial effects of liming to overcome the problems associated with soil acidity are examined in relation to the transformation and bioavailability of nutrients and heavy metals. More specifically, the development of methods to quantify lime-enhanced mobilization of nutrient ions and immobilization of heavy metals in soils and to explore the role of liming in remediating contaminated soils are discussed further.

II. PROCESSES OF ACID GENERATION IN SOILS

Understanding the processes involved in acid generation in soils and determining the underpinning causes are precursors to the implementation of preventive measures to reduce acid input to soils. These processes can be broadly grouped into two categories: (i) those occurring under natural ecosystems through industrial activities, and (ii) those occurring under managed ecosystems through farming activities. The various reactions involved in these processes are given in Table I.

A. NATURAL ECOSYSTEMS

The two most important acid generating processes under natural ecosystems resulting from industrial activities occur with acid drainage through pyrite oxidation, and acid precipitation (Longhurst, 1991; Evangelou, 1995). While the first process occurs at local level, the second process leads to acidification of sites further away from the origin of acid precipitation and hence warrants international collaborative effort to overcome the problems associated with this process (Reuss, 1986).

Table I
Proton Generation and Consumption Processes in Acid Precipitation, Pyrite Oxidation and C, N and S Biogeochemical Cycles

Process	Reaction equation	H^+ $(mol_c \cdot mol^{-1})$	Eq. No
	Acid precipitation		
Oxidation of sulfur dioxide	$2SO_2 + O_2 \rightarrow 2SO_3$	0	1
Hydrolyis of sulfur trioxide	$SO_3 + H_2O \rightarrow H_2SO_4 \rightarrow SO_4 + 2H^+$	+2	2
Photochemical oxidation of nitric oxide	$O_3 + NO \rightarrow N_2O_+O_2$	0	3
Hydrolyis of nitrogen dioxide	$2NO_2 + H_2O \rightarrow HNO_3 + HNO_2 \rightarrow NO_3 + H^+$	+1	4
	Pyrite oxidation		
Pyrite oxidation by oxygen	$2FeS_2 + 7O_2 + 2H_2O \rightarrow 2Fe^{2+} + 4SO_4^{2+} + 4H^+$	+2	5
Ferrous iron oxidation	$4Fe^{2+} + O_2 + 4H^+ \rightarrow 4Fe^{3+} + 2H_2O$	−1	6
Ferric iron precipitation	$Fe^{3+} + 3H_2O \rightarrow Fe(OH)_3 + 3H^+$	+3	7
Pyrite oxidation by ferric iron	$FeS_2 + 14Fe^{3+} + H_2O \rightarrow 15Fe^{2+} + 2SO_4^{2+} + 16H^+$		8
	Carbon cycle		
Dissolution of carbon dioxide	$CO_2 + H_2O \rightarrow H_2CO_3 \rightarrow H^+ + HCO_3^-$	+1	9
Synthesis of organic acid	Organic $C \rightarrow RCOOH \rightarrow RCOO^- + H^+$	+1	10
	Nitrogen cycle		
N fixation	$2N_2 + 2H_2O + 4R \cdot OH \rightarrow 4R \cdot NH_2 + 3O_2$	0	11
Mineralization of organic N	$RNH_2 + H^+ + H_2O \rightarrow R \cdot OH + NH_4^+$	−1	12
Urea hydrolysis	$(NH_2)_2CO + 3H_2O \rightarrow 2NH_4^+ + 2OH^- + CO_2$	−1	13
Ammonium assimilation	$NH_4^+ + R \cdot OH \rightarrow R \cdot NH_2 + H_2O + H^+$	+1	14
Ammonia volatilization	$NH_4^+ + OH^- \rightarrow NH_3 \uparrow + H_2O$	+1	15

Table I (*continued*)

Process	Reaction equation	H$^+$ (mol$_c$ mol^{-1})	Eq. No
Nitrification	$NH_4^+ + 2O_2 \rightarrow NO_3^- + H_2O + 2H^+$	+2	16
Nitrate assimilation	$NO_3^- + 8H^+ + 8e^- \rightarrow NH_3 + 2H_2O + OH^-$	−1	17
Denitrification	$4NO_3^- + 4H^+ \rightarrow 2N_2 + 5O_2 + 2H_2O$	−1	18
	Sulfur cycle		
Mineralization of organic S	$2\text{Organic S} + 3O_2 + 2H_2O \rightarrow 2SO_4^{2-} + 4H^+$	+2	19
Assimilation of sulfate	$SO_4^{2-} + 8H^+ + 8e^- \rightarrow SH_2 + 2H_2O + 2OH^-$	−2	20
Oxidation of S^0	$2S^0 + 2H_2O + 3O_2 \rightarrow 2SO_4^{2-} + 4H^+$	+2	21

1. ACID DRAINAGE

Acid drainage has various anthropogenic and natural sources, but the most extensive and widely known source originates from mining coal and various sulfide-rich metal ores, including copper, gold, lead and silver. Other human activities that contribute to acid drainage include various forms of land disturbances, such as industrial and residential development and farming (e.g., rice cultivation). Generally, strong acid forming processes in nature involve exposure of metal-sulfides enriched with heavy metals or metalloids to atmospheric air, which leads to oxidation and acidification of water bodies and their subsequent enrichment with total dissolved solids, including metals and metalloids. Other contributors to acid drainage production include mineral processing, manufacturing or recycling of batteries, electronics, wood pulp, paper and heavy steel industries, such as manufacturing of cars or heavy equipment, tanneries and textile manufacturing, food processing, and waste disposal/management industries. Oxidation of pyrite is considered as the major source of acid drainage prompting intensive efforts to minimize the production of pyrite–borne acid drainage and mitigation measures to alleviate its environmental impacts (Evangelou and Zhang, 1995; Frazer, 2001).

Pyrite is a mineral commonly associated with coal and various metal ores as well as mine deltas, wetlands, and rice fields. Often, pyrite becomes exposed to the atmosphere through various human activities including, mining, land development for agricultural purposes, and construction of highways, tunnels,

airports and dams. Pyrite exposure to the atmosphere leads to its oxidation and the subsequent production of extremely acidic drainage typically enriched with iron (Fe), Mn, Al and sulfate (SO_4^{2-}) and other heavy metals. The acidic drainage caused by pyrite oxidation not only acts as a source of heavy metals associated with the parent minerals but also serves as an agent for the solubilization and the transport of heavy metals in the soils through which it drains (Evangelou, 1995; Mays and Edwards, 2001).

Pyrite oxidation is mediated by biological and electrochemical reactions, some of which are given in Table I. Reactions (1) and (3) indicate that Fe^{3+} and O_2 are the major sources of electron acceptor for pyrite oxidation. At low pH (<4.5), Fe^{3+} oxidizes pyrite much more rapidly than does O_2 and more rapidly than O_2 oxidizing Fe^{2+} to Fe^{3+} (Evangelou and Zhang, 1995). For this reason, Reaction (6) is considered to be the rate-limiting step in pyrite oxidation. Reaction (7) is a readily reversible dissolution/precipitation reaction taking place at pH as low as 3, and is a major step in the release of acid to the environment. Abiotic oxidation of Fe^{2+} with O_2 is pH sensitive and is extremely slow in very acidic solution.

The mechanisms of pyrite oxidation mediated by microorganisms are grouped into (a) direct metabolic reactions, and (b) indirect metabolic reactions (Evangelou and Zhang, 1995). Direct metabolic reactions require physical contact between the bacteria and pyrite particles, while indirect metabolic reactions do not require such physical contact. During the indirect metabolic reactions, the bacteria typified by *Thiobacillus ferrooxidans* and *T. thiooxidans* oxidize Fe^{2+}, thereby regenerating the Fe^{3+} required for the chemical oxidation of pyrite. While *T. ferrooixdans* is active in the oxidation of both Fe^{2+} and sulfides, *T. thiooxidans* is involved only in the oxidation of sulfides. In the presence of *T. ferrooxidans*, Fe^{2+} oxidation is very rapid in acidic conditions. At neutral to alkaline pH, there is minimal bacterial involvement in pyrite oxidation and in such environment O_2 becomes a more important pyrite oxidant than Fe^{3+}. Under most conditions, however Fe^{3+} plays a major role in pyrite oxidation and O_2 is involved in the oxidation of Fe^{2+} (Evangelou and Zhang, 1995; Benner *et al.*, 2000; Frazer, 2001).

2. ACID PRECIPITATION

Carbon dioxide combines with water in the air to form a dilute solution of carbonic acid (H_2CO_3) at about pH 5.6. For this reason, acid precipitation is arbitrarily defined as precipitation with a pH below 5.6. The acidity of rain, snow and atmospheric particulates that fall upon much of the world appears to have increased significantly over the last four decades. In addition to natural sources of acid precipitation that results from geological weathering, volcanic eruption,

anaerobic decomposition of organic matter, air-borne sea salt sprays, and lightning, most of the increased acid precipitation burden has been attributed to consumption of fossil fuels, especially coal. Major anthropogenic sources include combustion of fossil fuels, smelting of ores, exhausts from internal combustion engines, and N fertilization of agricultural and forest lands (Binns, 1988; Longhurst, 1991).

Widespread occurrence of acid precipitation and dry deposition results in large part from industrial emissions of SO_x and NO_x (Longhurst, 1991). These gases are transformed in the atmosphere to sulfuric and nitric acids (Table I), transported over long distances and deposited on vegetation, soils, surface water, and building materials. While majority of the NO_x emissions are local/ natural origin, SO_x emissions are often transboundary in nature (Table II). The average annual ratio of sulfuric acid to nitric acid is about 2:1 in North America, but nitric acid is becoming progressively more important because of the installation of flue gas desulfurization (FGD) systems in coal-fired power stations (Dick *et al.*, 2000).

Acidification of lakes and streams in North America and Europe has altered their trace metal chemistry by (Adriano, 2001): (i) increasing total metal concentrations; (ii) shifting the speciation of dissolved metals toward free aqueous ions, typically the species most toxic to aquatic biota; and (iii) reducing particulate metal concentration in favor of higher dissolved levels. The impact of acidification on terrestrial ecosystems is less straightforward; forest health may be one casualty, but that could also be affected by increasing tropospheric ozone. Where

Table II
Annual Emission of Sulfur Dioxide and Nitrogen Oxide from Various Countries

Country	Emissions (10^3 tonnes)		Sulfur dioxide deposition (%)	
	Sulfur dioxide	Nitrogen oxide	Foreign	Domestic
USSR	24 000	2930	32	53
USA	20 800	19 400		
China	18 000	4130	–	90
Poland	4300	840	52	42
Germany	6400	2900	45	48
Canada	3727	1785	50	50
United Kingdom	3540	2900	12	79
Czechoslovakia	3040	1100	56	37
France	1845	1693	32	54
Finland	370	250	55	26
Sweden	272	305	58	18
Norway	100	215	63	8

however, acidic emissions have been reduced and where mitigating measures have been employed there is some evidence that affected ecosystems can recover (Longhurst, 1991).

B. MANAGED ECOSYSTEMS

The most significant H^+ and hydroxyl ion (OH^-) generating processes occur during the biogeochemical cycling of C, N and S (Table I). Although these processes occur both under natural and managed ecosystems, under the latter system, these processes are accelerated by the activities of humans through intensive land-based crop and animal production. In the case of the C cycle, dissolution of CO_2 to form H_2CO_3 in soil solution and synthesis and dissociation of carboxylic acids produced by plants and microorganisms are the two main sources of H^+ ions. The assimilation of CO_2 into carboxylic acids (including amino and fatty acids) in higher plants indirectly acidifies the soil explored by their roots.

In the case of the N and S cycles, mineralization and oxidation of organic N and S result in the production of H^+ ions. However, this will be balanced by OH^- generated through uptake and assimilation of $NO_3^- - N$ and $SO_4^{2-} - S$ by plant and microorganisms. Leaching of SO_4^{2-} and NO_3^- with a charge-balancing basic cation (Ca, Mg, potassium (K), or sodium (Na)) rather than the H^+ ions generated during oxidation results in permanent acidity remaining in the soil. This will be reflected in a decrease in pH in soils with low pH buffering capacity.

The processes involved in the generation of H^+ and OH^- ions during C, N and S cycling in soils can be grouped into two main categories: plant-induced—the uptake and assimilation of C, N and S; and soil-induced—the transformation of C, N and S in soils. These processes can have a bearing on the extent of bio-availability of certain plant nutrients, and the natural attenuation of heavy metals in the root zone (Adriano, 2001). In managed ecosystems used for agricultural production, regular fertilizer use is one of the major contributors of soil acidification.

