



Organic acid behavior in soils – misconceptions and knowledge gaps

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Abstract

Organic acids have been hypothesized to perform many functions in soil including root nutrient acquisition, mineral weathering, microbial chemotaxis and metal detoxification. However, their role in most of these processes remains unproven due to a lack of fundamental understanding about the reactions of organic acids in soil. This review highlights some of the knowledge gaps and misconceptions associated with the behavior of organic acids in soil with particular reference to low-molecular-weight organic acids (e.g., citrate, oxalate, malate) and plant nutrient acquisition. One major concern is that current methods for quantifying organic acids in soil may vastly underestimate soil solution concentrations and do not reveal the large spatial heterogeneity that may exist in their concentration (e.g., around roots or microbes). Another concern relates to the interaction of organic acids with the soil's solid phase and the lack of understanding about the relative importance of processes such as adsorption versus precipitation, and sorption versus desorption. Another major knowledge gap concerns the utilization of organic acids by the soil microbial community and the forms of organic acids that they are capable of degrading (e.g., metal-complexed organic acids, adsorbed organic acids etc). Without this knowledge it will be impossible to obtain accurate mathematical models of organic acid dynamics in soil and to understand their role and importance in ecosystem processes. Fundamental research on organic acids and their interaction with soil still needs to be done to fully elucidate their role in soil processes.

Introduction

Low-molecular-weight organic acids have been hypothesized to play key roles in many soil processes. These processes operate over a whole range of temporal and spatial scales (e.g., whole ecosystem through to the rhizosphere; Beyer and Bolter, 2000; Jones, 1998; Van Breemen, 2000). Most of these roles rely to a large extent on the ability of the organic acids to complex metal cations. For this reason, it has mainly been the divalent and trivalent organic anions that have been implicated in these processes (e.g., malate, citrate and oxalate; Pohlman and McColl, 1986). Although small amounts of organic acids enter the soil from atmospheric deposition and canopy throughfall, most

organic acids in soil arise from root exudation and lysis, and by release from soil microorganisms (Millet et al., 1997; Ryan et al., 2001).

Due to the difficulties in predicting the cumulative effect of organic acids over long time periods (10 to 1000 years), most studies to date have focused on the short-term impact of organic acids in soil with particular emphasis on the rhizosphere (Jones, 1998). With respect to rhizosphere processes, organic acids have been implicated as key drivers in events such as bacterial chemotaxis, nutrient uptake, anoxia alleviation, soil structural improvement and metal decontamination (Barbour et al., 1991; Grierson, 1992; Kelly et al., 1998; Ryan et al., 1995; Xia and Roberts, 1994). For plant and microbial nutrition, organic acids have been hypothesized to be involved in the mobilization and solubilization of poorly soluble nutrients such as

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Mn, Cu, Zn, Fe and P, in the detoxification of metals such as Zn and Al, and in the breakdown of wood (Delhaize et al., 1993; Hoffland, 1992; Marschner, 1995; Micales, 1997). Much of the evidence for these purported roles of organic acids comes from *in vitro* experiments performed under conditions which are vastly different from those that exist *in vivo*, and these studies have therefore drawn considerable criticism (Drever and Stillings, 1997; Jones, 1998; Parker and Pedler, 1988).

Since the realization that the root release of organic acids may confer aluminium resistance in plants, there has been great interest in the possibility of manipulating organic acid efflux by altering the expression of organic acid synthesis/efflux genes in plants (Delhaize et al., 2003; Ryan et al., 2001). After release from the root, however, organic acids can suffer a number of fates such as sorption, biodegradation and metal complexation, making their behavior difficult to predict. The aim of this review is to highlight current misconceptions and knowledge gaps surrounding the behavior of organic acids in soil with particular reference to plant nutrition. The review will focus on the main factors controlling the fate of organic acids in soil including their behavior in soil solution, nutrient-mobilization efficiency, sorption to the soil's solid phase, degradation by the soil microbial biomass and role in ecosystem processes. The generic term organic acids is used throughout this review, however, it should be acknowledged that in many soils these compounds are either partially or fully dissociated and as such could be referred to as organic anions.

Organic acid dynamics in soil solution

Across a broad range of ecosystems the concentration of organic acids in soil solution has been shown to be low, typically ranging from 1 to 50 μM (Baziramakenga et al., 1995; Krzysowska et al., 1996; Strobel, 2001). In comparison with many inorganic solutes in soil solution, such as NO_3^- , Cl^- , K^+ , Na^+ , Ca^{2+} and Mg^{2+} , these concentrations are an order of magnitude lower, however, they are similar to reports for other low-molecular-weight organic solutes (e.g., amino acids, sugars; Barber, 1995; Kielland, 1995). In the case of amino acids and sugars, significant reservoirs of these compounds exists in a polymeric form, with replenishment of the soil solution pool dependent upon the activity of extracellular enzymes (Stevenson, 1982). In contrast, replenishment of the

soil organic acid pool depends almost entirely upon a continued release from either plant or animal cells, and can therefore be expected to be more temporally variable. Based upon this assumption, it might be expected that soil solution organic acid concentrations would vary considerably over both space and time; however, current evidence suggests that this is not the case (Jones, 1998; Strobel, 2001). The question arises as to why organic acid concentrations in soil solutions are always so low and temporally constant? A number of explanations may account for this phenomenon including methods of sampling soil solutions, sorption characteristics and microbial reactions.

