Nitrogen and carbon mineralisation in agricultural soils of South Australia

by

ANGELA CLOUGH
Bachelor of Science (Honours) (Adel.)

Department of Agronomy and Farming Systems
Roseworthy Campus, Adelaide University,
South Australia, Australia

A thesis submitted in fulfilment of the requirements of the
degree Doctor of Philosophy in Soil Science

September 2001
CHAPTER 1 LITERATURE REVIEW

1.1 SOIL ORGANIC MATTER DECOMPOSITION
   1.1.1 Definition of soil organic matter
       1
   1.1.2 Factors affecting soil organic matter decomposition
       1
       1.1.2.1 Aggregate stability
           1
       1.1.2.2 Disturbance
           2
       1.1.2.3 Temperature
           3
       1.1.2.4 Moisture
           3
   1.2 NITROGEN CYCLING
       4
       1.2.1 Overview of the nitrogen cycle
           4
       1.2.2 Nitrogen mineralisation
           5
       1.2.3 Nitrogen immobilisation
           7
       1.2.4 Nitrogen inputs
           8
       1.2.5 Nitrogen losses
           10
   1.3 QUANTIFYING NITROGEN MINERALISATION
       12
       1.3.1 Net nitrogen mineralisation potentials
           12
       1.3.2 Benefits of measuring nitrogen mineralisation in situ
           13
       1.3.3 Techniques for measuring nitrogen mineralisation in situ
           14
       1.3.4 Laboratory techniques for estimating in situ nitrogen mineralisation
           16
   1.4 CARBON CYCLING
       17
       1.4.1 Overview of the carbon cycle
           17
1.4.2 Carbon inputs in soil
1.4.3 Carbon mineralisation
1.4.4 Carbon dioxide fixation and carbon immobilisation
1.4.5 Carbon losses from soil
1.4.6 Techniques for measuring carbon mineralisation in situ and in vitro
1.5 PHYSICAL AND CHEMICAL PROTECTION OF ORGANIC CARBON
1.5.1 Microbial attack
1.5.2 Clay content
1.5.3 Calcium bridging
1.5.4 Charcoal
1.5.5 Measuring organic carbon using the UV technique
1.6 MODELLING NITROGEN AVAILABILITY THROUGH TURNOVER OF ORGANIC CARBON
1.6.1 Simple nitrogen prediction models
1.6.2 Complex nitrogen prediction models
1.7 OBJECTIVES OF THIS RESEARCH
1.8 FLOW CHART

CHAPTER 2 IN SITU NET NITROGEN MINERALISATION IN AGRICULTURAL SOILS WITH DIFFERENT CONTENTS OF CALCIUM CARBONATE

2.1 INTRODUCTION
2.2 MATERIALS AND METHODS
2.2.1 Location, and soils
2.2.2 Initial soil sampling and soil analysis
2.2.3 Germination rates
2.2.4 Experimental design and agronomy
2.2.5 In-season soil sampling and net nitrogen mineralisation
2.2.6 Statistical analysis
2.3 RESULTS
2.3.1 Seasonal characteristics
<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1.2</td>
<td>Emergence and plant densities</td>
<td>46</td>
</tr>
<tr>
<td>2.3.3</td>
<td>Straw and grain yields and yield components at Yorke Peninsula</td>
<td>47</td>
</tr>
<tr>
<td>2.3.4</td>
<td>Straw and grain yields and yield components at Turretfi el</td>
<td>48</td>
</tr>
<tr>
<td>2.3.5</td>
<td>Soil moisture inside and outside soil cores</td>
<td>49</td>
</tr>
<tr>
<td>2.3.6</td>
<td>Effect of crop treatment on net nitrogen mineralisation rates</td>
<td>50</td>
</tr>
<tr>
<td>2.3.6.1</td>
<td>Within each site</td>
<td>50</td>
</tr>
<tr>
<td>2.3.6.2</td>
<td>Between sites</td>
<td>51</td>
</tr>
<tr>
<td>2.3.7</td>
<td>Effect of crop treatment on inorganic nitrogen loss through leaching</td>
<td>52</td>
</tr>
<tr>
<td>2.3.7.1</td>
<td>Within each site</td>
<td>52</td>
</tr>
<tr>
<td>2.3.7.2</td>
<td>Between sites</td>
<td>54</td>
</tr>
<tr>
<td>2.4</td>
<td>DISCUSSION</td>
<td>56</td>
</tr>
<tr>
<td>2.4.1</td>
<td>Crop growth</td>
<td>56</td>
</tr>
<tr>
<td>2.4.2</td>
<td>Differing soil moisture contents</td>
<td>57</td>
</tr>
<tr>
<td>2.4.3</td>
<td>Effect of variability</td>
<td>57</td>
</tr>
<tr>
<td>2.4.4</td>
<td>Effect of season</td>
<td>58</td>
</tr>
<tr>
<td>2.4.5</td>
<td>Extrapolating within a soil group</td>
<td>59</td>
</tr>
<tr>
<td>2.4.6</td>
<td>Effect of calcium</td>
<td>60</td>
</tr>
<tr>
<td>2.5</td>
<td>CONCLUSIONS</td>
<td>61</td>
</tr>
<tr>
<td>2.6</td>
<td>IMPLICATIONS FOR FUTURE EXPERIMENTS</td>
<td>61</td>
</tr>
<tr>
<td>3.1</td>
<td>INTRODUCTION</td>
<td>63</td>
</tr>
<tr>
<td>3.2</td>
<td>MATERIALS AND METHODS</td>
<td>64</td>
</tr>
<tr>
<td>3.2.1</td>
<td>Soil preparation</td>
<td>64</td>
</tr>
<tr>
<td>3.2.2</td>
<td>$^{14}$Carbon labelled straw extract</td>
<td>65</td>
</tr>
<tr>
<td>3.2.3</td>
<td>Experimental design and incubation</td>
<td>66</td>
</tr>
<tr>
<td>3.2.4</td>
<td>Carbon dioxide sampling and analysis</td>
<td>66</td>
</tr>
<tr>
<td>3.2.5</td>
<td>Statistical analysis</td>
<td>67</td>
</tr>
<tr>
<td>3.3</td>
<td>RESULTS</td>
<td>68</td>
</tr>
</tbody>
</table>