1. PLANT-INDUCED PROCESSES

CARBON ASSIMILATION. In higher plants, C is first assimilated as carbohydrates during the photosynthetic process. The subsequent metabolism of the photosynthates results in the synthesis of organic acids, such as malic and oxalic acids. At the cytoplasmic pH of the plants (pH 7.2–7.4), some of the carboxyl groups of simple acids, amino acids, proteins and more complex structural carbohydrates (e.g., pectin) dissociate to produce H^+ ions (Raven,

1985). The excess H^+ ions are disposed of by neutralization resulting from decarboxylation, by transport into the vacuole, or by transport via the phloem into the roots and thence into the soil solution. Excretion of H^+ into the surrounding aqueous medium is the usual means of pH regulation in aquatic plants. In the case of terrestrial plants, some species counteract the change in cytoplasm pH by excreting H^+ ions into the soil solution, at the same time taking in a basic nutrient cation to balance the charge (Felle, 1988).

UPTAKE AND ASSIMILATION OF NITROGEN. Plants utilize N in three main forms—as an anion (nitrate, NO_3^-), as a cation (ammonium, NH_4^+), or as a neutral N_2 molecule (N_2 fixation) (Marschner, 1995). Depending upon the form of N taken up and the mechanism of assimilation in the plant, excesses of cation or anion uptake may occur. To maintain charge balance during the uptake process, H^+, OH^- or bicarbonate (HCO_3^-) ions must pass out of the root into the surrounding soil. The H^+ ions may be derived from the dissociation of organic acids within the cell, and OH^- and HCO_3^- ions from the decarboxylation of organic acid anions. It has been shown that while the uptake of NH_4^+ and N_2 fixation results in a net release of H^+ ions, uptake of NO_3^- can result in a net release of OH^- ions (Haynes, 1990).

(i) *Nitrogen fixation.* In the case of N_2 fixation, the neutral N_2 can be assimilated into protein and no charge imbalance is generated across the soil/root interface. Many legumes, however, commonly export H^+ ions into their rhizosphere when actively fixing N_2 (Haynes, 1983; Liu *et al.*, 1989). Part of the H^+ ions generated within the legume root comes from the dissociation of the carboxyl groups of amino acids. The acidity generated by legume fixation of N_2 has been found to be equivalent to the excess uptake of cations over anions by the plant and to vary from 0.2 to 0.7 mol H^+ mol^{-1} of fixed N (Helyar, 1976; Bolan *et al.*, 1991; de Klein *et al.*, 1997).

The amount of H^+ ions released during N_2 fixation is a function of C assimilation and therefore depends mainly on the form and amount of amino acids and organic acids synthesized within the plant (Raven, 1985). Some tropical legumes apparently do not acidify their rhizosphere as much as do temperate legumes when actively fixing N_2 (Israel and Jackson, 1978; Tang *et al.*, 1997). Part of the reason for this is that their N assimilation products appear to be ureides (allantoin and allantoic acid) that have high pK_a values (e.g., allantoin pK_a 8.96) and are therefore unlikely to dissociate and donate H^+ ions under cytoplasmic and xylem pHs. Thus many tropical legumes accumulate less cations than do temperate legumes (Andrew and Johnson, 1976). The ability of N fixing plants to accumulate metal cations can be considered as a means of enhancing phytoremediation of metal-contaminated soils.

(ii) *Ammonium and nitrate assimilation.* When NH_4^+ assimilation occurs in roots, deprotonation of NH_4^+ releases one mole of H^+ per mole of NH_4^+ (Eq. (14)). Additional small amounts of H^+ ions are generated during the assimilation

of the deprotonation product, R·NH$_2$ into amino acids and proteins which have isoelectric pHs lower than the cytoplasmic pH (Raven, 1985). When plants take up N in the form of NO$_3^-$ ion, the NO$_3^-$ ion is first reduced to NH$_4^+$, which is subsequently assimilated into amino acids. When NO$_3^-$ is reduced in roots, for every mole of NO$_3^-$ reduced to NH$_4^+$ one mole of OH$^-$ ion is produced (Eq. (17)). When NH$_4^+$ is assimilated into amino acids, small amounts of H$^+$ ions are produced through the dissociation of the carboxyl groups of amino acids. The net excess of OH$^-$ ions can either be excreted into the rooting medium or can be neutralized by H$^+$ ions produced during the dissociation of organic acid (Raven, 1985).

UPTAKE AND ASSIMILATION OF SULFUR. Sulfate is assimilated into S-containing amino acids (cysteine, cystine and methionine) in the form of sulfydryl ($-$SH) group (Saggar *et al.*, 1998). This reduction process is similar to NO$_3^-$ assimilation and produces two net moles of OH$^-$ for each mole of S assimilated (Eq. (20)). Upon deprotonation of sulfydryl-containing amino acids, two H$^+$ ions are generated for each mole of $-$SH oxidized to SO$_4^{2-}$. Since plants require 10 times less S than N, assimilation of SO$_4^{2-}$ has only a small effect on H$^+$ balance in plants, and likewise deprotonation of S-containing proteins contributes little to H$^+$ generation in soils.

2.   SOIL-INDUCED PROCESSES

DECOMPOSITION OF ORGANIC MATTER. As microorganisms decompose soil organic matter, they respire CO$_2$, which dissolves in water to form H$_2$CO$_3$ (Eq. (9)). The continuous production of CO$_2$ through soil and root respiration increases the concentration of CO$_2$ in the soil air space, so the extent of soil acidity from this source is considerably greater than that from CO$_2$ dissolved in rainwater. However, acidic soil solutions at around pH 5 hold very little CO$_2$. Thus, respiration is unlikely to cause soil pH to drop below 5.

Soil microorganisms produce organic acids when decomposing plant litter that is rich in organic compounds but low in basic cations (Eq. (10)). A number of low-molecular-weight organic acids have been isolated from soils (Uren, 2001). Depending upon the nature of the plants growing in a particular soil, different amounts and diversity of organic acids are generated from the litter. In general, forest soils that have thick litter layer tend to be more acidic than grassland soils. Further, the litter from conifers tends to produce more organic acids when decomposed than the leaf fall from deciduous woodlands (Parfitt *et al.*, 1997).

TRANSFORMATION OF NITROGEN. Nitrification and ammonia (NH$_3$) volatilization processes result in the release of H$^+$ ions. Both heterotrophic and

autotrophic microorganisms are involved first, in the conversion of organic forms of N to NH_4^+–N (ammonification), and subsequent oxidation of NH_4^+ to NO_3^- (nitrification). While the ammonification process results in the release of OH^- ions, the nitrification process results in the release of H^+ ions. Combined ammonification (Eq. (12)) and nitrification (Eq. (16)) of organic N compounds, including urea, in theory generate one net mole of H^+ for every mole of N transformed.

Ammonium ions in an alkaline medium dissociate into gaseous NH_3, which is subject to volatilization loss (Eq. (15)). During NH_3 volatilization, the pH of the soil decreases due to the consumption of OH^- ions (or release of H^+ ions) as NH_4^+ is converted to NH_3. Ammonia volatilization occurs when the soil pH is high (>7.5). When N is applied in the form of urea (e.g., urea fertilizer and animal excreta) the initial increase in soil pH through the ammonification process is likely to result in NH_3 volatilization.

TRANSFORMATION OF SULFUR. In aerobic soils, large proportion of S is present in organic form in roots, undecomposed litter and humified organic matter. Sulfur in soil organic matter and plant litter is mainly present as sulfydryl (–SH) groups in proteins, nucleic acids and sulfolipids and bonded directly to C (Saggar *et al.*, 1998). Protons are produced during the mineralization and subsequent oxidation of S in soil organic matter (Eq. (19)). As soil bacteria and fungi grow on plant litter and soil organic matter rich in C and poor in S, soil solution SO_4^{2-} may be immobilized. In this case Eq. (19) in Table I is reversed and becomes a H^+-consuming reaction as SO_4^{2-} is assimilated to microbial protein.

In periodic anaerobic conditions that occur following aerobic generation of SO_4^{2-}, O_2 concentration may be depleted by rapidly growing bacteria. Some bacteria have the capacity to use SO_4^{2-} as a terminal electron acceptor for fermentation. The result is H^+ consumption as SO_4^{2-} is reduced along a chain of intermediate compounds to H_2S. It is common for H_2S to react with metal ions to precipitate as metal sulfides (Cowling *et al.*, 1992). This process is a H^+-consuming process. However, when these metal sulfides are reoxidized, they generate H^+ and acidify the soil (acid drainage). This sequence of reactions are common in soils used for lowland rice cultivation and results in a phytophillic neutral pH when waterlogged, but can create low phytotoxic pH when the soil is in the aerobic state (Li *et al.*, 2001).

3.   FERTILIZER USE AND SOIL ACIDIFICATION

Fertilizer application in managed ecosystems used for agricultural production is a major contributor to soil acidification and it is important to understand

Table III
Nutrient Content and Acidity Equivalent of Various Fertilizers

Fertilizer	Chemical formula	Nutrient content (% w/w)				Acidity [a] equivalent
		N	P	K	S	
Ammonium sulfate	$(NH_4)_2SO_4$	21	0	0	24	110
Ammonium chloride	NH_4Cl	26	0	0	0	93
Ammonium nitrate	NH_4NO_3	33	0	0	0	60
Diammonium phosphate	$(NH_4)_2HPO_4$	18	20	0	0	74
Monoammonium phosphate	$NH_4H_2PO_4$	11	21	0	0	55
Urea	$CONH_2CO$	46	0	0	0	79
Potassium nitrate	KNO_3	14	0	39	0	-23
Calcium nitrate	$Ca(NO_3)_2$	14	0	0	0	-50
Sodium nitrate	$NaNO_3$	16	0	0	0	-29
Nitrogen fixation	–	–	–	–	–	$70-250$
Single superphosphate	$Ca(H_2PO_4)_2. CaSO_4.2H_2O$	0	10	0	12	8
Triple superphosphate	$Ca(H_2PO_4)_2$	0	18	0	1	15
North Carolina phosphate rock	$Ca_{10}(CO_3)_x(PO_4)_{6-x}F_2$	0	13	0	0	-50
Calcium sulfate	$CaSO_4.2H_2O$	0	0	0	18	-57
Potassium sulfate	K_2SO_4	0	0	50	18	-64
Elemental sulfur (S^0)	S^0	0	0	0	100	310

[a]Acidity equivalent is the number of parts by weight of pure lime (calcium carbonate) required to neutralize the acidity caused by 100 parts of the fertilizer. Negative values indicate the liming value (kg $CaCO_3$/100 kg) of the fertilizer.

the mechanisms involved in the acidifying effects of different fertilizers. The effects on soil acidification of various fertilizers used as sources of the major nutrients N, P, and S are discussed in the following section. The nutrient contents and the acidifying effects of the most common fertilizers used in agricultural production are presented in Table III.

NITROGEN FERTILIZERS. Nitrogen is derived from fertilizer and manure applications and also from biological fixation of the atmospheric N by leguminous plants. Fixation of atmospheric N and the subsequent leaching of NO_3^- formed from the mineralization of the fixed N result in soil acidification, the extent of which depends on the amount and the fate of N fixed. It has been shown that in high producing pastures, approximately $400-550$ kg $CaCO_3$ ha^{-1} is required annually to neutralize the acidity produced by these processes (Bolan et al., 1991; de Klein et al., 1997).

Application of N fertilizers, such as urea and ammonium sulfate to soils produces H$^+$ by two processes: nitrification (Eq. (16)) and NO_3^- leaching. Part of the H$^+$ produced is neutralized by OH$^-$ released by the plants during

the subsequent uptake of the NO_3^- ions (Eq. (17)). The negatively charged NO_3^- ions carry positively charged basic cations (Ca, K, Mg and Na) in order to maintain the electric charge on the soil particles. The depletion of these basic cations during the leaching of NO_3^- ions accelerates the acidification process. In cases where ammonium sulfate is used the transport of both the SO_4^{2-} and the NO_3^- ions in the soil causes greater depletion of basic cations. With urea, the initial conversion of amide N to NH_4^+–N (ammonification) releases OH^- ions (Eq. (13)) which neutralize part of the H^+ produced during the subsequent oxidation of NH_4^+ ions to NO_3^- ions, which explains why urea-based N fertilizers are less acidifying than the NH_4^+-based fertilizers (Table III).

PHOSPHATE FERTILIZERS. Superphosphates are the most common phosphate fertilizers used and monocalcium phosphate (MCP) is the principal P component present in superphosphate fertilizers. Dissolution of MCP in soils results in the formation of dicalcium phosphate with a release of phosphoric acid close to the fertilizer granules. Phosphoric acid subsequently dissociates into phosphate ($H_2PO_4^-$) and H^+ ions. Part of H^+ is subsequently neutralized by the OH^- ions released during the adsorption of the $H_2PO_4^-$ ions by soil particles. Since the $H_2PO_4^-$ ions are strongly adsorbed by most soils, $H_2PO_4^-$-induced leaching of basic cations is unlikely to occur.