Problems with sampling soil solutions for organic acids

The purported role of organic acids in mineral weathering has recently been questioned based upon the premise that the concentration of organic acids in soil solution is too low to have any significant effect on mineral dissolution rates (Drever and Stillings, 1997). Their central argument, however, relies on the accurate quantification of organic acids in soil. To date, there has been relatively little work investigating the impact of soil solution extraction technique on the concentration of organic acids detected, however, based upon other reports this is likely to highly influence the results obtained (Giesler et al., 1996; Grieve, 1996; Jones and Edwards, 1993; Smethurst, 2000; Tyler, 2000). Organic acid analysis, typically involves the bulk removal of water from large volumes of soil by centrifugal drainage, ceramic suction samplers or water extracts. Given the various hypothesized functions of organic acids in soil and the spatial heterogeneity of soil resources such as P, it is likely that the concentration of organic acids may also be highly spatially localized (Figure 1). Although soil solution microsampling techniques have been developed at the millimeter scale (Göttlein et al., 1996), due to the very low diffusion coefficients of most organic acids in soil (e.g., citrate, oxalate; Darrah, 1991), the size of these hot spots may be only a few μm in diameter if release occurs from the tip of a root hair, fungal hyphae or bacterial cell. This is supported by mathematical modeling and experimental simulations of organic acid diffusion in the rhizosphere (Darrah, 1991; Jones et al., 1996a). We hypothesize that current extraction techniques vastly underestimate soil solution organic acid concentrations by maybe up to several orders of magnitude within soil microsites. In addition, soil

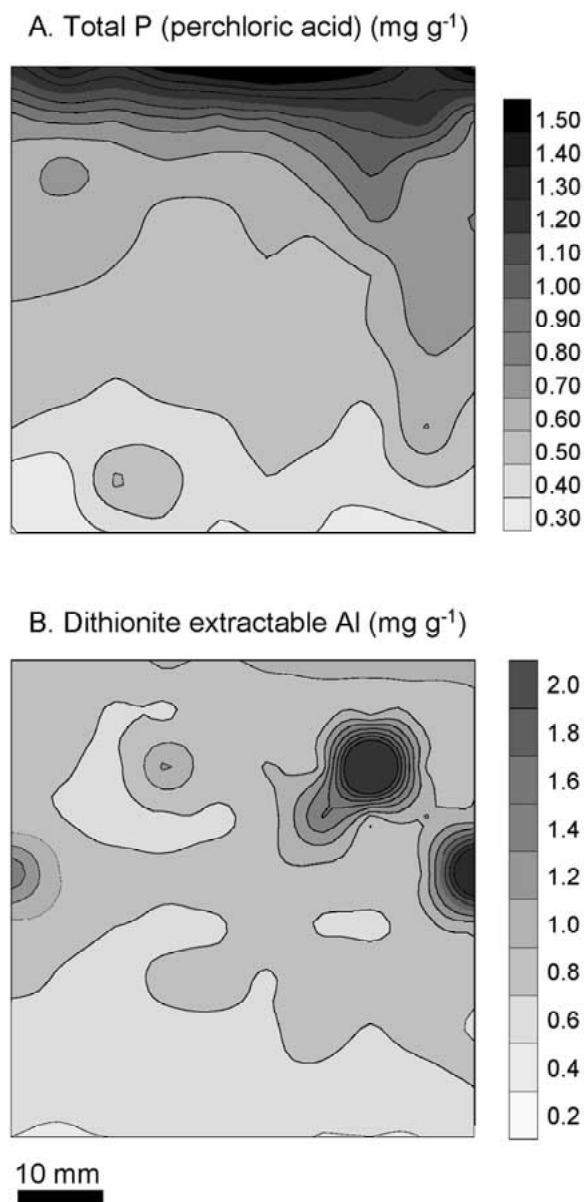


Figure 1. Spatial distribution of phosphorus and aluminium in a 50 mm wide, 50 mm deep block of podzolic soil collected from under an acid grassland in the UK. Soil P and Al analysis was performed at 5 mm intervals and the data interpolated using a computerized minimum curvature routine to obtain a concentration map. The data are representative of other soil blocks analyzed at the same location.

