

Secondary Immobilization as a Phase of N mineralization Dynamics of Soil Organic Inputs

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Abstract: Current understanding of nitrogen (N) mineralization from organic soil inputs considers three alternative processes: immediate net mineralization of N, net immobilization followed by net mineralization, or exclusively net immobilization. The three processes are compatible and linked with the C:N ratio rule. However, research evidence from a number of incubation studies incorporating processed materials like manures, composts, manure composts, or already decomposed plant residues suggest the presence of a second N immobilization phase. The mechanisms and conditions of this process, which is against the prevailing theory of soil N cycling, have not been ascertained, but they should most likely be attributed to impeded dead microbial biomass turnover. The transfer of mineral forms of N to the organic N pool may reasonably be explained by the chemical stabilization of nitrogenous compounds with secondary products of lignin degradation, which occurs late after incorporation of an organic input in soil. Secondary immobilization questions the reliability of the C:N ratio and most likely of other quality indices if proved to be real, even to some extent, while it may also have significant consequences on the management of soil organic additives applied as fertilizers.

Keywords: net N mineralization; organic additives; gross immobilization; C:N ratio; microbial biomass turnover



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1. Introduction

The description of N dynamics following plant residue, manure, or compost input in soil has long been a central issue in soil ecology research. A thorough knowledge of it may allow the prediction of soil mineral N availability, which is an important variable in ecosystem processes and a key component of soil management in the agricultural context. The nutrient mineralization rate of soil organic amendments (applied as fertilizer) constitutes the main parameter controlling nutrient availability for plant uptake and, therefore, nutrient use efficiency as well as losses to water bodies.

The amount of mineral N accumulated over aerobic soil incubations represents net N mineralization and can be defined as the balance of gross N mineralization (or gross ammonification), and microbial N fixation (or immobilization). It is also well shown that net N mineralization dynamics in control soils lacking any amendments are very often described by first order kinetics [1,2], whereas these processes become more complex when soil is mixed with organic additives. The ultimate N release to the soil is directly determined by the decomposability of the organic substances added and the availability of N for microbial growth.

The theoretical kinetic models in Figure 1 (modified from [3]) show the three alternative dynamic processes of mineral N concentration in soil following the addition of organic inputs, given that there is no interference of root uptake, leaching, or aerial losses. To this effect, research data that fit well to these kinetic models are typically obtained by soil incubation trials without plants. Kinetic curves in Figure 1 were extended (dashed lines)

to show that all three processes would end up in net mineralization which would plateau at a certain level if the experiments or simulation exercises were prolonged in time [4–6]. However, long-term incubations are rare as relevant experiments typically intend to give insights on N dynamics for the first growing season after application. Therefore, plateaus are provided from the estimated asymptote of kinetic curves fitting on data. The value of the asymptote represents the theoretical maximum amount of N or the percentage of initial organic N that could be mineralized.