In legume-based pasture and crop production systems, phosphate fertilizers are added mainly to promote the N fixation by the legumes by overcoming soil deficiency of P. It is important to point out that irrespective of P fertilizer source, application of P to legume-based systems promotes N fixation, thereby indirectly causing soil acidification. The amount of acidity produced indirectly by N fixation depends mainly on the extent of NO_3^- leaching and is higher than that produced directly by the dissolution of MCP in superphosphate fertilizer granules (Table III).

In recent times, increasing amounts of phosphate rocks (PRs), such as North Carolina Phosphate rock (NCPR) are added directly to soils as a source of P. Unlike superphosphate fertilizers, PRs neutralize acids, thus adding some liming value. The liming action of PRs is discussed in Section IV.

SULFATE FERTILIZERS. Gypsum, a component of single superphosphate, and S^0 are the most common sources of S in pasture soils. Since gypsum contains both Ca^{2+} and SO_4^{2-} ions, leaching of SO_4^{2-} is unlikely to completely deplete the added Ca^{2+}. Elemental sulfur (S^0) is frequently used as an acidifying agent, slow-release S fertilizer, or in a finely divided form as a fungicide. When S^0 is added to soils, it is oxidized to sulfuric acid which dissociates into SO_4^{2-} ions and H^+ ions (Eq. (21)). In some soils, part of the acidity is neutralized by the OH^- ions released during the ligand-exchange adsorption of SO_4^{2-}. Increases in soil pH due to the ligand-exchange adsorption of SO_4^{2-}, commonly referred to as "self-liming

effect," has often been observed in soils rich in variable charge components, such as Fe and Al oxides (Reeve and Sumner, 1972).

CHANGES IN SOIL pH DUE TO FERTILIZER ADDITION. When plants are grown in unbuffered nutrient medium supplied with different forms of N, the release of H^+ and OH^- ions alters the pH of the medium. In soils, however, acidification is effected either by a decrease in soil pH or by a decrease in ANC. The extent of soil acidification depends mainly on the pH buffering capacity of soils. Soil constituents, such as organic matter, Fe and Al oxides and $CaCO_3$ (in calcareous soils) contribute to the pH buffering capacity of soils. Thus soils vary in their pH buffering capacity. For example, New Zealand soils generally have higher buffering capacity than Australian soils. In Table IV, the amount of acidity produced and the number of years required to reduce the pH by one unit for the top 7.5 cm of two soils (with different pH buffering capacities) due to fertilizer additions are presented. It is obvious that continuous application of ammonium sulfate and ammonium phosphates is likely to acidify the soils more quickly, particularly in soils with low pH buffering capacity. Although S^0 can be used as an acidifying agent, at the normal application rate of 30 kg S ha^{-1}, the acidity produced by the oxidation of S^0 is negligible when compared to the ability of most New Zealand soils to resist pH change. Similarly the acidity produced from the dissolution of superphosphate is unlikely to cause any significant measurable change in the pH of the bulk soil.

Table IV
Acidifying Effects of Various Fertilizers

Fertilizer	Acidity equivalent[a]	Acidity produced (kmol H^+ ha^{-1})[b]	Number of years required to reduce the pH by one unit[c]	
			Tokomaru	Egmont
Ammonium sulfate (AS)	110	2.60	8	26
Diammonium phosphate (DAP)	74	2.06	10	33
Urea	79	0.86	25	78
Single superphosphate (SSP)	8	0.48	45	140
Triple superphosphate (TSP)	15	0.50	43	135
Elemental sulfur (S^0)	310	1.55	14	43

[a]kg $CaCO_3$100 kg^{-1} fertilizer.
[b]AS, DAP and Urea added at the rate of 25 kg N ha^{-1} year^{-1}; SSP and TSP at the rate of 30 kg P ha^{-1} year^{-1}; and S^0 at the rate of 30 kg S ha^{-1} year^{-1}.
[c]pH buffering capacity (kmol H^+ ha^{-1}) = 21.7 and 67.5 for the Tokomaru and the Egmont soil, respectively.

III.   EFFECT OF SOIL ACIDITY ON NUTRIENT AND HEAVY METAL TRANSFORMATION IN SOILS

Acidification affects the transformation and biogeochemical cycling of both nutrients and heavy metals through its effect on the physical, chemical and biological characteristics of soils. According to Adriano (2001), the pH can be viewed as the master variable of all the driving factors because it can affect the surface charge and subsequent adsorption of solutes by variable charge soil components, such as layer silicate clays, organic matter, and oxides of Fe and Al. In addition to the effect on the sorption of metal cations and anions in soils, it also influences metal speciation, complexation of metals with organic matter, precipitation/dissolution reactions, redox reactions, mobility and leaching, dispersion of colloids, and the eventual bioavailability of trace metals.

A number of soil physical and chemical properties are controlled by the nature and the amount of surface charge and the variation of surface charge with soil solution characteristics. The surface reactions of charged particles are essential to the biogeochemical cycling of nutrients and pollutants, and the pathway of detoxification of the latter when present at hazardous concentrations (Sposito, 1984; Sparks, 1995; Bolan et al., 1999a). It is important to first understand the effect of acidification on surface charge so that the surface charge can be manipulated to take advantage of solid phase interactions relating to the movement of nutrient and pollutant ions in soils, the degradation of pesticides and the decontamination of soils.

Soil solution pH is one of the major factors controlling surface properties of variable charge components (Sposito, 1984; Barrow, 1985; Sparks, 1986). pH affects the surface charge through the supply of H^+ for adsorption onto the metal oxides and the dissociation of the functional groups in the soil organic matter. An increase in pH increases the net negative charge (often referred to as cation exchange capacity or CEC) and a decrease in pH increases the net positive charge (often referred to as anion exchange capacity or AEC) (Singh and Uehara, 1986). Thus, change in surface charge is a major reason for the effect of pH on anion and cation adsorption. Lower pH values also elevate the concentration of Al in soil solution, taking up a greater proportion of the cation exchange sites and reducing base saturation. On the other hand, precipitation of Al at high pH values could block the exchange sites with positively-charged Al hydrous oxides, leading to a decrease in CEC; when these soils are acidified, Al is resolubilized from the negatively charged soil particle coatings, exposing more negatively charged surface leading to an increase in CEC (Ritchie, 1989).

Sumner et al. (1991) wrote a comprehensive review on nutrient status and toxicities in acid soils. In the following section, a brief discussion on the direct effects of acidification on the transformation of nutrients and heavy metals is given. The beneficial effects of liming to neutralize the acidity in relation to

the mobilization of nutrients and the immobilization of heavy metals will be discussed in detail in Section V (Tables VII–IX).

A. PLANT NUTRIENTS

1. PRIMARY NUTRIENTS

NITROGEN. Acidity, by virtue of governing the type, number and activity of microorganisms, regulates the rate of organic matter mineralization, thereby reducing the number of simple organic molecules available for further decomposition and eventually rendering N and other constituent elements (P and S) soluble (Alexander, 1977). In highly acid conditions, organic matter accumulates giving rise to vast storehouse of nutrients that can be exploited by liming.

Nitrification is markedly reduced below pH 6 and is undetectable below pH 4.5 (Alexander, 1977). On the other hand, ammonification reactions are insensitive to acidity over a range of pH typified in agricultural soils, resulting in the accumulation of NH_4^+–N. Thus, the effect of acidity on the soluble N status of most agricultural soils is limited to nitrification, implying that for plants which use both NH_4^+ and NO_3^-, acidity plays little role in determining the availability of N. For certain crops unable to use NH_4^+–N, acidification can result in restricted uptake of N or even NH_4^+ toxicity. Use of NH_4^+–N by both higher plants and by certain groups of algae usually will result in even higher H^+ accumulation exacerbating acidification (Marschner, 1995).

Acidity has a deleterious effect on the symbiotic relationship between *rhizobia* and legumes, and generally in soils with pH below 6, poor nodulation and N fixation result. Several physiological reasons have been attributed to this phenomenon including: (i) inhibition of infection of legume roots by nodule bacteria, decreasing nodule formation; (ii) inhibition of nitrogenase enzyme activity in the nodule due to modification of the nitrogenase iron protein; (iii) decrease in bacterial membrane potential and the inhibition of the leghaemoglobin; and (iv) decrease in the supply of photosynthate to the *rhizobium* due to the poor supply of major nutrients, such as P. The inhibitory effect of acidity on biological N fixation has also been attributed to the poor supply of Mo and Ca which are essential for N fixation. Thus, when nutrient deficiencies, especially Ca and Mo are overcome in acid soils, biological N fixation can be improved (Munns *et al.*, 1977; Coventry *et al.*, 1985; Unkovich *et al.*, 1996).

PHOSPHORUS. Much has already been reported on the effect of acidity on the solubility of soil P (Haynes, 1984). A decrease in soil pH initially increases the concentration of Fe and Al in soil solution thereby increasing the adsorption/ precipitation of P. For example, when water-soluble P fertilizers, such single and

triple superphosphates are added to soils, the H^+ ions produced from the dissolution reactions (Eq. (22)) reduce the pH around the fertilizer granules to a very low level (pH $<$ 2). This dissolves the Fe and Al compounds in the soil resulting in the adsorption/precipitation of P.

$$Ca(H_2PO_4)_2 + H_2O \rightarrow CaHPO_4 \cdot H_2O + H_3PO_4 \qquad (22)$$
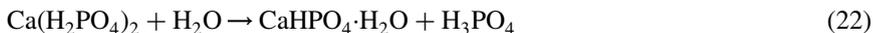
In variable charge soils, a decrease in pH increases the AEC, increasing the retention of P (Bolan *et al.*, 1999a). As a consequence, liming acid soils results in the release of P for plant uptake. This effect is often referred to as "*P sparing effect*" of lime which will be discussed later (see Section V). However at very low pH, solubilization of P compounds in soils results in an increase in the concentration of P in soil solution. It has often observed acidification caused by continuous use of NH_4^+–N results in the release of P for plant uptake (Soon and Miller, 1977).

Studying anion adsorption at a range of pH values, Hingston (1981) obtained a relationship between the apparent Langmuir maxima for a range of anions and pH. This was termed the "adsorption envelope" and the apparent maxima in the envelope were found at the pK_a values for anions with conjugate acids. A good linear relationship was obtained between points of inflection in the adsorption envelope and pK_a values for conjugate acids. Based on this he demonstrated the sharp decrease in $H_2PO_4^-$ adsorption at pH values above 6.8, which coincided with the pK_a value of orthophosphate.

POTASSIUM. Under acid conditions, weathering liberates K from micaceous and feldspar minerals enhancing it to enter the soluble and exchangeable pools (Barshad and Kishk, 1970). However, in variable charge soils, increasing acidity decreases CEC reducing the ability of the soil to retain K, resulting in more soil solution K. This solution K would then be prone to leaching (Blue and Ferrer, 1986; Alibrahim *et al.*, 1988).

2. SECONDARY NUTRIENTS

SULFUR. In many soils, organic matter is the main source of S and since mineralization of organic matter is affected by acidity, the release of S for plant uptake decreases with increasing acidity. Further, in highly weathered acid soils, SO_4^{2-} is adsorbed by sesquioxide surfaces, precipitated as an Al–OH–SO_4 type mineral, such as alunite and basulminite and/or held as simple exchangeable anions on positively charged sites on sesquioxides under acid conditions (Marsh *et al.*, 1987). As subsoil of most highly weathered soils are acid, they represent a potential storehouse for SO_4^{2-}–S against leaching, and provided roots are able to enter these zones, this S should contribute significantly to plant requirements.

CALCIUM AND MAGNESIUM. One of the major consequences of acidification is the decline in basic cations, such as Ca and Mg, leading to deficiency of these cations for plant growth. In acid soils, most of the Ca present would exist in soluble form, but both soluble and exchangeable Ca decreases with decreasing soil pH (Haynes and Ludecke, 1981). Further more at low pH, the bioavailability of Ca is retarded by high concentration of Al.

With increasing soil acidification, decreasing amounts of Mg remain in exchangeable form due to reduction in variable charge, and more is present in solution, liable to leaching losses. Also since Mg is a poor competitor with Al and Ca for the exchange sites, it tends to accumulate in the solution phase and is therefore prone to leaching (Edmeades *et al.*, 1985; Myers *et al.*, 1988).

3.   ESSENTIAL TRACE ELEMENTS

In general, the solubility and phytoavailability of metals are inversely related to soil pH. In very acid soils, Cu deficiency is likely to occur due to reduced retention. Since Cu is complexed with organic matter, the slow rate of decomposition of organic matter in acid soils decreases the release of Cu (Cavallaro and McBride, 1980; Jeffery and Uren, 1983). However, Cu toxicities have been reported on acid soils receiving repeated application of Cu pesticides (Alva *et al.*, 1995; Adriano, 2001). Temminghoff (1998) observed that a decrease in soil pH increased the free Cu and Cu bound by the fulvic fraction, while Cu bound by the humic fraction decreased. At pH 3.9, about 30% Cu in solution was bound by dissolved organic carbon (DOC), whereas at pH 6.6, Cu-DOC composed of $>99\%$.