solution sample preparation (e.g., soil storage, etc) and analytical errors may also cause the underestimation of organic acid concentrations in soil (Chapman et al., 1997; Piombo et al., 1996). Unfortunately, due to the lack of specific dyes, electrodes and chemical probes for organic acids, their spatial heterogeneity in

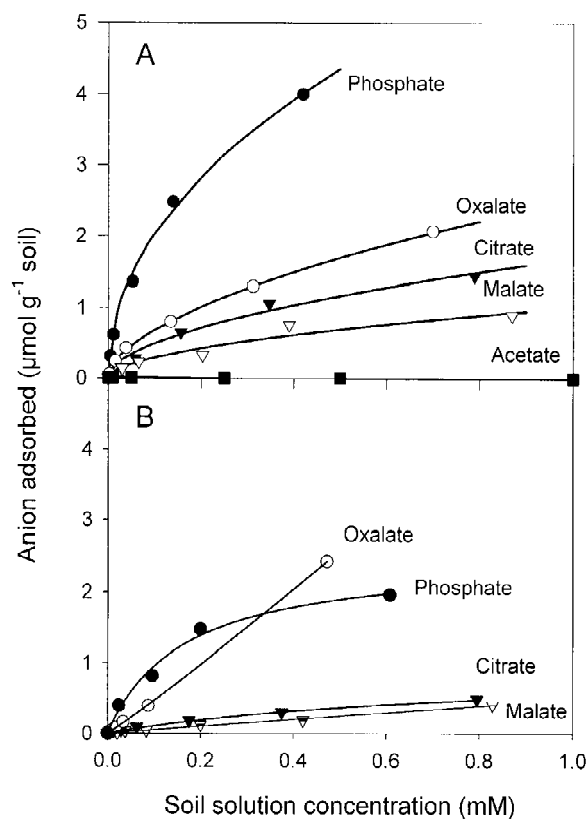


Figure 2. Organic acid and phosphorus sorption on (A) a gleyed subsoil and (B) a calcareous topsoil. Symbols represent experimental data points while lines represent optimized fits to the Langmuir sorption equation. Further details of the soils and experimental procedures can be found in Jones and Brassington (1998) and Ström et al. (2002a,b).

soil remains unknown. One solution to this problem could be the development of marker gene bioassays, which involves the tagging of soil bacteria and fungi with reporters based on green fluorescent protein (gfp) or luciferase (lux) that respond to exogenous organic acids (as has been achieved for C, P and amino acids in soil; Killham and Yeomans, 2001; Farrar et al., 2002).

In the case of organic acid-mediated metal detoxification by plant roots, the concentration in the root apoplasm may be more important than the external soil solution concentration (e.g., in malate-induced Al detoxification; Delhaize et al., 1993). To date, there has been no evaluation of apoplastic concentrations, however, this is certainly worthy of further consideration.

Solid phase buffering of soil solution concentrations

Another explanation for the observed near-constant

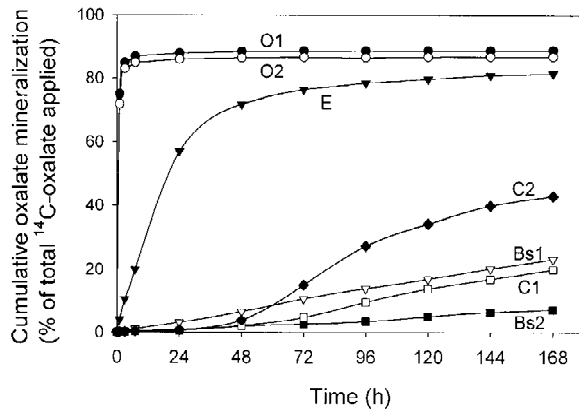


Figure 3. Oxalate mineralization in different horizons of a *Picea abies* forest soil from Sweden. The initial ^{14}C -oxalate concentration was $500\ \mu\text{M}$. Further details of the soils and experimental procedures can be found in Van Hees et al. (2002).

organic acid concentrations in soil solution may be the high degree of buffering by the soil's solid phase. In contrast to amino acids and sugars, di- and tri-carboxylic acids become strongly associated with the solid phase through the processes of adsorption and precipitation (Jones and Edwards, 1998). In the case of oxalate, if there are significant quantities of free Ca^{2+} in solution, oxalate concentrations will rarely exceed $50\ \mu\text{M}$, due to the formation of insoluble Ca^{2+} -oxalate (Ström et al., 2002a,b). Additionally, at low organic acid solution concentrations ($<50\ \mu\text{M}$) the soil's solid phase possesses a high affinity and large capacity for organic acid adsorption (e.g., for citrate, malate and aconitate), and these processes will also help maintain low soil solution concentrations (Figure 2).