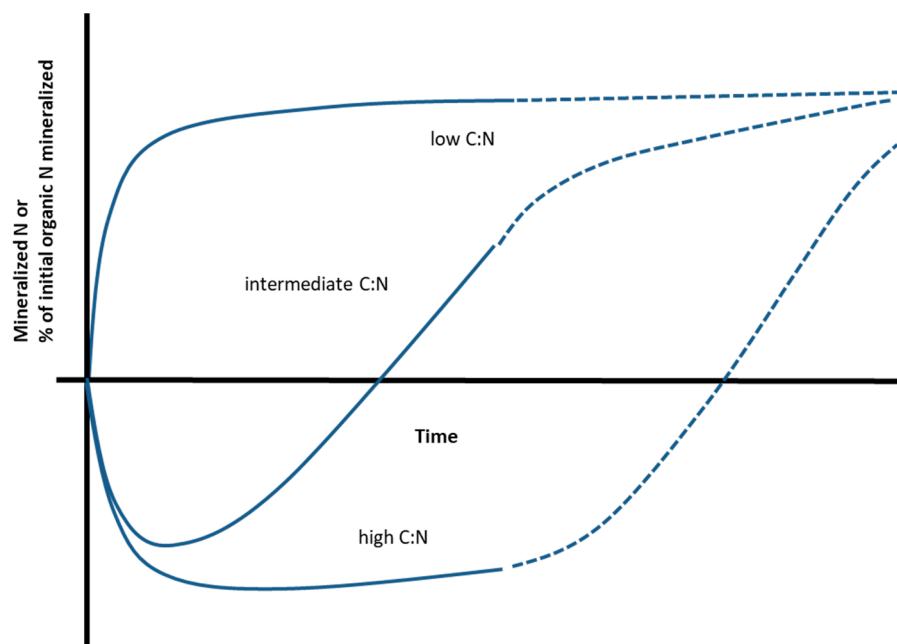


Figure 1. Alternative dynamics of soil inorganic N after the addition of organic residues (modified from [3]).

The three alternative N release trajectories of Figure 1 do not predict for secondary decreases in mineral N; therefore, no explanatory support has been given until now for such a decrease.

The theoretical considerations behind the three alternative processes of immobilization–mineralization (Figure 1) are compatible and closely linked with the C:N ratio concept. Organic C concentration in soil drops during the immobilization phase as CO_2 is released into the atmosphere. On the other hand, organic N concentration increases as ammonium and nitrates are taken up by microorganisms and transferred to the live and dead microbial biomass, which are thereafter considered as parts of the organic N pool of the input. Therefore, the C:N ratio of the sum of the original and derived organic forms of N decreases (e.g., results on litter decay by [7]) and net mineralization occurs when this ratio decreases below a certain value. From then onwards, organic N concentration becomes lower (though to a smaller rate compared with that of C), resulting in the steady decrease in the C:N ratio until the point where it becomes almost equal to that of the microbial biomass (Figure 2). The % of initial organic N that is mineralized is typically smaller than the % of initial C that is mineralized [8,9] indirectly indicating that the C:N ratio of a material decreases during decomposition in soil. Hence, when nitrogen mineralization kinetic data are fitted well by any of the curves of Figure 1, the validity of the C:N rule is not contradicted.

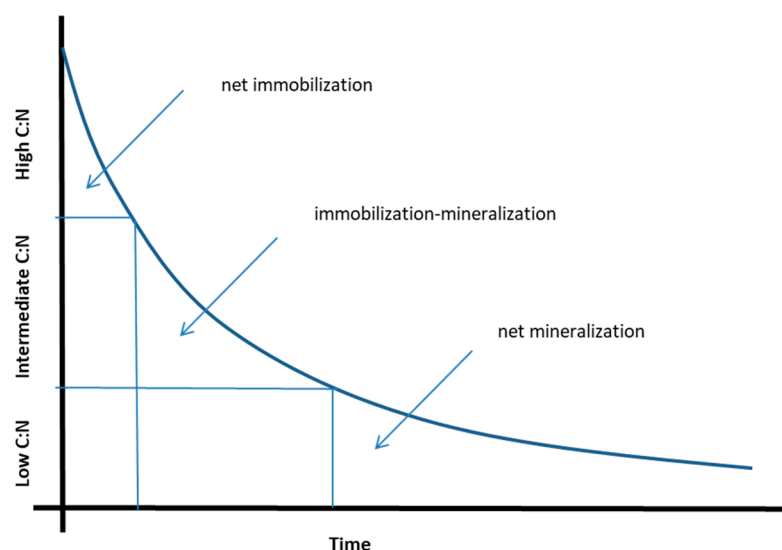


Figure 2. The evolution of C:N ratio of organic inputs during the course of their decomposition in soil.

A secondary decrease in mineral N concentration would undermine the relationship between the C:N ratio and N dynamics. Such a decrease infers that although the C:N ratio narrows, N is immobilized. Hence, apart from scrutinizing published information on the long-term N mineralization dynamics of organic inputs in order to reveal whether secondary immobilization actually occurs in incubation studies, the literature data citing a direct comparison between mineral N release and the C:N ratio were also reviewed.