Zinc (Zn) activity increases rapidly with decreasing pH, indicating that Zn nutritional problems are seldom encountered in soils at pH value below 5.5 provided they contain sufficient Zn. The pH-dependent solubility of Zn in soils is governed by a complex mixture of mechanisms including adsorption on sesqui-oxides, co-precipitation with Al, and complexation with organic matter (Barrow, 1986; Shuman, 1986; Stahl and James, 1991). Hesterberg *et al.* (1993) modeled changes in the solubility of some trace elements in soil as a result of acidification and found Zn, Cd, and Al solubilities increased exponentially with decreasing pH and Ca concentration.

One of the important effects of acidification is the increase in Mn toxicity in plants (Shuman, 1986; Ritchie, 1989; Sumner *et al.*, 1991; Patra and Mohanty, 1994). A decrease in pH results in increasing levels of soluble Mn and below pH 6, Mn can be expected to become soluble in toxic quantities which can adversely affect the growth of sensitive crops (Jones and Fox, 1978). The toxic levels of Mn can be reduced by the addition of organic matter through chelation (Foy, 1984). In addition to being pH sensitive, Mn is also very sensitive to changes in redox

potential. The effect of redox conditions is much greater than that of acidity in determining the level of soluble Mn in soils.

Because of low solubility of iron (Fe) even under very acid conditions (Lindsay, 1971), redox reactions are likely to be of greater importance in the rhizosphere in solubilizing sufficient Fe to meet the requirements of plants (Marschner, 1995). Under acid conditions, boron (B) occurs in solution as the uncharged H_3BO_3 molecule and is strongly adsorbed by soil containing sesquioxides, organic matter and soluble Al as the pH is raised. Thus, B availability is increased with decreasing pH (Bingham *et al.*, 1971). Unlike other anions, Mo is highly insoluble in low pH conditions and hence becomes less available in acid soils. The beneficial effect of liming on Mo availability is discussed in Section V.

In general, enhanced solubility of certain metal cations is an important consequence of soil acidification. The resulting toxicity of those elements, which are essential to plant growth, appears to be partly due to a nutrient imbalance brought about by abnormal accumulation in plant tissue (Sumner *et al.*, 1991).

B. Heavy Metals

One of the major consequences of soil acidification is the increase in concentration of Al and Mn which are highly toxic to plant growth. One of the primary aims of liming soils for agricultural production is to decrease the concentration of these elements. While Mn toxicity is related directly to the metabolic requirements of plants, the effect of Al toxicity appears to be largely manifested as malformation and malfunction of the root system, a syndrome which is exacerbated by low levels of solution Ca in acid soils (Hechtbuchholz and Foy, 1981).

Acidification affects the transformation of heavy metal ions through: (a) modification of surface charge in variable charge soils; (b) altering the speciation of metals; and (c) influencing the reduction and oxidation reactions of the metals.

In most countries, cadmium (Cd) has been identified as the major heavy metal reaching the food chain through animal transfer in pastoral agriculture. This is one of the main reasons why this element has been studied extensively in relation to soil and plant factors affecting its bioavailability. It has been observed that the adsorption of Cd increased with decreasing pH (Tiller *et al.*, 1979; Basta and Tabatabai, 1992; Naidu *et al.*, 1994; Bolan *et al.*, 1999b). Three reasons have been advanced for this phenomenon: firstly, in variable-charge soils, an increase in pH causes an increase in surface negative charge resulting in an increase in cation adsorption (Naidu *et al.*, 1994). Secondly, an increase in soil pH is likely to result in the formation of hydroxy species of metal cations which are adsorbed preferentially over the metal cation. Naidu *et al.* (1994) observed that CdOH$^+$ species are formed above pH 8 which have a greater affinity for adsorption sites

than just Cd^{2+}. Thirdly, precipitation of Cd as $Cd(OH)_2$ is likely to result in greater retention at pH above 10 (Naidu et al., 1994).

Attempts have been made to relate the pH-induced increases in surface charge to Cd adsorption by variable charge soils (Boekhold et al., 1993; Naidu et al., 1994; Bolan et al., 1999b). For example, Bolan et al. (1999b) observed that approximately 50% of the pH-induced increase in surface negative charge in variable charge soils was occupied by Cd. The remaining surface negative charge was presumed to be occupied by the H^+ and K^+ ions, added in acid and alkali solutions to alter the soil pH. This indicates that the increased Cd adsorption with increasing pH is attributable to increasing negative charge. Similarly, Naidu et al. (1994) demonstrated that the effect of ionic strength on Cd adsorption operates through its effect on surface charge.

The effect of pH on metal sorption has also been related to the exchange of H^+ for the metal ions. On this basis, Christensen (1984) and Boekhold et al. (1993) modified the Freundlich equation to account for the effect of pH on Cd sorption in soils (Eq. (23)).

$$S = K_f C^n (H^+)^m \qquad (23)$$

The exponent, m is considered as a stoichiometric coefficient indicating relative replacement ratio of H^+ by Cd^{2+} (moles H^+ replaced by one mole of Cd). A range of m values ranging from 0.5 to 1.8 (Boekhold et al., 1993; Naidu et al., 1994; Filius et al., 1998) have been obtained for Cd adsorption in soils, indicating that depending on the soil and solution composition, varying amounts of H^+ are released per unit Cd sorbed. Kinniburgh and Jackson (1981) tabulated H^+ release values for a number of metal ions on a range of adsorbents illustrating that the value of m can vary widely and is generally high for Fe and Al oxides.

Filius et al. (1998) observed that while a decrease in soil pH decreased the adsorption of Cd it caused the opposite effect on desorption. With increasing pH, the sorption/desorption isotherms became less continuous in the transition zone from adsorption to desorption. The equilibrium solution concentration at which zero sorption–desorption occurred (called nut point) decreased with increasing pH, indicating that even at low solution concentration adsorption continued to occur at high pH values. For example, at the lowest pH (4.68) the soil sample released 50 μmol Cd kg^{-1} soil at an equilibrium Cd concentration of 0.1 μM, but at the same concentration, the soil with the highest pH (6.81) was still adsorbing Cd from the solution. Generally with increasing pH, increasing amount of irreversibly bound Cd occupies specific sorption sites whereby the proportion of Cd bound reversibly to non-specific exchange sites becomes less pronounced.

In general, Cd uptake by plants increases with decreasing pH. For example, higher Cd concentrations were obtained for lettuce and Swiss chard on acid soils

(pH 4.8–5.7) than on calcareous soils (pH 7.4–7.8) (Mahler *et al.*, 1978). Consequently, it is recommended that soil pH be maintained at pH 6.5 or greater in land receiving biosolids containing Cd (Adriano, 2001).

Acidification affects the leaching and residence time of many trace elements. Taylor (1975) observed that the amounts of trace elements released from the mor soils of Sweden increased with decreasing pH of the acid precipitation. Approximately 85% of the total Cd was released at pH 2.8 and the estimated length of time for a 10% decrease through leaching in the total concentration of Cd in the mor horizon would be 1.7 years at pH 2.8, 4–5 years at pH 3.2, and 20 years at pH 4.2.

The effect of soil acidity on the adsorption of metalloids, such as arsenic (As) and selenium (Se) is manifested through two interacting factors—the increasing negative surface potential on the plane of adsorption and increasing amount of negatively charged ionic species present in soil solution. For example, while the first factor results in a decrease in As(V) adsorption, the latter factor is likely to cause the opposite effect. Thus, the effect of pH on As(V) adsorption has been shown to be dependent on the nature of the mineral surface. In soils with low oxides content, increasing the pH had little effect on As(V) adsorption, while in highly oxidic soils, adsorption decreased with increasing pH (Smith *et al.*, 1998). In general, adsorption of As(V) decreases with increasing pH. In contrast to As(V), however, adsorption of As(III) tends to increase with increasing pH (Adriano, 2001).

Soil acidification affects the solubility of Cr through its effect on adsorption/precipitation and oxidation/reduction reactions (Bartlett, 1991; James, 1996). While the adsorption of Cr(VI) in soil increases with decreasing pH, the adsorption of Cr(III) decreases (Bartlett and Kimble, 1976). Similarly, while the reduction of Cr(VI) to Cr(III) (a H^+ consumption reaction) increases with decreasing soil pH (James, 1996), the oxidation of Cr(III) to Cr(VI) (a H^+ donation reaction) decreases (Bartlett and James, 1979). The reduction of Cr(VI) to Cr(III) occurs readily in most soils due to the presence of organic matter (Eq. (24)); whereas the oxidation of Cr(III) to Cr(VI) requires the presence of oxidized Mn in the soil as an electron acceptor for the reaction to proceed (Bartlett and James, 1979).

$$2Cr_2O7 + 3C^0 + 16H^+ \rightarrow 4Cr^{3+} + 3CO_2 + 8H_2O \tag{24}$$

In general, with the exception of Se and Mo, trace elements are more soluble in soils at low pH due to the dissolution of the carbonates, phosphates, and other solid phases. Low pH also lowers the CEC of organic matter and mineral surfaces, thereby weakening the sorption of metals to specific adsorption sites.

IV. AMELIORATION OF SOIL ACIDITY THROUGH LIMING

Three approaches may be taken to minimize the rate of acidification and its subsequent negative impacts on sustainable agricultural production and environmental protection (Gregan *et al.*, 1989; Helyar, 1990): (i) reduce the amount of H^+ ions generated, (ii) reduce the uncoupling of H^+ and OH^- ions generation processes, and (iii) neutralize the acid produced. In the case of acidity caused by industrial activities, the rate of acid generation can be retarded by reducing NO_x and SO_x gaseous emissions and by reducing the oxidation of pyrite (Longhurst, 1991; Frazer, 2001). But in the case of managed ecosystems used for agricultural production, the rate of acid generation can be altered by selecting the fertilizer type that produce less acid, selecting plant species that do not accumulate cation excesses, and reducing the losses of C, N and S from the system (Gregan *et al.*, 1989).

Traditionally liming is the most common practice used to overcome the impact of soil acidification. However, an integrated approach involving liming, cultural practices and plant tolerance will probably be necessary, particularly where the acidification potential is high and its effect likely to extend into the subsoil. These approaches are discussed in detail by Bolan and Hedley (2001) which is not within the scope of this review.

A. Liming Materials

A range of liming materials are available, which vary in their ability to neutralize the acidity. These include calcite ($CaCO_3$), burnt lime (CaO), slaked lime ($Ca(OH)_2$), dolomite ($CaMg(CO_3)_2$) and slag ($CaSiO_3$). The acid neutralizing value of liming materials is expressed in terms of calcium carbonate equivalent (CCE), defined as the acid neutralizing capacity of a liming material expressed as a weight percentage of pure $CaCO_3$ (Table V). A neutralizing value > 100 indicates greater efficiency of the material relative to pure $CaCO_3$. The amount of liming material required to rectify soil acidity depends on the neutralizing value of the liming material and pH buffering capacity of the soil. Recently the potential value of other Ca-containing compounds in overcoming the problems associated with acidification has been evaluated (Dick *et al.*, 2000). Some of these materials include PRs, FGD gypsum, fluidized bed boiler ash, fly ash, and lime stabilized organic composts.

Increasing amounts of PRs are added directly to soils mainly as a source of P. Unlike soluble P fertilizers, such as superphosphates, PRs can also have a liming value in addition to supplying P and Ca. The liming action of PRs can occur through two processes. Firstly, most PRs contain some free $CaCO_3$ which

Table V
Neutralizing Value of Liming Materials

Liming material	Chemical formula	Neutralizing value[a]	Reference
Burnt lime	CaO	179	Brady and Weil (1999)
Slaked lime	$Ca(OH)_2$	136	Brady and Weil (1999)
Dolomite	$CaMg(CO_3)_2$	109	Brady and Weil (1999)
Lime	$CaCO_3$	100	
Slag	$CaSiO_3$	86	Brady and Weil (1999)
Phosphogypsum	$CaSO_4\cdot2H_2O$	0.33	Bolan *et al.* (1991)
Mined gypsum	$CaSO_4\cdot2H_2O$	12.4	Bolan *et al.* (1991)
FGD gypsum (The Netherlands)	$CaSO_4\cdot2H_2O$	0.42	Bolan *et al.* (1991)
FGD gypsum (USA)	$CaSO_4\cdot2H_2O$	0.1	Bolan *et al.* (1991)
FBA (New Zealand)	Variable	65	Wang *et al.* (1999)
Coal fly ash		Variable	Dick *et al.* (2000)
Alkaline biosolid		Variable	Basta (2000)

[a]Expressed as a weight percentage of pure $CaCO_3$.

itself can act as a liming agent. Secondly, the dissolution process of the P mineral component (i.e., apatite) in soils consumes H^+, thereby reducing the soil acidity. It is estimated that every 1 kg of P dissolved from PRs generates a liming value equivalent to 3.2 kg $CaCO_3$. From the amounts of P and free $CaCO_3$ present in the PR it may be possible to calculate its total liming value. For example, a tonne of North Carolina Phosphate Rock (NCPR) which contains 13.1% P and 11.7% free $CaCO_3$ can have a potential liming value of 536 kg $CaCO_3$ (132 kg free $CaCO_3$ + 3.2 × 132 = 419 kg $CaCO_3$ upon dissolution).