Microbial regulation of soil solution organic acid concentrations

A third possible explanation for the low organic acid concentrations detected in soil solution is the continual removal by the soil microbial community. In support of this, organic acid mineralization across a wide range of soil types has been shown to be rapid (Figure 3; Jones, 1998). Further, soil solution concentrations reported in the literature are often close to the minimum concentration at which transporters can generate net organic acid uptake (i.e. influx $>$ efflux; 0.1 to $1\ \mu\text{M}$; Barber, 1995; Jones et al., 1996b). We hypothesize that the soil microbial community plays an active role in scavenging this readily utilizable source of C from the soil solution thereby preventing the accumulation of organic acids in soil.

Where do the organic acids in soil come from?

In many ecosystems root turnover provides the primary source of C entering the soil (Norby and Jackson, 2000). Based upon the typical composition of root sap ($40\ \text{mM}$ sugars, $10\ \text{mM}$ organic acids, $10\ \text{mM}$ amino acids; Marschner, 1995; Ryan et al., 2001), organic acids can form a major component of the solutes lost from plant cells upon lysis. However, in comparison with the polymeric reservoirs of sugars and amino acids in root tissue (ca. 20 to 40% of total root dry weight), organic acids provide only a minor fraction of the primary C entering the soil system (ca. 1 to 3% of total root biomass and a minor component of root exudates; Farrar and Jones, 2000). As organic acids possess similar soil solution concentrations and half lives to sugars and amino acids (see later), it implies that the rates of production of all three groups of compounds in soil must be similar. We conclude therefore that most of the organic acid entering the soil solution pool must be produced from a source other than plants (e.g., secondary organic acids produced and excreted by microorganisms formed during the breakdown of other C substrates). Further work is therefore required to elucidate the critical control points of organic acid production in soil.

Measuring total organic acids in soil

Although some methods have been presented for quantifying total organic acids in soil, the results obtained with such methods remain difficult, if not impossible, to interpret (Piombo et al., 1996). The main problem of these techniques is that they measure the sum of all soil pools, many of which may have no direct relationship with the question being asked in the study (e.g., the internal microbial pool in a soil P solubilization study). The main methodological problem that needs to be overcome is finding a way of separating organic acids bound to the solid phase from those held in the microbial biomass. In our studies, we have found that organic acids in organic forest soils can be completely recovered by extraction with KH_2PO_4 ($50\ \text{mM}$); however, recovery of organic acids from mineral subsoils remained incomplete even at high KH_2PO_4 concentrations ($500\ \text{mM}$; Table 1). Full removal of organic acids from mineral horizons therefore requires extraction with strong acids, which inevitably releases large amounts from soil microorganisms. We estimate that for a typical topsoil the

Table 1. Recovery of ^{14}C -citrate from two *Picea abies* forest soils by KH_2PO_4 (1, 50 and 100 mM) and HCl (10 mM). The soil was CHCl_3 -fumigated for 2 days, 50 nmol g^{-1} ^{14}C -citrate added (pH 4.5), the soil incubated with a CHCl_3 atmosphere for 7 days and then the soil extracted with either KH_2PO_4 (1, 50 or 100 mM) or HCl (10 mM) for 15 min (5:1 v/w solution:soil). Values represent the means of both soils \pm SEM ($n=2$). Further details of the Swedish forest soils (Heden and Nyänget) can be found in Van Hees et al. (2002)

Horizon	Adsorbed on the solid phase (% of total) ^a	Extractant type for citrate recovery from soil			
		1 mM KH_2PO_4	50 mM KH_2PO_4	100 mM KH_2PO_4	10 mM HCl
		(% of total ^{14}C citrate added)			
O1	19 \pm 12	100 \pm 3	102 \pm 3	102 \pm 0	96 \pm 2
O2	31 \pm 23	95 \pm 5	97 \pm 3	96 \pm 1	96 \pm 6
E	80 \pm 18	40 \pm 20	46 \pm 17	52 \pm 13	44 \pm 16
Bs1	97 \pm 2	4 \pm 3	16 \pm 9	21 \pm 7	5 \pm 4
Bs2	97 \pm 2	6 \pm 5	19 \pm 10	29 \pm 13	5 \pm 4
C1	98 \pm 1	6 \pm 3	23 \pm 8	36 \pm 11	5 \pm 2
C2	98 \pm 1	6 \pm 1	26 \pm 1	39 \pm 4	7 \pm 2

^aEstimated from sorption isotherms (Van Hees et al., 2002).