2. The Relationship between N mineralization and C:N Ratio for Processed Materials

Research results concerning the N mineralization of processed materials (i.e., litter at advanced stages of decomposition, compost, manure, and manure compost) very often show a lack of correlation with the C:N ratio. Four distinct manures incubated in a microcosm study by [10] of immobilized N from soil and the N dynamics lacked any relation with the initial C:N ratio of used manures. Similarly, the C:N ratio was not a good predictor of the extractable inorganic N concentrations in soil amended with fresh and composted cattle manures [11]. Maturity parameters of composts including the C:N ratio were poorly correlated with the rate and extent of mineralization [12,13]. It is also underlined that manures and composts typically have C:N ratios below 25 and, although they are expected to result in net mineralization in this range, they often provoke net N immobilization [6].

3. Secondary Immobilization

Secondary N immobilization or N re-immobilization phases are illustrated in mineralization dynamics graphs by a drop of mineral N ($\text{NH}_4^+-\text{N} + \text{NO}_3^--\text{N}$) at the late stages of organic material decomposition in soil, regardless of whether or not an initial immobilization phase occurred (Figure 3).

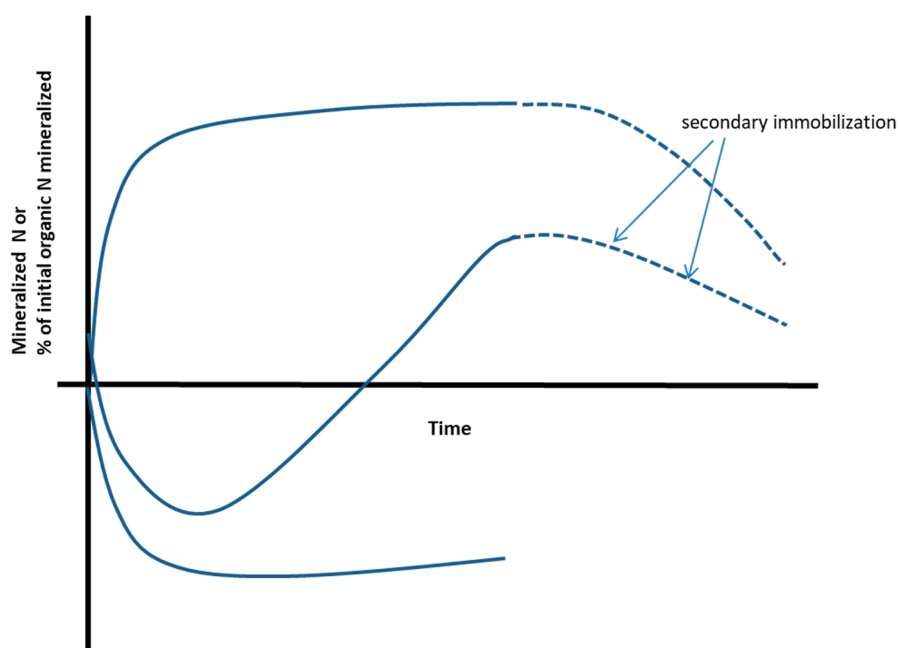


Figure 3. Alternative dynamics of soil inorganic N after the addition of organic residues illustrating secondary immobilization.

Interestingly, scientific data concerning secondary immobilization processes are not uncommon. Such data refer to the decomposition of tree leaf litter of either legume or non-legume species [14–18], above-ground biomass of crop residues and tree weed species [19], and especially different types of manure [20–27] and composts [13]. Some of these studies showed that the re-immobilization phase was followed by re-mineralization, thus suggesting a wave-like pattern of N release dynamics [16,21,25].

4. Potential Interpretations

Decreases in cumulative net N release are not discussed in some research articles either because they were considered as not important or as measurement inaccuracies. Before attempting to provide some plausible explanations, a brief discussion is given indicating the reasons why secondary immobilization cannot be due to volatilization or denitrification.