The liming values of various PRs are presented in Table VI, which ranges from 450 to 560 kg $CaCO_3$ tonne^{-1} of PR and most of the liming value in PRs is derived from the dissolution of the apatite. While the free $CaCO_3$ in PRs dissolves reasonably fast providing a small amount of immediate liming value, the apatite dissolves at a variable but generally slower rate providing liming value over a longer period of time. Certain unreactive PRs, such as Christmas Island PR, Nauru PR, and Duchess PR also have significant amounts of potential liming value, but since they are unlikely to dissolve in soils, there is no benefit from adding these PRs either as a P source or as a liming material.

Alkaline stabilized biosolids are increasingly being used as an agricultural lime substitute, soil amendment and surrogate soil. Alkaline stabilization of biosolid utilizes a combination of high pH, heat, and drying to kill pathogens and stabilize organic matter. A range of alkaline materials are used for this purpose, including, cement kiln dust, lime kiln dust, lime, limestone, alkaline coal fly ash, FGD, other coal burning ashes, and wood ash (Basta, 2000).

Logan and Harrison (1995) examined the value of a commercial alkaline stabilized biosolid product called "N-Viro" soil as a soil substitute. N-Viro is

Table VI
Theoretical Liming Value of Phosphate Rocks

Phosphate rock	Total P (% w/w)	Free $CaCO_3$ (% w/w)	Liming value (kg $CaCO_3$ Mg^{-1})[a]
North Carolina phosphate rock	13.1	11.7	536
Sechura phosphate rock	13.1	5.1	470
Gafsa phosphate rock	13.4	7.1	500
Chatham rise phosphorite	8.9	27.6	560
Arad phosphate rock	14.1	8.2	533
Youssafia phosphate rock	13.8	5.4	495
Khourigba phosphate rock	14.4	6.1	520
Egyptian phosphate rock	13.0	4.9	465
Jordan phosphate rock	13.4	7.7	505
Nauru phosphate rock	15.6	4.1	540
Christmas Island	16.4	2.1	545
Duchess phosphate rock	13.5	1.8	450

[a]Amount of acidity neutralized, expressed as an equivalent weight of pure $CaCO_3$ per tonne (Mg) of phosphate rock, through dissolution of apatite, and free $CaCO_3$.

produced by heat treatment of a mixture of cement kiln dust and municipal sewage sludge. Addition of this material improved the physical and chemical properties of a degraded mine soil. Such alkaline materials are effective in reducing the acidity produced during the nitrification of NH_4^+ in biosolids, thereby reducing the bioavailability of heavy metals in biosolid-amended soils (Brown *et al.*, 1977; Basta, 2000; Dinel *et al.*, 2000).

To minimize metal mobility and bioavailability in biosolid-amended soils, the USEPA recommends the application of alkaline-stabilized biosolids and other liming agents to increase the soil pH to 6.5 or greater. In France, application of lime combined with organic matter has been used for more than 30 years to reduce Cu phytotoxicity in vineyards receiving regular application of Cu-based fungicides (Mench *et al.*, 1994).

B. EFFECTS OF LIMING

Liming enhances the physical, chemical and biological characteristics of soil through its direct effect on the amelioration of soil acidity and through its indirect effects on the mobilization of plant nutrients, immobilization of toxic heavy metals, and the improvements in soil structure and K_s (Haynes and Naidu, 1998).

1. PHYSICAL AMELIORATION

Dispersion and flocculation of colloid particles are often manifested through changes in surface potential and charge densities. Thus manipulation of particle-charge density assists management of dispersive soils. Such charge manipulations has often been obtained by the use of inorganic salts including liming materials (Bolan *et al.*, 1999a). Dispersion is caused by mutual repulsion of soil particles because of surface charge. If the repulsive forces are predominant, the soil becomes dispersed and virtually unmanageable in an agronomic sense. It is the balance of attractive and repulsive forces that determines whether a soil is flocculated or dispersed.

Factors which affect the surface charge of soil particles determine the extent of dispersion, and include electrolyte concentration of the soil solution, the valence of the dominant cation occupying the exchange sites, and pH. pH can influence the dispersion, and the sensitivity of K_s to pH change depends on the quantity of variable charge minerals and organic matter present in the soil (Chiang *et al.*, 1987).

Liming influences flocculation/dispersion through its effect on soil pH and Ca concentration in soil solution. Bolan *et al.* (1996) observed that the effect of pH on dispersion varied between the Na- and the Ca-saturated soils. At the same value of net charge, the Ca^{2+}-saturated soils exhibited less dispersion than the Na-saturated soils. This can partly be explained by the increased surface charge screening mechanism of Ca than Na. It has often been observed that the dispersion of clay decreases as the percentage Ca-saturation increases, which has been related to the decrease in charge density (Rengasamy, 1983). The thickness of the diffuse-double layer (DDL) in Ca-saturated soil is likely to be smaller than that of the Na-saturated soil (Bolan *et al.*, 1996). As the DDL becomes smaller, the soil particles are attracted to each other resulting in increased flocculation and greater K_s (Rengasamy, 1983).

Liming has often been shown to improve soil structure and K_s of soils. The Ca in the liming materials helps in the formation of soil aggregates, thereby improving soil structure (Chan and Heenan, 1998). The lime-induced improvement in aggregate stability and K_s is manifested through the effect of liming on dispersion and flocculation of soil particles.

2. CHEMICAL AMELIORATION

The primary purpose of liming arable soils is to overcome the chemical problems associated with soil acidity that include high concentrations of acid ions (H^+ and Al^{3+}) and toxic elements (Mn^{2+}), and low concentrations of basic cations (Ca and Mg) and other nutrient ions, such as Mo and P. In relation to environmental pollution, soil acidity enhances the solubility and the subsequent

bioavailability of heavy metals. The hydrolysis of the basic cations in lime produces OH^- ions which neutralize the H^+ ions, thereby decreasing the activity and bioavailability of Al and Mn. But liming also increases the solubility of Mo and P, thereby increasing their availability. Lime provides the basic nutrient cations (Ca and Mg), and also reduces the solubility of heavy metals, thereby minimizing their bioavailability and mobility in soils. Thus lime can interact with nutrient and heavy metal transformation and bioavailability, as discussed in detail in Section V.

Elevation in pH due to addition of lime results in the precipitation of exchangeable Al (with the vacated sites being mostly occupied by Ca) and increases the negative charge or CEC. In many soils, the increase in negative charge is mainly due to dissociation of H^+ from weakly acidic functional groups of organic matter (Thomas and Hargrove, 1984; Curtin et al., 1996). It has been estimated that raising pH by one unit increases the CEC of soil organic matter by about 30 cmol $(+)$ kg^{-1} (Helling et al., 1964). The CEC of the soil mineral component is generally far less pH-dependent than that of soil organic matter. For example, the CEC of soil clay may only increase by as little as 3 or 4 cmol $(+)$ kg^{-1} per pH unit (Helling et al., 1964; Curtin et al., 1996). However, the pH-dependence of mineral CEC can vary considerably depending on the nature of the component minerals. Mineral constituents that dissociate H^+ when lime is added include hydroxy-Al polymers associated with the surfaces of phyllosilicate minerals, amorphous and short-range ordered aluminosilicates, and ruptured surfaces of silicates and oxides (Thomas and Hargrove, 1984). Thus, mineral soils whose CEC varies substantially with pH (sometimes described as *variable charge soils*) generally are high in allophonic materials, hydrous oxides of Al and Fe, or 1:1 layer silicates, such as koalinite and halloysite.

3. BIOLOGICAL AMELIORATION

Liming has been shown to provide optimum conditions for a number of biological activities that include N fixation, and mineralization of N, P and S in soils. The enhanced mineralization of these nutrient ions is likely to cause an increase in their concentration in soil solution for plant uptake and for leaching (Lyngstad, 1992; Arnold et al., 1994; Neale et al., 1997). Nitrogen fixing bacteria in legume plants require Ca, hence liming is likely to enhance N fixation (Muchovej et al., 1986).

Liming is often recommended for the successful colonization of earthworm in pasture soils. The lime-induced increase in earthworm activity may influence the soil structure and macroporosity through the release of polysaccharide and the burrowing activity of earthworm (Springett and Syers, 1984).

Liming has been shown to cause short-term increases in microbial biomass and soil enzyme activity (Haynes and Swift, 1988). Increased microbial activity and the subsequent production of extracellular polysaccharides which act as a binding agent can increase soil aggregate stability.

Although an increase in pH through liming is likely to enhance the solubilization of soil organic matter, an increase in the coagulation of DOC can be expected with a decrease in negative charge of DOC. The charge on the DOC is influenced by the nature and the valency of the cation. Calcium is found to be very effective in decreasing the negative charge on DOC, which may be a reason for the decrease in the leaching of DOC with liming (Temminghoff, 1998).

V.   LIME, NUTRIENT AND HEAVY METAL INTERACTIONS

Liming influences the transformation and uptake of nutrients and heavy metals by plants through its direct effect on the neutralization of soil acidity and its indirect effect on the physical, chemical and biological characteristics of soils. The processes involved in the liming-induced transformation and phytoavailability of nutrients and heavy metal ions are given in Tables VII–IX.

A. PLANT NUTRIENTS

1.   PRIMARY NUTRIENTS

NITROGEN. Liming has often been shown to enhance the mineralization of organic matter, thereby releasing inorganic plant nutrients such as N, S and P to soil solution. Unless these nutrients are actively taken up plants they are liable for leaching losses. Lime-induced greening of plant leaves is often associated with enhanced availability of N (Ogata and Caldwell, 1960; Nyborg and Hoyt, 1978). Nitrate, being weakly retained by soil particles, is subjected to leaching. Liming exacerbates the leaching of NO_3^- because an increase in pH through liming decreases the positive surface charges in variable charge soils. Further, liming also provides basic cations (Ca and Mg) as a companion ion for NO_3^- leaching (Tinsley, 1973; Adams, 1986).

Liming affects both the chemical and microbial transformation of N in soils. In general, NH_4^+–N is nitrified more rapidly on addition of lime due to an increase in the activity of microorganisms involved in nitrification (Lyngstad, 1992; Puttanna *et al.*, 1999). The efficiency of nitrification inhibitors decreases with the addition of lime. This is probably due to an increase in nitrifier activity and also due to an increase in general microbial activity (Slangen and Kerkhoff, 1984),

Table VII
Selected References on the Effects of Liming on the Transformation and Plant Uptake of Primary and Secondary Nutrients in Soils

Nutrient	Effects	Reference
Nitrogen	Increased mineralization/nitrification	Gardner *et al.* (1965), Nyborg and Hoyt (1978), Edmeades *et al.* (1981), Carter (1986), Curtin and Smillie (1986), Klemmedson *et al.* (1989), Clay *et al.* (1993), Stevens and Laughlin (1996), Unkovich *et al.* (1996), and Curtin *et al.* (1998a)
	Increased ammonium volatilization	Winter *et al.* (1981), Sommer and Ersboll (1996), and Howard and Essington (1998)
	Increased biological N fixation	Munns *et al.* (1977), Coventry *et al.* (1985), Peoples *et al.* (1995), Unkovich *et al.* (1996), and Raychaudhuri *et al.* (1998)
	Increase in plant uptake	Ogata and Caldwell (1960), Rosolem and Caires (1998), and Raychaudhuri *et al.* (1998)
	Decrease in plant uptake	Ogata and Caldwell (1960) and Bailey (1995)
Phosphorous	Increased mineralization of organic P	Trasarcepeda *et al.* (1991), Condron *et al.* (1993), and Fernandes and Coutinho (1999)
	Increased adsorption/precipitation	Badora and Filipek (1988), Naidu *et al.* (1990), Holford *et al.* (1994), Agbenin (1996), Mongia *et al.* (1997), and Fransson *et al.* (1999)
	Increase in plant uptake	Lucas and Blue (1973), Friesen *et al.* (1980b), Hemphill *et al.* (1982), Bhella and Wilcox (1989), and Raychaudhuri *et al.* (1998)
	Decrease in plant uptake	Wahab and Shah (1952) and Amarasiri and Olsen (1973)
Potassium	Increase in adsorption	Magdoff and Bartlett (1980), Blue and Ferrer (1986), and Alibrahim *et al.* (1988)
	Decrease in adsorption	Bolan *et al.* (1999a)
	Increase in plant uptake	Abraham *et al.* (1980) and Mason *et al.* (1994)
	Decrease in plant uptake	Magdoff and Bartlett (1980)
Sulfur	Increased mineralization of organic S	Bolan *et al.* (1988) and Valeur *et al.* (2000)