Table 2. Amount of organic acids in the soil solution or associated with the solid phase in the surface horizon of a calcareous Typic rendoll (USDA Soil Taxonomy) soil and in the surface organic and lower mineral horizon of a *Picea abies* forest podzolic soil. Soil solution concentrations were measured directly and the amount associated with the solid phase at this soil solution concentration calculated from sorption isotherms. The values were derived from data presented in Ström et al. (2001, 2002a,b) and Van Hees et al. (2002). n.d. indicates not determined

	Typic rendoll Ah horizon		Podzolic O horizon		Podzolic Bs horizon	
	Soil solution	Adsorbed	Soil solution	Adsorbed	Soil solution	Adsorbed
	pmol mm ⁻³		(pmol mm ⁻³)		(pmol mm ⁻³)	
Citrate	0.11	0.35	19.5	3.8	0.3	225
Oxalate	0.12	2.76	1.2	30.4	0.9	967
Malate	0.10	0.34	n.d.	n.d.	n.d.	n.d.

amount of organic acids held in the soil microbial biomass is between 0.5 to 100 pmol mm⁻³ soil, given an internal cell concentration of 1 to 10 mM. These concentrations are of a similar magnitude to those held on the soil's solid phase, and therefore extractions should take this factor into account (Ström et al., 2001, 2002a,b; Table 2).

Organic acid-mediated nutrient solubilization and mobilization

One of the main hypothesized functions of organic acids in soil is the solubilization and mobilization of nutrients by plants and microorganisms. Recently, there have been suggestions that organic acid release from plants may provide a practical, green solution for combating declining fertility within resource-poor agroecosystems such as those in parts of South Amer-

ica, Sub-Saharan Africa and Australia (Lopez-Bucio et al., 2000). In the case of nutrients such as P, its solubilization by organic acids such as oxalate and citrate is highly soil dependent (Figure 4). In a screen of 20 contrasting soil types, we found that organic acids mobilized significant amounts of P in 65% of the soils tested ($P < 0.05$, in comparison with water) with large amounts of P mobilized in 35% of the soils. The reason for the large differences in the response of the various soil types remains unclear; however, the amount of P mobilized did not correlate well with either total soil P, soil pH, P-sorption capacity or total Fe ($r^2 < 0.5$; data not presented). These differential soil type responses are also supported by the study of Ström et al. (2002a) in which oxalate was capable of increasing plant P acquisition while citrate could not. This result highlights the problems in recommending organic acids as a blanket strategy for enhancing P mo-

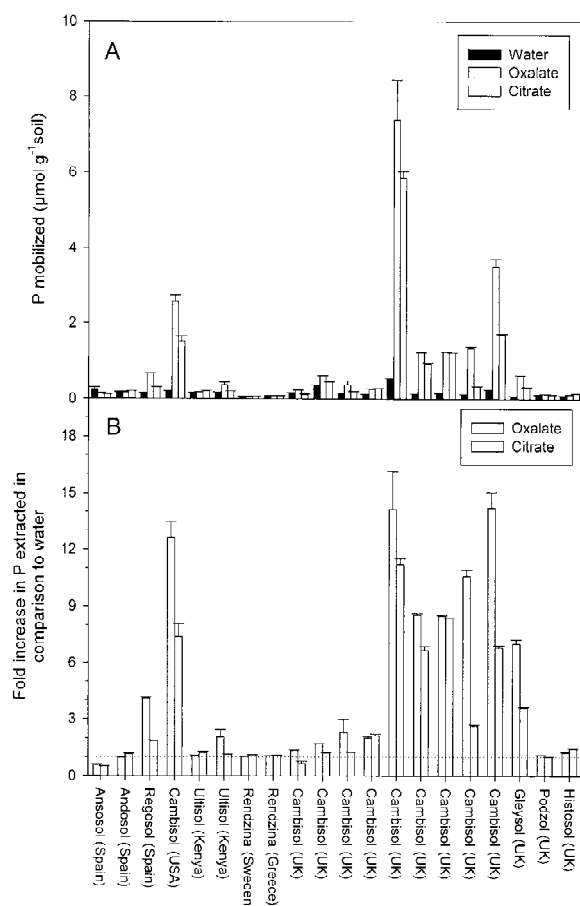


Figure 4. Organic acid-mediated phosphorus solubilization in 20 contrasting soils. Panel A (upper) shows the amount of P solubilized when soils were shaken with either water (control), oxalate (1 mM), or citrate (1 mM) for 30 min at a soil:solution ration of 1:10 (w/v). Panel B (lower) shows the magnitude of the change in P solubilization by oxalate and citrate in comparison to the water extractions. A value of 1 (no enhanced P solubilization) is represented by the dotted line. Further details of the experimental procedures can be found in Jones and Darrah (1994). Values represent means \pm SEM ($n=3$).

bilization in soil. Similar arguments also exist for other proposed organic acid-mediated nutrient mobilization strategies (e.g., Fe, Zn, Cu) and metal detoxification mechanisms (e.g., Al, Cd).