Ammonia volatilization in some cases represents an important loss of N from the soil, especially in alkaline conditions. For example, the equilibrium between ammonium and ammonia shifts towards ammonia and significant gaseous losses of N may occur after manure incorporation in an arable alkaline soil [28]. However, the secondary decrease in mineral N in the above-cited studies could hardly be attributed to volatilization because it concerns a process typically appearing after many weeks of incubation. It also appears even when the principal form of mineral N in soil is the nitrate form, which leads to soil acidification.

Denitrification might also be seen as the reason for N losses. It particularly occurs when soil is at or near water saturation leading to limited O₂ diffusion, and when a recent addition of available carbon to the soil has stimulated heterotrophic microbial activity. The process may certainly be taking place inside anaerobic microsites even in the otherwise aerobic conditions of incubations. To this effect, the rates of mineral N accumulation in soil would decrease and maximum N release would be pushed down, as expressed by the curve asymptote. This would be an unlikely reason though for the abrupt drop in measured mineral N. Such decreases are typically observed in closed systems, where O₂ is depleted at a certain point, rather than in aerobic incubations where an equilibrium between O₂ diffusion and microbial consumption is achieved. Moreover, at late decomposition stages when the rate of microbial respiration significantly decreases, O₂ consumption reaches its lowest level. Additionally, by studying the effects of nitrate (NO₃[−]) concentration

on emissions of denitrification gases, Wang et al. [29] showed that N aerial losses are proportional to nitrate availability. These results can justify a decreased rate of nitrate accumulation in soil, but not a sudden drop in mineral N.

Robust explanations for the secondary decrease in mineralized N can be provided by processes appearing or becoming more effective at the late stages of decomposition.

Three potential interpretations of the reported late decreases in extracted mineral N during incubations are suggested:

1. Secondary immobilization could be the outcome of a replacement of the initial microbial community by a microbial biomass having a significantly lower C:N ratio. Such a replacement could justify the increased microbial N uptake rates as a result of elevated needs for this element for protein formation. However, suggestions of a stoichiometric alteration of communities during microbial succession or a shift to more bacteria-dominated communities, which are known to have lower C:N ratios than fungi, are not empirically supported.

2. Late decreases of mineral N could be obtained during the decomposition of residue mixtures or of a material composed of two chemical fractions which are characterized by contrasting N dynamics, i.e. one promoting net N mineralization and the other net N immobilization. Figure 4 is a graphic demonstration of secondary N immobilization appearing in such mixtures as the cumulative result of their component decomposition with no interaction. Composts and manures mixed with bedding material often contain substances of contrasting lability.

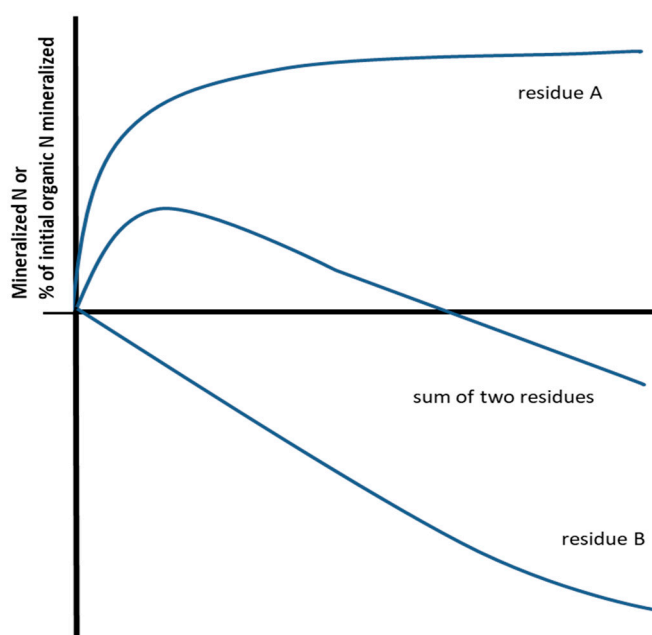


Figure 4. Illustration of late mineral N decrease obtained during the decomposition of a mixture (middle line) composed of two residues with very different N dynamics and no interaction: residue A would show net mineralization if decomposed separately and, residue B would show net immobilization.