Table VII (*continued*)

Nutrient	Effects	Reference
	Decreased adsorption	Marsh *et al.* (1987) and Bolan *et al.* (1988)
	Increased leaching	Korentajer *et al.* (1983) and Bolan *et al.* (1988)
	Increase in plant uptake	Martini and Mutters (1984)
	Decrease in plant uptake	Korentajer *et al.* (1983) and Kemper and Sorensen (1984)
Calcium	Increase in exchangeable and solution Ca	Curtin and Smillie (1983), Edmeades *et al.* (1983), and Curtin and Smillie (1995)
	Increase in plant uptake	Crouchley (1981) and Bhella and Wilcox (1989)
Magnesium	Increased adsorption/*fixation*	Grove *et al.* (1981), Riggs *et al.* (1995a) and Wheeler (1997)
	Increase in plant uptake	Bhella and Wilcox (1989) and Mason *et al.* (1994)
	Decrease in plant uptake	Crouchley (1981)

Table VIII

Selected References on the Effects of Liming on the Transformation and Plant Uptake of Trace Element Nutrients in Soils

Nutrient	Effects	Reference
Copper	Increased adsorption	Msaky and Calvet (1990), De Vera and Pocsidio (1998), and Federer and Sticher (1999)
	Increased organic matter complexation	McBride and Bouldin (1984) and Hodgson *et al.* (1966)
	Increase in plant uptake	Adcock *et al.* (1999)
	Decrease in plant uptake	Bates (1971), John and van Laerhoven (1976), Anderson and Siman (1991), Preer *et al.* (1995), Fang and Wong (1999), and Tyler and Olsson (2001)
Zinc	Increased adsorption	Friesen *et al.* (1980a), Shuman (1986), Harter (1991), and Federer and Sticher (1999)
	Increase in plant uptake	Adcock *et al.* (1999)
	Decrease in plant uptake	Lee and Craddock (1969), MacLean *et al.* (1972), John and van Laerhoven (1976), Chang *et al.* (1982), Pepper *et al.* (1983), Sanders *et al.* (1987), Bhella and Wilcox (1989), Anderson and Siman (1991), Preer *et al.* (1995), Brallier *et al.* (1996), Chowdhury *et al.* (1997), Fang and Wong (1999), Ye *et al.* (1999), Oste *et al.* (2001), and Tyler and Olsson (2001)
Cobalt	Increased adsorption	Backes *et al.* (1995)
	Decrease in plant uptake	Deram *et al.* (2000) and Tyler and Olsson (2001)
Boron	Increased adsorption	Bingham *et al.* (1970) and Parker and Gardner (1982)
	Increase in plant uptake	Bingham *et al.* (1970), Peterson and Newman (1976) and Su *et al.* (1994)
	Decrease in plant uptake	Bingham *et al.* (1970), Gupta (1972), Bartlett and Picarelli (1973), Gupta and MacLeod (1973), Peterson and Newman (1976), Blamey and Chapman (1979), Brown (1979), Lipsett *et al.* (1979), Haddad and Kaldor (1982), Hemphill *et al.* (1982), Su *et al.* (1994), and Tyler and Olsson (2001)
Selenium	Increased bimethylation	Frakenberger and Karlson (1994)
	Increase in plant uptake	Cary *et al.* (1967), Cary and Allaway (1969), and Gupta *et al.* (1982)
	Decrease in plant uptake	Gupta and Winter (1975) and Tyler and Olsson (2001)

Table VIII (*continued*)

Nutrient	Effects	Reference
Iron	Decrease in plant uptake	Patra and Mohanty (1994) and Franzen and Richardson (2000)
Molybdenum	Decreased adsorption	Robinson *et al.* (1951)
	Increase in plant uptake	Robinson *et al.* (1951), Vlek and Lindsay (1977), Gupta (1979), Gupta and Kunelius (1980), Crouchley (1981), Coventry *et al.* (1985), Coventry *et al.* (1987), Mason *et al.* (1994), and Wheeler (1998)

Table IX
Selected References on the Effects of Liming on the Transformation and Plant Uptake of Toxic Heavy Metals in Soils

Metal	Effects	Reference
Aluminium	Increased adsorption	MacLean *et al.* (1972), Badora and Filipek (1988), Hochman *et al.* (1992), Unkovich *et al.* (1996), Mongia *et al.* (1997), and Mora *et al.* (1999)
	Decrease in plant uptake	MacLean *et al.* (1972), Haynes and Ludecke (1981), Edmeades *et al.* (1983), Wang *et al.* (1999), and Tyler and Olsson (2001)
Manganese	Increased adsorption	MacLean *et al.* (1972) and Jauregui and Reisenauer (1982)
	Increased precipitation as manganocalcite	Jauregui and Reisenauer (1982)
	Decrease in plant uptake	Godo and Reisenauer (1980), Haynes and Ludecke (1981), Edmeades *et al.* (1983), Adcock *et al.* (1999), and Tyler and Olsson (2001)
Cadmium	Increased adsorption/ precipitation	MacLean (1976), Estan *et al.* (1987), He and Singh (1994), Brallier *et al.* (1996), Hooda and Alloway (1996), Filius *et al.* (1998), Krebs *et al.* (1998), Federer and Sticher (1999), and Gray *et al.* (1999)
	Decreased desorption	Filius *et al.* (1998)
	Increase in plant uptake	Li *et al.* (1996)
	Decrease in plant uptake	Lagerwerf (1971), John and van Laerhoven (1976), Chaney *et al.* (1977), Bingham *et al.* (1979), Hortenstine and Webber (1981), Adriano *et al.* (1982), Pepper *et al.* (1983), Albasel and Cottenie (1985), Anderson and Siman (1991), Jackson and Alloway (1991), Sparrow *et al.* (1993), He and Singh (1994), Preer *et al.* (1995), Brallier *et al.* (1996), Han and Lee (1996), Hooda and Alloway (1996), Oliver *et al.* (1996), Maier *et al.* (1997), Redente and Richards (1997), Sparrow and Salardini (1997), Krebs *et al.* (1998), Singh and Myhr (1998), Vasseur *et al.* (1998), Fang and Wong (1999), Fernandes *et al.* (1999), Gray *et al.* (1999), Lehoczky *et al.* (2000), Oste *et al.* (2001), and Tyler and Olsson (2001)

Table IX (*continued*)

Metal	Effects	Reference
Arsenic	Increased immobilization	Bothe and Brown (1999)
	Decreased adsorption	Jones *et al.* (1997)
	Increase in plant uptake	Heeraman *et al.* (2001)
	Decrease in plant uptake	Jiang and Singh (1994) and Tyler and Olsson (2001)
Mercury	Increased reduction to Hg^0	Frear and Dills (1967) and Landa (1978)
	Decreased reduction of Hgo	Alberts *et al.* (1974)
	Increased adsorption	Farrah and Pickering (1978)
	Increased uptake	Heeraman *et al.* (2001)
	Decreased uptake	Tyler and Olsson (2001)
Lead	Increased adsorption	Chlopecka *et al.* (1996)
	Increase in hydroxy species	Roy *et al.* (1993) and Chlopecka *et al.* (1996)
	Decrease in plant uptake	Cox and Rains (1972), John and van Laerhoven (1972), Zimdahl and Foster (1976), Reddy and Patrick (1977), Ye *et al.* (1999), and Tyler and Olsson (2001)
Nickel	Increased adsorption/precipitation at high pH	Pratt *et al.* (1964)
	Decrease in plant uptake	Bisessar (1989), Brallier *et al.* (1996), and Tyler and Olsson (2001)
Chromium	Increased Cr(III) oxidation	Bartlett and James (1979)
	Decreased Cr(VI) adsorption	Bartlett and James (1979) and Bolan and Thiagarajan (2001)
	Increased Cr(III) adsorption	Bolan and Thiagarajan (2001)
	Decrease in plant uptake	Bolan and Thiagarajan (2001) and Tyler and Olsson (2001)

resulting in rapid biodegradation of nitrification inhibitors. All these processes result in an increase in NO_3^- concentration, leading to NO_3^- leaching, especially in the absence of active plant uptake. Although an increase in pH due to liming is likely to enhance the volatilization losses of NH_3 gas, the enhanced effect of liming on NH_3 volatilization has not been documented under field conditions (Winter *et al.*, 1981; Sommer and Ersboll, 1996; Howard and Essington, 1998).

PHOSPHORUS. A reason commonly given for liming-induced improvement in plant growth in acid soils was to increase P availability. It is well established that, in strongly acid soils, Al toxicity can have a substantial inhibitory effect on the uptake and translocation of P (Chen and Barber, 1990). Haynes (1984) noted that the effects of liming on Al toxicity and P deficiency could be difficult to delineate. In soils high in exchangeable and soluble Al, liming may increase plant P uptake by decreasing Al, rather than by increasing P availability *per se*. This may be due to improved root growth where Al toxicity is alleviated, allowing a greater volume of soil to be explored (Friesen *et al.*, 1980b). Interactions between P and Al in acid soils were already covered in detail by Haynes (1984).

In situations where Al toxicity is not a factor, the impact of liming on P availability is not clear-cut. It has become apparent that generalizations on the direction (positive or negative) of the response of available P to lime can be misleading (Haynes, 1984). Lack of a consistent response can be attributed to the fact that liming may change several factors that regulate the concentration of P in the soil solution (Barrow, 1984). Some of these changes tend to increase soluble P concentration whereas others can have the reverse effect.

In many soils, adsorption–desorption reactions regulate the concentration of P in the soil solution. Barrow (1984) suggested that several major factors influence the relations between pH and P adsorption. When pH is increased, the proportion of the divalent phosphate ion (HPO_4^{2-}), the P species considered to be adsorbed, also increased. This change in phosphate speciation promotes adsorption but at the same time, surface electrostatic potential becomes more negative as pH increases thus lowering the AEC. The resultant effect of these two competing tendencies has a large bearing on whether P adsorption could be altered by liming. The pH-dependence of surface potential is sensitive to factors, such as exchangeable cation composition and ionic strength of the soil solution (Barrow, 1984), both of which change when lime is applied. Other possible effects of liming on P availability include the precipitation of P as calcium phosphate, often cited as the cause of increased P retention as pH approaches 7 (Naidu *et al.*, 1990).

Liming may accelerate the rate of organic P mineralization due to increased rates of microbial activity, but the practical significance of this effect remains unclear because of the difficulty in measuring P mineralization rates. At a long-term experimental site in New Zealand, Condron and Goh (1989) attributed declines in organic P in the 0–7.5 cm soil layer between 1971 and 1974 to increased mineralization as a result of liming in 1972.

The net effect on P availability of the various soil chemical and biochemical changes upon liming is difficult to predict. Approaches to measuring effects of lime on P availability include studies of its effects on P adsorption (Naidu *et al.*, 1990; Holford *et al.*, 1994; Agbenin, 1996), P release to extractants (Rhue and Hensel, 1983; Sorn-Srivchai *et al.*, 1984; Curtin and Syers, 2001) and P uptake by plants (Mansell *et al.*, 1984; Fernandes and Coutinho, 1999). Studies using chemical extractants have shown that the response of extractable P to lime is influenced by the nature of the extractant. In a fertilized soil in which lime increased soil solution P from 0.29 mg l^{-1} (pH 4.7) to 0.67 mg l^{-1} (pH 6.2), Curtin and Smillie (1984) observed that acidic extractants gave similar values suggesting that liming had little effect on P availability whereas alkaline extractants (0.1 M NaOH) indicated that lime indeed decreased available P. There is evidence that the commonly-used Olsen bicarbonate test may give artificially low values for limed soil because of precipitation of calcium phosphate resulting from a combination of high pH (~ 8.5) and soluble Ca in the extract (Sorn-Srivchai *et al.*, 1984). Recently, Curtin and Syers (2001) also confirmed that Olsen P tends to decrease when pH was raised; however, water-extractable P also decreased by liming, suggesting that the lime-induced decreases in Olsen P were due to increased P adsorption rather than to Ca–P precipitation. It appears then that the least ambiguous way of evaluating the effect of liming on the solubility of P is by measuring the levels of P in soil solution. While this approach has been successfully used in some studies (Adams *et al.*, 1982; Curtin and Smillie, 1984), procedures for the displacement of soil solution are too laborious for routine use in soil testing laboratories.