CHAPTER 3  ASSESSING THE VALIDITY OF USING ALKALI TRAPS AS A MEANS OF MEASURING CARBON MINERALISATION IN CALCAREOUS SOIL

<table>
<thead>
<tr>
<th>Section</th>
<th>Title</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.1</td>
<td>INTRODUCTION</td>
</tr>
<tr>
<td>3.2</td>
<td>MATERIALS AND METHODS</td>
</tr>
<tr>
<td>3.2.1</td>
<td>Soil preparation</td>
</tr>
<tr>
<td>3.2.2</td>
<td>$^{14}$Carbon labelled straw extract</td>
</tr>
<tr>
<td>3.2.3</td>
<td>Experimental design and incubation</td>
</tr>
<tr>
<td>3.2.4</td>
<td>Carbon dioxide sampling and analysis</td>
</tr>
<tr>
<td>3.2.5</td>
<td>Statistical analysis</td>
</tr>
<tr>
<td>3.3</td>
<td>RESULTS</td>
</tr>
</tbody>
</table>
3.3.1 Recovery of respired carbon dioxide-C 68
3.3.2 Recovery of carbon dioxide-C after addition of sulphuric acid 69
3.4 DISCUSSION 71
3.4.1 Retention of 14C-carbon labelled carbon dioxide 71
3.4.2 Release of carbon from carbonates 73
3.4.3 Effect of soil characteristics on carbon mineralisation 73
3.5 CONCLUSIONS 74

CHAPTER 4 MINIMISING THE EFFECT OF SOIL DISTURBANCE UPON NET NITROGEN AND CARBON MINERALISATION THROUGH REPACKING SIEVED SOIL TO FIELD BULK DENSITY

4.1 INTRODUCTION 75
4.2 MATERIALS AND METHODS 76
4.2.1 Soils 76
4.2.2 Sample preparation 77
4.2.3 Experimental design 78
4.2.4 Incubation 78
4.2.5 Carbon dioxide and inorganic nitrogen sampling and analysis 79
4.2.6 Statistical analysis 79
4.3 RESULTS 80
4.3.1 Cumulative carbon mineralisation 80
4.3.2 Daily carbon mineralisation rates 80
4.3.3 Cumulative net nitrogen mineralisation 81
4.3.4 Incremental net nitrogen mineralisation rates 84
4.4 DISCUSSION 87
4.4.1 Effect of soil treatments on carbon mineralisation 87
4.4.2 Effect of soil treatments on net nitrogen mineralisation 88
4.4.3 Variability between replicates 90
4.4.4 Differences between soils 91
4.5 CONCLUSIONS 93
6.2.5 Acid treatment

6.3 RESULTS

6.3.1 Soil fractionation

6.3.2 Ultra-violet photo-oxidation treatments

6.3.3 Photo-oxidation with a sulphur dioxide solution pre-treatment

6.3.4 13C Carbon cross polarisation magic angle spinning Nuclear Magnetic Resonance spectroscopic analysis

6.4 DISCUSSION

6.4.1 Degradability of organic matter

6.4.2 Retention of organic carbon after ultra-violet photo-oxidation treatment

6.4.3 Physical protection of organic matter within micro-aggregates

6.4.4 Physical protection of organic matter is the presence of calcium carbonate

6.4.5 Chemical protection of organic carbon

6.5 Implications for mineralisation studies and nitrogen fertiliser recommendations

CHAPTER 7 CONCLUSIONS AND RECOMMENDATIONS

7.1 Conclusions

7.1.1 Effect of calcium on net nitrogen mineralisation

7.1.2 Effect of calcium on gross carbon mineralisation

7.1.3 Mechanism for the effect of calcium carbonate on carbon mineralisation

7.1.4 Chemical protection of organic matter

7.1.5 Implications for nitrogen fertiliser applications

7.1.6 Recommendations for future research, development and extension

References
SUMMARY

Changes in the form of soil nitrogen (N) are difficult to measure on a routine basis suitable for predicting the amount of soil N that becomes available to a crop in a growing season. However, soil organic carbon (SOC) is relatively simple to measure. Thus, the relationship between SOC and N is used in models to predict the change in available soil N over time and hence anticipate a crop’s fertiliser N requirements.