3. All mechanistic explanations of immobilization–mineralization processes require the acceptance of turnover of dead microbial biomass and derived materials. Nitrogen in organic input is introduced into the N of soil organic matter, which is mineralized and assimilated again by the microbial biomass; however, turnover is stalled by stabilization processes, either chemical or physical. Organo–mineral associations are very important for stabilizing the microbial necromass in soil. Restricted accessibility of enzymes to biomolecules or the reduced activity of enzymes due to the conformational changes of molecules when they are attached to particle surfaces may be components of these processes [30]. It has been found that N-rich microbial metabolites can attach directly to

mineral particle surfaces or form associations with the existing mineral-bound organic matter, thus increasing their stabilization [31]. Humification processes during the decomposition in soil may also lead to the chemical condensation of organic forms of N and the production of complex assemblages (heteropolycondensation) which are highly resistant to further degradation [32].

The reason for organo–mineral complexes or chemical stabilization processes to abruptly intensify in the late stages of decomposition remains to be clarified. Either the contact of secondary metabolites with mineral constituents of the soil become stronger after a certain degree of biochemical processing or chemical condensation requires the existence of some particular chemical organic molecules to appear first. For example, Mellilo et al. [33] suggested that lignin degradation is the essential process provoking late N immobilization. These authors considered two phases of N immobilization during litter decay and suggested that lignin-shielded cellulose was the dominant carbon source for the microbes during the second period. Phenolics, which are the products of lignin degradation, recondense with nitrogenous compounds thus leading to elevated N-pool concentration. Starting from the well-supported observation that the limit value of total litter mass loss was negatively correlated with the N concentration of litter, Berg [34] also suggested that low-molecular N reacts with lignin remains forming recalcitrant aromatic compounds. The retardation of litter decomposition and the stabilization of N in these aromatic compounds starts when celluloses have almost disappeared and lignin degradation has become the dominant process.

Chemical condensation of nitrogenous compounds likely represents the most plausible explanation of secondary immobilization transforming the turnover of dead microbial biomass and derived materials from a process of N release to a process channeling mineral N to the organic N pools.

The invoked transformation of mineral N to organic N is a natural soil humification process contributing to gross N immobilization. This process becomes stronger in the late stages of decomposition, especially of processed materials, when gross immobilization frequently surpasses gross mineralization. Hence, long-term incubations simply allowed this process to be revealed in graphical plots of mineral N evolution as a distinct phase. In field conditions, where plants continuously remove N from the soil solution and, therefore, mineral forms of N do not accumulate as in incubation samples, the suggested process can be regarded as a microbially-mediated one that is antagonistic to plant uptake.

5. Concluding Remarks

Re-immobilization seems to be a relatively common and underestimated process in N dynamics, the exact mechanism of which remains unclear. It affects the general view that, even if there is an initial stage of immobilization, N will ultimately be released in soil. There are still many research gaps, including the timing and conditions under which N is re-immobilized and the requirements for it to become available again to plants. However, it certainly undermines the relationship between the C:N ratio of an organic input in soil and its N mineralization and makes the establishment of any quality index more difficult. Moreover, if secondary immobilization phases are actual components of N dynamics, the management of organic application in soil becomes much more complex, and synchrony much more difficult to achieve.

The great heterogeneity and individuality of organic inputs combined with a reduced reliability of quality indices as predictors of N mineralization renders the incubation of a soil + input mixture as a realistic approach to estimate mineralization potential. Although a time-consuming method, soil + input mixture incubation under controlled conditions that extends for a period of time equivalent to the first growing season after application, remains a valuable approach.

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