There have been relatively few studies in which the so-called *P-sparing effect* of lime (Tillman and Syers, 1982) has been quantified under field conditions. The *P-sparing effect* of lime is a term which is specific to a situation in which lime increases the actual availability of P to the plant. It excludes situations where plant P uptake is increased as a result of elimination of Al (or Mn) toxicity by liming. Mansell *et al.* (1984) evaluated the results of 25 field experiments that investigated the effects of P and lime on pasture production in New Zealand for evidence of a P-sparing effect of lime. Only 11 of the trials gave evidence of a P-sparing effect and only 4 of these showed effects large enough to be of practical significance (i.e., 11–20 kg P ha^{-1}year^{-1} in some sedimentary-type soils at low pH (< 5.5) at the normal liming rates). An increase in the availability of P can only be expected on soils which have accumulated some reserve (in this case organic P or inorganic "fixed" P) of this element. Unfortunately, field situations where liming might result in worthwhile reductions in fertilizer P requirement is not predictable. Mansell *et al.* (1984) concluded that, because of the scarcity and unpredictability of important P-sparing effects, it would seem unwise to recommend to farmers to reduce fertilizer P inputs after lime has been applied. Therefore liming should not be practiced with the expectation that fertilizer P input can be reduced in the long term.

In summary, the information on lime-phosphate interactions that has been published since the topic was last reviewed in *Advance in Agronomy* (Haynes, 1984) further suggests that, once pH is high enough to eliminate Al/Mn toxicity ($\sim$pH 5), liming will neither have a large nor consistent effect on the efficiency of use of soil or applied P.

POTASSIUM. Comprehensive reviews have been published in which the forms and availability of soil K have been described (e.g., Syers, 1998). Assessment of the plant-availability of K is somewhat more complex than that of Ca or Mg because non-exchangeable form of the element (i.e., K fixed by micaceous minerals and K in the lattice of K-containing primary minerals) can supply significant amount of the K for crop uptake (Syers, 1998).

Effects of lime on soil K availability to plants are not well documented however. In theory, a number of processes that control the concentration of K in the soil solution could be influenced by liming. Liming could alter the equilibrium between soil solution K and exchangeable K due to increases in CEC and removal of Al from exchange sites or because of competition for exchange sites with lime-derived Ca. In laboratory studies, the concentration of K in soil solution decreased after liming due to increased K adsorption (Curtin and Smillie, 1983). Although the ratio of Ca to K in soil solution can increase substantially when soil is limed (Curtin and Smillie, 1995), there is no evidence that this antagonistic effect of Ca reduces the uptake of K by plants. The efficiency of fertilizer K use in variable charge soils may improve after liming because increased CEC may result in less leaching of K.

It is possible that, by reducing the intensity of acid weathering, liming could slow down the release of non-exchangeable K. Measurement made 17 years after liming showed that exchangeable K decreased from 1.0 to 0.7 cmol $(+)$ kg^{-1} as pH increased from 4.5 to 6.1 (Curtin and Smillie, 1995). Such a trend could be due to increased plant uptake of K or possibly insignificant release of non-exchangeable K when the soil was limed.

Since liming also increases the concentration of Ca in soil solution, the adsorption of cations, such as K, can be affected. For example, in batch experiments, the decrease in K adsorption induced by liming was attributed to the increase in Ca concentration in soil solution (Galindo and Bingham, 1977) and to a decrease in charge density (Goedert *et al.*, 1975). Thus, in the absence of competition from Ca, the increased negative charge at higher pH-induced by liming is likely to result in an increase in K retention.

There is clearly a need for greater understanding of K-lime interactions. As recently pointed out by Syers (1998) "the extent to which K fertilizer application rates should be varied as soil pH varies requires further evaluation."

2. SECONDARY NUTRIENTS

SULFUR. Addition of lime has often been observed to increase the concentration of anions, such as SO_4^{2-} in soil solution (Bolan *et al.*, 1988) and several reasons have been proposed to explain this (Korentajer *et al.*, 1983). These include: (i) SO_4^{2-} mineralized from soil organic matter by microorganisms growing in a more favorable pH environment; (ii) SO_4^{2-} released from organic matter by chemical hydrolysis; (iii) adsorbed SO_4^{2-} released from the soil surface; and (iv) SO_4^{2-} released from sparingly soluble Fe and Al hydroxy sulfates, which become more soluble at higher pH.

After liming an acid soil, Elkins and Ensminger (1971) observed an increase in the SO_4^{2-} concentration in the soil solution with a corresponding increase in the S content of soybean plants grown in the soil. However, Bolan *et al.* (1988) indicated that in the absence of active uptake by plants, any SO_4^{2-} released into soil solution by liming is susceptible to leaching and may be lost to subsoil horizons.

Because general aspects of S biogeochemical cycling in the soil–plant system have already been reviewed elsewhere (e.g., Saggar *et al.*, 1998) the focus here will be on ways in which liming affects the processes that regulate S cycling. The two processes that are most likely to be affected by liming include S adsorption/desorption (Bolan *et al.*, 1988) and S mineralization (Grego *et al.*, 2000).

Although the precise mechanism by which SO_4^{2-} is adsorbed by soil components is still arguable, it is clear that SO_4^{2-} retention decreases rapidly with increasing pH. As a general rule, many soils adsorb little, if any, SO_4^{2-} once pH exceeds about 6 (Marsh *et al.*, 1987; Bolan *et al.*, 1988).

Liming of variable charge soils has often been shown to decrease the retention of anions, such as SO_4^{2-} (Marsh *et al.*, 1987; Bolan *et al.*, 1988) and HPO_4^{2-} (Naidu *et al.*, 1990) and increase the retention of cations, such as nutrient ions (Adams, 1984) and heavy metals (Helmke and Naidu, 1996). In general, liming invariably increases soil pH, thereby decreasing the positive charge (i.e., AEC) and hence the adsorption of SO_4^{2-} and HPO_4^{2-}; whereas an increase in Ca concentration through liming can increase anion retention.

Calcium-induced anion adsorption by variable charge soils has been reported. For example, Bolan *et al.* (1993) observed that the adsorption of SO_4^{2-} ions by variable-charge soils was higher in the presence of Ca than K. Various hypotheses have been postulated for the increase in SO_4^{2-} adsorption in the presence of Ca. Firstly, the increase in SO_4^{2-} adsorption in the presence of Ca has been related to the formation of a surface complex between the anion and Ca. This involves coordination of one Ca to two adsorbed anion groups, reducing the repulsive force between two adjacent anion groups, thereby enhancing further adsorption. Secondly, increased adsorption of SO_4^{2-} at higher levels of Ca addition has been attributed to precipitation reactions occurring at high pH (>7.0). Thirdly, specific adsorption of Ca by hydrous oxides has been

shown to increase the positive charge on the surface, thereby increasing the adsorption of anions. Bolan *et al.* (1993) observed that the increase in positive charge with Ca adsorption accounted for most of the increase in SO_4^{2-} adsorption at low levels of Ca (<0.002 M) in solution. The role of positive charge in SO_4^{2-} adsorption by soils has been well documented (Marsh *et al.*, 1987).

Soil column studies have demonstrated that SO_4^{2-} adsorption capacity of the soil is a major factor determining leaching of SO_4–S. Leaching of SO_4^{2-} from a New Zealand soil with high S retention capacity increased several-fold when pH was increased from 4.7 to 7.0 by application of $CaCO_3$ (Bolan *et al.*, 1988). The lime-induced leaching of SO_4^{2-} was attributed mainly to the large decrease in SO_4^{2-} adsorption that occurred when pH was raised and, possibly, to greater S mineralization in the limed soil. In situations where S supply is marginal, enhanced SO_4^{2-} leaching after liming could lead to S deficiency. Decreases in the uptake of S by corn (*Zea mays* L.) from two limed soils which were subjected to leaching under green house conditions provided some evidence that leaching-induced S losses may lead to S deficiencies in plants grown in limed soils (Korentajer *et al.*, 1983). Unfortunately, similar data for field-grown crops are lacking.

Several authors allude to the possibility that liming may accelerate the mineralization of organic S (Korentajer *et al.*, 1983; Bolan *et al.*, 1988), though the significance of this effect is open to question. Recent reviews of organic S transformations in cultivated and grassland soils (Saggar *et al.*, 1998) do not list pH amongst the factors affecting S mineralization. Under field conditions, very little is known about S mineralization rates and there is no documented evidence that S mineralization rates are pH-sensitive.

Concern over the effects on S nutrition in crops impacted by low or declining atmospheric inputs in some countries has renewed the interest in soil S, particularly in the 1980s (McGrath and Zhao, 1995). Much work has been conducted on lime-sulfate interaction and leaching of SO_4^{2-} in simplified soil systems (e.g., repacked columns containing homogeneous soil). However, more information is needed to develop ways of predicting the effects of lime on S leaching under field conditions. Sulfate leaching models that incorporate soil pH as a driving variable would be a useful advance on existing, empirical SO_4^{2-} leaching indices (McGrath and Zhao, 1995).

CALCIUM AND MAGNESIUM. Liming materials supply Ca and Mg to soil and one of the primary purposes of liming is to overcome the deficiency of basic cations. An increase in pH through liming increases the net negative charge, thereby increasing the adsorption of cations; whereas an increase in Ca in soil solution through liming is likely to decrease the adsorption of other cations. Therefore the resultant effect of liming on the adsorption of cations depends largely on the concentration of Ca in soil solution. Under natural leaching

conditions where most of the Ca is lost from soil solution, liming of soils may not necessarily cause increased leaching of subsequently added K and Mg (Goedert *et al.*, 1975; Grove *et al.*, 1981). It is possible, however, that liming a soil may lead to displacement of other cations already present in the soil, hence inducing leaching if there is a water flux (Edmeades, 1982).

Increasing CEC without Mg addition reduces Mg saturation and such lime-induced Mg deficiencies can be quite striking. As soil pH is raised to the vicinity of 5.5, Mg has been shown to precipitate possibly as a mixture of Al, Mg double hydroxide or as poorly ordered Mg silicate, rendering it less soluble and available to plants (Grove *et al.*, 1981).

Plants derive their nutrients including the cations (Ca, Mg, and K) directly from the soil solution. The concentrations of Ca, Mg, and K in the soil solution are determined primarily by cation exchange equilibria (Curtin and Smillie, 1995). Addition of lime can alter the solution concentrations of these cations as a consequence of: (a) the input of Ca (and Mg in the case of dolomitic lime), and (b) pH-induced changes in the extent and nature of the cation exchange complex, which may shift the equilibrium between solution and exchangeable cations.

Addition of lime usually increases the contribution of organic matter to CEC (Helling *et al.*, 1964; Curtin *et al.*, 1998a). As organic and mineral exchange sites differ considerably in their affinity or selectivity for cations (Baes and Bloom, 1988; Suarez and Simunek, 1997), changes in the relative proportions of organic and mineral sites may have some effect on the distribution of cations between the exchange and solution phases of soil. Several studies have demonstrated that organic matter exhibits a preference for Ca over Mg. For example, Suarez and Simunek (1997) and Curtin *et al.* (1998b) reported a selectivity constant for Ca–Mg exchange of about 4 for organic matter compared to ∼ 1 (i.e., little or no preference) for smectite clay. An increase in the proportion of organic sites following liming might be expected to lead to greater selectivity for Ca over Mg but experimental results have been inconsistent. Edmeades and Judd (1980) reported that liming New Zealand soils generally increased selectivity for Ca over Mg. In contrast, Curtin *et al.* (1998b) concluded that Ca–Mg selectivity was insignificantly affected by pH in Canadian prairie soils. Information of the effects of pH on K selectivity is sparse. Data for a sandy loam from South Carolina indicated increased selectivity for Ca relative to K when pH was increased under laboratory conditions (Rhue and Mansell, 1988).

Negative charge sites activated when soils are limed are mostly occupied by Ca with minimal effects on the levels of exchangeable Mg (Hochman *et al.*, 1992). However, there have been frequent reports of decreases in exchangeable Mg following the use of calcitic limestone (Grove *et al.*, 1981; Edmeades *et al.*, 1985; Myers *et al.*, 1988; Riggs *et al.*, 1995a). This phenomenon has been associated mainly with highly weathered soils (Oxisols and Ultisols), but it has also been observed in less weathered soils in Great Britain (Riggs *et al.*, 1995a). The magnitude of the effect may be large enough to be of some concern in

relation to Mg supply to plants and grazing animals. In a laboratory study, for example, raising pH of Iowa soils (initial pH 3.8–5.1) to near neutrality reduced exchangeable Mg by 17–34% of that initially present (Myers *et al.*, 1988). Riggs *et al.* (1995a) showed that the decrease in exchangeable Mg in British soils treated with calcitic lime was directly proportional to the initial exchangeable Al content. Adsorption of soluble Mg on to newly-precipitated hydroxy-Al polymers (a process referred to as Mg *fixation*) has been proposed as a mechanism responsible for lime-induced reduction in exchangeable Mg (Grove *et al.*, 1981).