In the case of Zn and P, a drop in soil pH often enhances the plant availability of these nutrients. The importance of an associated soil pH change on the nutrient mobilization/solubilization efficiency of organic acids, either as a result of the direct release of H^+ with the organic acid (e.g., H^+ -citrate) or indirectly from associated H^+ -ATPases, also requires further investigation. Similarly, additional work is required to determine the critical concentration of organic acids

or anions in the soil that are sufficient to cause a significant increase in plant nutrient uptake. In summary, more research is required to understand the factors that control organic acid-mediated nutrient release in different soil types.

Organic acid biodegradation by soil microorganisms

One of the primary mechanisms by which organic acids are removed from the soil solution is through uptake by soil microorganisms (Jones et al., 1996b; Lundström et al., 1995). Along with other low-molecular-weight compounds such as sugars and amino acids, organic acids represent one of the most labile sources of C in soil and, due to their ubiquity in soil, it can be expected that most soil organisms will be capable of their utilization. A number of studies have shown that the rate of organic acid turnover in soil is extremely rapid with half-lives ranging from 1 to 5 h in organic topsoils, to 5 to 12 h in subsoils (Jones, 1998). This is comparable to the rate of utilization of many other low-molecular-weight solutes in soil (e.g., amino acids, glucose; Coody et al., 1986; Jones, 1999). The finding that organic acid turnover is very fast and that soil solution concentrations are maintained at low concentrations (1 to 50 μ M) suggests that the flux through the soil solution is highly dynamic with the free organic acid pool turning over between 500 and 3000 times annually. If the total organic acid pool is considered (i.e. sorbed plus free in solution) the rate of turnover can be estimated to be of the same order of magnitude in organic topsoils where the degree of sorption is low (Table 2). In mineral subsoils, however, where the degree of sorption is much higher and the rate of degradation much lower, the total organic acid pool may turn over at a much slower rate (ca. 0.5 to 10 times annually).

One question that has yet to be adequately resolved is the degree to which soil microorganisms can act as both sources and sinks of organic acids in the soil solution. The excretion of organic acids by soil microorganisms in laboratory liquid cultures is well documented; however, there have been few studies conducted in soil (Dutton and Evans, 1996; Gallmetzer and Burgstaller, 2001; Heyer and Krumbein, 1991; Takao, 1965). It is clear that ectomycorrhizal fungi can release large quantities of organic acids (particularly oxalate and citrate); however, whether they simultaneously act as sources and sinks remains unknown. It

could be hypothesized that in these circumstances, distinct spatial regulation of organic acid exudation and uptake occurs in the mycelium in response to localized soil environmental conditions. In the case of silicate weathering by fungal hyphae (Van Breemen et al., 2000), we hypothesize that organic acid exudation occurs primarily at the hyphal tip region with organic acid consumption in basal areas away from the weathering front. This is supported to some extent by laboratory studies with bacteria in which the level of influx is directly regulated by external organic acid supply (Jones et al., 1996b). Hopefully the genome sequencing of various soil bacteria (e.g., *Rhizobium*), combined with the development of molecular tools such as green fluorescent protein marking (Errampalli et al., 1999), will help address issues such as the temporal and spatial dynamics of organic acid transport gene expression in soil microorganisms.

Another consideration in the biodegradation of organic acids is the extent to which organic acids can be accessed when they are either sorbed or fixed to the soil's solid phase or present in a precipitate. Although there have been insufficient studies on this to draw definitive conclusions, the limited information available suggests that organic acids held strongly to the soil's exchange phase (i.e. fixed) are not biodegraded, at least in the short term (Boudot, 1992; Jones and Edwards, 1998). In contrast, organic acids held loosely on soil exchange sites can be rapidly mineralized (Jones and Edwards, 1998). The latter scenario relies on the continual removal of organic acids from solution, which leads to a continual desorption of organic acids off the solid phase. In the case of precipitated organic acids (e.g., Ca-oxalate), indirect studies in calcareous soils have indicated that their rate of biodegradation is extremely slow, although again definitive studies are lacking (Ström et al., 2001).

The extent to which organic acids complexed with metals (e.g., Al-citrate) can be degraded by the soil microbial community remains controversial (Jones, 1998). Studies in liquid culture media have demonstrated that both bacteria and fungi have transporters capable of taking up specific organic acid metal complexes (e.g., Fe-citrate, Ca-citrate) while other reports suggest that these metals are capable of being taken up but not assimilated (Brynhildsen and Allard, 1994; Brynhildsen and Rosswall, 1989; Francis et al., 1992; Madsen and Alexander, 1985). Studies in soil, however, suggest no distinction between the utilization of metal complexed or non-metal complexed organic acids (Brynhildsen and Rosswall, 1997; Jones et al.,

2001). This contradiction may be simply due to the degree of adaption in each experimental system. In culture media, it is likely that many 'environment' genes are down-regulated, and therefore when challenged with organic acid-metal complexes not previously exposed to, the cellular machinery is not present. Alternatively, C is provided by another component of the media, making utilization of the organic acids unnecessary. If these complexes are common in their natural environment (e.g., Al-citrate in a podzolic soil) it can be expected that the microbes will possess the transporters capable of using this labile substrate (given that organic acids do not accumulate in soil). Again definitive studies are required to clarify this.