Previous Australian studies have highlighted two potential weaknesses in these fertiliser requirement prediction models. Firstly, studies with soils amended with calcium carbonate (CaCO₃) or lime showed that the presence of CaCO₃ reduced C mineralisation rates. Secondly, using total OC in models may not be valid because not all OC is necessarily available for mineralisation due to chemical and physical protection. The effect of these two factors on N fertiliser requirement models has not been determined and might be important in regions with calcareous soils and a history of burning. The objective of the research presented in this thesis was to fill this knowledge gap and apply the information to calcareous Xeralfs in South Australia.

Field experiments were established at two sites with different CaCO₃ contents to determine whether CaCO₃ affected net N mineralisation rates under two cropping treatments. Results were inconclusive with high variability between replicates (coefficient of variation (cv) up to 637%) despite intensive soil sampling equivalent to 900 samples ha⁻¹. High variability was due to the net N mineralisation rates having high spatial variability (cv > 100%) and being very close to zero (< 0.5 μg⁻¹ N g soil⁻¹ day⁻¹). All further experiments were conducted under laboratory conditions.

Before starting a long term in vitro mineralisation experiment, two technical experiments were conducted to establish techniques for generating mineralisation rates that represented field conditions as closely as possible. The first technical experiment compared two Xeralfs subjected to three soil treatments; sieving only, sieving plus repacking, and intact soil cores.
Recovery of total CO₂-C from sieved plus repacked cores averaged at least 94% of that recovered from intact cores. Total amounts of C mineralised were highest in the sieved only treatment and least in the intact treatment. Net N mineralisation was statistically the same across all soil treatments in the calcareous soil. In the non-calcereous soil net N mineralisation was in the order intact < repacked, sieving only.

The other technical experiment showed that mineralisation of glucose-C could be used on mildly alkaline and calcareous Xeralfs to monitor C mineralisation rates without glucose-C becoming trapped in the soil. Further, evolved CO₂ was not derived from CaCO₃. Using results from the two technical experiments, a 231 day incubation compared the net N and C mineralisation rates in four Xeralfs with different CaCO₃ contents collected from two locations in South Australia.

The 231 day incubation showed that mineralisation of SOC and labelled glucose-C differed between soils. Net N mineralisation rates produced a similar trend to C mineralisation. The effect of soil type suggested that the form or availability of SOC differed between soils. The total proportion of C mineralised was up to 8.9% less in soil with added CaCO₃ compared to non-calcereous soil. However, the effect of CaCO₃ was only due to differences in the mineralisation rates of glucose-C, not SOC. Differences in net mineralisation rates of substrate N and native soil N were less discernible than for substrate C.

Explanations for the effect of SOC and CaCO₃ on mineralisation rates were determined using high energy ultra-violet (UV) photo-oxidation followed by cross polarisation magic angle spinning (CP/MAS) ¹³C NMR. Analysis of <53 μm soil fractions showed that between 17% and 40% of SOC was in a condensed aromatic form, most likely charcoal. Adjusting the total amounts of C mineralised during the 231 day incubation to account for the presence of charcoal reduced the differences between soils. However, the soils with CaCO₃ still mineralised less OC than the non-calcereous soils which indicated that physical protection of OC by calcium – organic matter (Ca-OM) bridging also reduced mineralisation rates (Muneer and Oades, 1989c).
The concept that organic material remaining after photo-oxidation may be physically protected within Ca-OM aggregates was investigated by treating soils with a mild acid prior to photo-oxidation. More organic material was protected in the calcareous than the non-calcareous soils regardless of whether the calcium (Ca) occurred naturally or was an amendment. Acid treatment showed that the presence of exchangeable Ca reduced losses of organic material upon photo-oxidation by 7% due to calcium bridging. The finding that OM is protected in the presence of Ca has implications for C sequestration in soils. Larger amounts of C may be retained in calcareous soils than in non-calcareous soils with low exchangeable Ca. Further research is warranted to quantify this difference between soils.

The implications of these findings for N fertiliser prediction models is that in soils with charcoal, the active OC pool is overestimated when a conventional method such as Walkley-Black is used to determine the soil’s OC content. Overestimation leads to higher rates of N mineralisation being assumed than actually occurs and therefore predicted N fertiliser requirements are underestimated. Using UV photo-oxidation to assess soils’ OC content overcomes the problem of overestimating OC. However, presently the method is too expensive and time consuming to be used in routine analysis. With regards to the effect of CaCO₃ on N fertiliser prediction models, the effect is small and unlikely to have an effect that impacts upon N fertiliser recommendations in calcareous soils similar to those used in this study. This conclusion may not hold true in highly calcareous soils (> 50%) such as those farmed at the southern tip of Yorke Peninsula, and far western Eyre Peninsula, South Australia. The effect of calcium on N mineralisation in highly calcareous soils may be significant and warrants further investigation especially where the soil has high amounts of exchangeable calcium.