There is evidence that lime-induced reductions in exchangeable Mg may occur even in low Al soils where Mg fixation is unlikely (Edmeades *et al.*, 1985). The concentration of Mg in soil solution can either increase or decrease after liming (Curtin and Smillie, 1983). Increased concentrations of soluble Mg can be attributed to displacement of exchangeable Mg by lime-Ca. In an open system where leaching can occur, this may result in lime-induced loss of Mg from the soil, as suggested by Edmeades *et al.* (1985). Decreases in soil solution Mg following liming (Curtin and Smillie, 1986) could be due either to adsorption of Mg by newly activated cation exchange sites or to Mg fixation. Changes in the concentration of soluble Mg as a result of liming are usually small compared with the large increase in the solution concentration of Ca. Thus, the ratio of Mg-to-Ca in the soil solution is invariably decreased by liming (Curtin and Smillie, 1995).

Even when soil available Mg is not affected by liming, plant Mg may be depressed because of the antagonistic effect of Ca on Mg uptake (Edmeades *et al.*, 1983). Decreased herbage Mg associated with low soil Mg/Ca ratios is believed to be a factor causing increased incidence of hypomagnesemia (grass tetany) in animals grazing limed pastures (Thomson, 1982). Calcium-induced Mg deficiency has also been proposed as a possible cause of negative plant yield responses to lime. Carron (1991) observed Ca-induced Mg deficiency in pot-grown clover (*Trifolium repens* L.) when the ratio of exchangeable Ca to exchangeable Mg exceeded 20. Awareness of the potential for Mg deficiency in plants and animals after use of calcitic lime has stimulated an interest in use of dolomitic limestone. Although the use of dolomitic limestone is more likely to provide adequate levels of Mg for plants and grazing animals than is calcitic limestone, neither exchangeable Mg nor the ratio of exchangeable Mg to Ca adequately predicted Mg availability to pot-grown ryegrass (*Lolium perenne* E.) (Riggs *et al.*, 1995b).

3. TRACE ELEMENTS

With the exception of Mo, plant availability of most other trace element nutrients decreases with liming mainly due to decrease in the concentration of

these elements in soil solution. For example, most problems with Fe nutrition are encountered when pH is raised by liming, resulting in a sufficient depression of Fe solubility to limit uptake in crops (Marschner, 1995). This phenomenon is often referred to as "lime-induced iron chlorosis." The effect of pH > 6 in lowering free metal ion activities in soils has been attributed to the increase in pH-dependent surface charge on oxides of Fe, Al, and Mn (Stahl and James, 1991), chelation by organic matter, or precipitation of metal hydroxides (Lindsay, 1971).

At pH above 7.0 the bioavailability of Zn to crops is substantially reduced. Severe Zn deficiencies are often associated with alkaline and calcareous soils; in these soils, acidification of root zone may prove an efficient method to increase the bioavailability of Zn to plants (Fenn *et al.*, 1990). The effect of pH on the activity of Zn in solution in naturally acid soils is found to decrease with increasing pH. The gradual decrease in Zn activity with increasing pH is attributed to increasing CEC (Shuman, 1986). Similarly, Stahl and James (1991) observed that increasing surface charge due to liming increased Zn retention. In general, both the CEC and the total amount of Zn removed from soil solution increased with liming.

On the other hand, strong complexation of Cu by soil organic matter is believed to be an important factor in explaining why Cu deficiencies are not as prevalent as Zn deficiencies in limed soils, even though the two cations show similar diminution in solubility with increasing pH (Lindsay, 1971). Precipitation of Cu contaminated industrial waste is usually achieved using lime or sodium hydroxide (caustic). Precipitation as cupric oxide, which is very effective between pH 9 and 10.3 using lime seems to offer distinct advantages with respect to cost and handling. For example, residual concentration of $0.2-1.1$ mg l^{-1} has been achieved for Cu in the timber treatment effluent using lime precipitation (Patterson, 1985).

Unlike most other trace elements, bioavailability of Mo in soils is greatest under alkaline pH than under acidic condition. Liming acid soils often helps to correct Mo deficiency; liming may substitute for Mo fertilization by releasing Mo from soils into forms readily bioavailable for plant uptake. Conversely, plant response to application of Mo under field conditions is more effective on acid soils (Adriano, 2001). However, liming could only increase the amount of plant-available Mo on soils which have a reserve of Mo. There are some soils in New Zealand (e.g., some highly weathered "gumland" soils of Northland and deep acid peats in the Waikato) that have no reserve Mo and hence liming is ineffective in raising available Mo. In such cases Mo must be applied as a fertilizer.

B. HEAVY METALS

Liming is increasingly being accepted as an important management tool in reducing the toxicity of heavy metals in soils. In addition to the traditional

agricultural lime, a large number of studies have examined the potential value of other liming materials as immobilizing agents in reducing the bioavailability of a range of heavy metals in soils (Table IX). In this regard Cd contamination of agricultural soils is of particular concern because this metal reaches the food chain through regular use of Cd containing fertilizer materials, such as single superphosphates. Also it remains mobile even at about neutral pH.

Low soil pH and soils of low CEC induce a greater uptake of soluble Cd by plants. The Cd in soils can be immobilized by increasing the soil pH through the addition of liming materials. One benefit arises from the antagonistic effect from Ca added through liming, which may serve to depress Cd uptake by competing for exchange sites at the root surface. Limited Cd uptake may also arise from increases in Cd adsorption caused by increases in pH that induce increases in negative charge (Temminghoff, 1998). However, adsorption may decrease with an increase in Ca concentration due to a decrease in activity coefficient, increase of inorganic complexation and increase in Ca competition. The resultant effect of liming on Cd adsorption and uptake depends on the relative change in pH and Ca concentration in soil solution.

Liming, as part of the normal cultural practices, has often been shown to reduce the concentration of Cd and other heavy metals in the edible parts of a number of crops (Table IX). Addition of other alkaline materials such as coal fly ash has also been shown the decrease the Cd contents of plants (Lagerwerf, 1971; Adriano *et al.*, 1982). In these cases, the effect of liming materials in decreasing Cd uptake by plants has been attributed to both decreased mobility of Cd in soils and to the competition between Ca and Cd ions on the root surface. It is also possible that above pH 7, solubility and uptake of Cd can be enhanced due to facilitated complexation of Cd with humic or organic acids (Naidu and Harter, 1998).

Arsenic can be precipitated using sodium sulfides, lime, ferric sulfate, ferric chloride and alum. The primary mechanism of As removal is by precipitation as hydroxide. Lime has been considered as a better and cheaper treatment chemical for As in industrial wastewater. Arsenic in industrial waste, which also contains other heavy metals in solution, can be concurrently co-precipitated upon precipitation of the heavy metals.

The effect of liming soils on As mobility has been rather inconsistent. Calcium from lime forms calcium arsenate ($Ca(AsO_4)_2$) and because the solubility product constant of this compound is greater than that for Fe and Al arsenates, the role of Ca in the sorption process of As is not as clear cut as the role of Fe and Al. For this reason, liming is not practiced widely to overcome As toxicity in soils, although liming has been shown to reduce the concentration of water soluble As in soils (Jones *et al.*, 1997). Recently, Heeraman *et al.* (2001) have observed that liming of acid mine-soils contaminated with Hg and As has resulted in an increase in the uptake of these elements because of the lime-induced improvement in plant growth. In a limed loamy soil treated with $HgCl_2$, reduction of Hg salts to $Hg°$

increased, resulting in increased volatilization losses (Frear and Dills, 1967; Landa, 1978).

Manganese uptake by plants is more closely related to the soil pH than is the uptake rate of any other micronutrient (Marschner, 1995). Marked increases in the bioavailability of Mn should be expected when soil pH decreases below 5.5. Manganese toxicity in acidic soils can be easily alleviated through adsorption and precipitation reactions by lime application at rates sufficient to raise the soil pH to about 6.5 (Jauregui and Reisenauer, 1982).

Phytotoxicity of nickel (Ni) can be alleviated rather easily by increasing the levels of Ca through liming; Ca competes with Ni for plant uptake, thereby reducing the uptake of Ni. Thus liming serpentine soils containing toxic levels of Ni and agricultural soils treated with alkaline stabilized biosolid helps to overcome the phytotoxicity of Ni (Bolton, 1975).

Selenium (Se) is quite bioavailable in well-aerated, alkaline soils where it occurs primarily as selenates. In acid soils selenite is formed which is sparingly soluble and generally unavailable to plants. In general, liming the soil could enhance the uptake of Se by plants (Adriano, 2001).

The uptake of lead (Pb) is often found to decrease with liming, which is attributed to increased adsorption/precipitation at high pH, and competition between Pb and other cations for uptake (Cox and Rains, 1972). Basta and Tabatabai (1992) observed positive correlation between Pb sorption by soils and soil pH. Calcium addition through liming causes an inhibition of the translocation of Pb from root to shoot.

Removal of Cr (III) from industrial effluent is achieved using lime or magnesium oxide to precipitate as chromic hydroxide. Precipitation is reported to be most effective at pH 8.5–9.5, due to the low solubility of chromic hydroxide in that range (Patterson, 1985). This method will decrease Cr concentration to very low levels of Cr and hence precipitation systems are very widely accepted by major tanneries. Recently, Bolan and Thiagarajan (2001) examined the effect of liming materials on the adsorption and plant availability of Cr(V) and Cr(III) species. Addition of liming materials to soils increased the retention of Cr(III) but had the opposite effect on the retention of Cr(VI). The liming materials were found to be effective in reducing the phytotoxicity of Cr(III) but not Cr(VI). Addition of the liming materials decreased the concentration of the soluble Cr(III), the main reason for the decrease in the phytotoxicity of Cr(III) in the presence of liming material.

VI.   CONCLUSIONS AND FUTURE RESEARCH NEEDS

Soil acidification is a natural process, but it can be accelerated by certain industrial and farming activities. Pyrite oxidation causing acid drainage and acid

precipitation through the emission of SO_x and NO_x gases are the two most important industrial-borne processes of acidification. However, under managed farming systems, most of the acidity is generated from fertilizer application and from C, N and S biogeochemical cycles in soils. Soil acidification reduces the availability of major plant nutrients and induces the solubilization of metals that can lead to phytoaccumulation.

Various liming materials are used to neutralize the acidity, there by overcoming the problems associated with acidification. The primary objective of liming soils used for agricultural production is to reduce the concentrations of Al and Mn, which are more soluble in acid soils and can be phytotoxic. Liming also enhances the rate of decomposition of organic matter and the subsequent transformation and release of nutrient ions from it. For example, liming has been identified for the enhanced leaching of NO_3^- in cultivated soils and the consequential contamination of ground water. This is attributed to increased mineralization and nitrification of organic N and the supply of co-cation (Ca) for NO_3^- movement in soils.

Liming has been shown to reduce the amount of P fertilizer required to boost yield in some soils. This reduction in P requirements results directly from an increased solubilization of soil P and its subsequent uptake and/or indirectly from an increase in P uptake due to reduced Al and Mn toxicity. This is termed as lime-induced P-sparing effect that has been observed at normal liming rates to generate $11-20$ kg P ha^{-1} year^{-1} in some sedimentary-type soils having low pH (<5.5).

Liming is increasingly being practiced as a management tool to immobilize heavy metals in soils, biosolids and mine tailings, thereby reducing their availability for plant uptake and leaching to ground water. In fact, alkalinization of biosolids is commonly practiced to enhance their immobilization potential for heavy metals (Hsiau and Lo, 1998). Several reasons have been attributed to the lime-induced immobilization of heavy metals: increases in negative charge (CEC) in variable charge soils; formation of strongly-bound hydroxy metal species; precipitation of metals as hydroxides; and sequestration due to enhanced microbial activity. However, in soils with low cation exchange capacity, liming may increase the plant availability of heavy metals due to the exchange of lime-borne Ca with the heavy metal ions and subsequent increase in their concentration in soil solution. The net effect of liming on heavy metal transformation in these soils largely depends on the extent of pH change and Ca release from the liming material.

Lime is used to enhance the natural attenuation of metals in contaminated soils. Alkaline stabilized biosoilds are now becoming increasingly popular as a liming material because of the complementary mitigating effect from organic matter in immobilizing metals in sols. Lime-induced mobilization of nutrient ions and immobilization of heavy metals are important in sustainable agricultural production and soil environmental protection. Future research should aim to focus on the development of methods to quantify lime-enhanced mobilization of

nutrient ions and lime-induced immobilization of heavy metals in soils under field conditions and to explore further the role of liming in remediating contaminated soils. This will entail elucidation of the role of liming in various biogeochemical processes in the rhizosphere and the direct effects on microbial consortium and root-mycorrhizal association.

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