Organic acid interactions with the solid phase

Individual organic acids interact differently with the soil's solid phase. Generally, the degree of association is directly related to the amount of charge the organic acid carries and the solution pH (Figure 2; Jones and Brassington, 1998; Karlton, 1998; Ström et al., 2001; Van Hees et al., 2002). Monovalent organic acids such as acetate, lactate and propionate are weakly adsorbed to the soil's solid phase, whereas divalent organic acids such as malate, fumarate and succinate are adsorbed to a greater degree (Figure 2). The greatest adsorption occurs for trivalent organic acids such as citrate, isocitrate and aconitate, with the degree of sorption often being similar to that for phosphate (Figure 2). A major problem that remains to be resolved, however, exists in the interpretation of conventional sorption isotherm experiments. This mainly centers around the issue of whether these experiments actually measure an adsorption process in its strictest sense. Typically, sorption isotherms for organic acids have been constructed using the standard methodology applied to phosphate which involves shaking soil with known concentrations of organic acids at a high soil:solution ratio (e.g., 1:10 w/v; Kuo, 1996). This methodology may not be appropriate for organic acids or P for a number of reasons (Li and Stanforth, 2000). Firstly, unless steps are taken to sterilize the soil, significant microbial degradation of the organic acids can occur during the shaking process, thereby overestimating the degree of sorption. Degradation of organic acids by the soil microbial community can be suppressed through the addition of high concentrations of chemical sterilants (e.g., Na-azide or HgCl₂; de Maagd et al., 1998), but many of these

also interact with the soil's solid phase, possibly reducing organic acid sorption. Moreover, they can cause the lysis and release of competing anionic substances from microbial cells. Alternatives, including chloroform fumigation, may also release significant quantities of potentially competing substances into the soil solution from ruptured microbial cells, while autoclaving significantly affects the structure and chemistry of Fe- and Al-hydroxide sorption surfaces (Otabbong and Barbolina, 1998; Xie and Mackenzie, 1991). To reduce organic acid microbial degradation, short shaking times have been advocated (5 to 10 min; Jones and Brassington, 1998). Whilst this will reduce microbial degradation, it probably also greatly underestimates the amount of sorption. Evidence for this comes from studies on phosphate where sorption is a multiphasic process involving a fast sorption phase which typically reaches equilibrium within 1 h, and a second slower sorption phase, which may not reach equilibrium for many days (Hope and Syers, 1976). Given the short residence time of organic acids in the rhizosphere, it could be argued that for plant nutrient uptake only the first sorption phase is important, however, for pedogenic processes the second phase becomes more important. Other experimental factors such as the soil:solution ratio, the background ionic strength, the control of solution pH during the shaking period, the organic acid balancing cation (Na^+ , H^+ , Ca^{2+} , etc.) are also major considerations which may affect the final result (Courchesne, 1991; Rupa et al., 2001). As yet there have been no studies to address the importance of these issues.

Of greater concern is the extent to which these experiments are actually measuring adsorption *per se* or other chemical events such as precipitation. Here we define sorption as the reversible binding of organic acids to the soil's solid phase. In contrast, we define fixation as the process by which organic acids become bound to soil particles in an almost irreversible manner unless extreme chemical conditions, which rarely occur in the soil, are employed to remove them (e.g., 1 M HCl). While sorption and fixation are reactions occurring at the surface of minerals, precipitation can occur purely in the solution phase. Using the current experimental procedures for quantifying sorption, precipitates formed in the soil solution will be accounted for as being adsorbed (e.g., Ca-oxalate). The differences in sorption between free organic acids (e.g., $\text{H}_3\text{-citrate}^0$, citrate^{3-}) and organometallic complexes (e.g., Fe-citrate^0 , Al-citrate^0) also remains unknown but deserves further study.

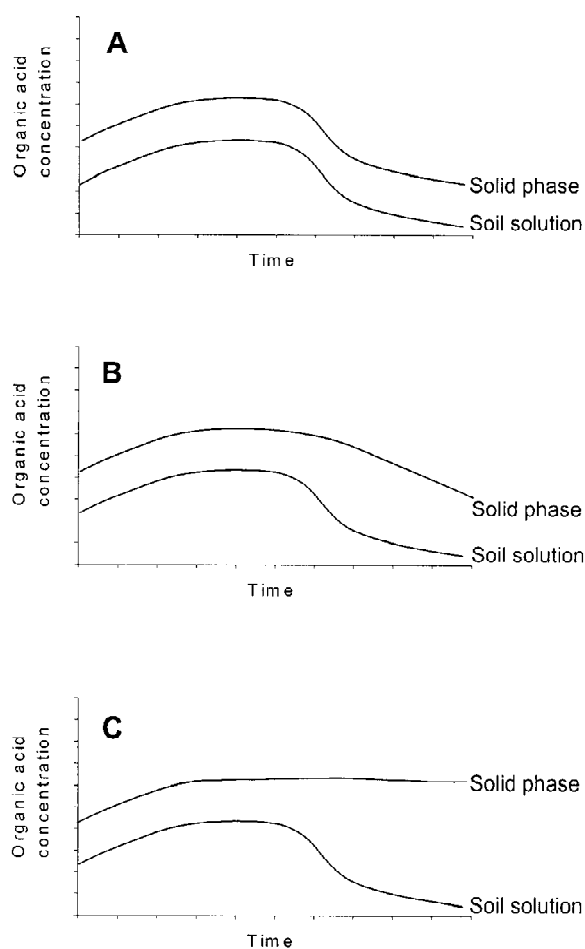


Figure 5. Schematic representations of the sorption and desorption reactions of organic acids in soil. Panel A (upper) illustrates the fast equilibrium reaction between organic acids held in solution and on the solid phase. Panel B (middle) shows a slow rate of desorption compared to the rate of sorption. Panel C (lower) shows almost no desorption when soil solution concentrations fall. See text for further details.

Another major issue that is rarely considered, and which would help address the issues raised above, is the rate of desorption of organic acids from the solid phase. Studies on the fate of organic acids in soil have mainly focused on the removal of organic acids from the soil solution as this directly affects the efficiency of rhizosphere-based nutrient acquisition or metal detoxification reactions (Ryan et al., 2001). However, desorption is also important, particularly in the computer modelling of organic acid dynamics where it is often assumed that the rate of sorption and desorption from the solid phase are identical (Barber, 1995). Typically this reaction is described by a constant, the

buffer power (b), which is defined as

$$b = (OA_{tot}/OA_{sol}), \quad (1)$$

where OA_{tot} is the total amount of organic acid in the soil (sorbed plus solution) and OA_{sol} is the amount of organic acid in solution. The extent to which this relationship holds, however, remains unknown. Three different scenarios are shown in Figure 5 to illustrate the point. At low soil solution concentrations the strength of organic acid binding to the solid phase is typically high but at higher soil solution concentrations organic acid binding to the solid phase becomes weak (Figure 2). As most reported soil solution concentrations are $<100 \mu\text{M}$, we will only consider the lower part of the isotherm where Equation 1 is satisfied (i.e. a linear relationship between OA_{sol} and OA_{tot}). Figure 5A shows the assumed situation in Equation 1 where the concentration of organic acids in solution is always in equilibrium with the soil solid phase. Figure 5B shows the situation where the rate of desorption is not as fast as the rate of sorption, while Figure 5C illustrates very slow desorption or fixation/precipitation. Which of these scenarios occurs in a particular soil remains unknown. From the available evidence, we hypothesize that monovalent and some divalent organic acids (e.g., malate, oxaloacetate etc.) will conform to the pattern observed in Figure 5A at all solution concentrations in both mineral and organic horizons. Divalent organic acids like oxalate, which undergo strong sorption and precipitation at mineral surfaces will probably conform to pattern Figure 5C in mineral soils. In the case of trivalent TCA cycle organic acids such as citrate and aconitate, our results indicate that in highly organic soil horizons sorption follows the pattern shown in Figure 5A (Table 2). In contrast, in mineral soil horizons (e.g., Bs, Ah horizons), at high solution concentrations where sorption is weak, they will conform to the pattern of Figure 5A but at low solution concentrations where sorption is strong they will follow Figure 5B.

The preceding discussion on organic acid solid phase reactions highlights our poor understanding of how organic acids behave in soil. Without this information, mathematical modeling will only remain purely speculative, and our understanding of rhizosphere and pedogenic processes involving organic acids rudimentary.

Concluding remarks

Organic acids have been hypothesized to be important in many soil processes; however, consideration of the importance of these processes at the ecosystem level has rarely been explored. This is partly due to a lack of fundamental knowledge about their behavior in soil and the short-term nature of many experiments. More effort is therefore required to unravel the complexities of organic acids in soil with specific emphasis on gaining greater spatial and temporal resolution in measurements and also in validating the procedures used in these studies. Further work is also required to clarify the sequence of events and importance of the various fates of organic acids in the rhizosphere.

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