SOLUTE LEACHING STUDIES IN CROPPED FIELD PLOTS AND LABORATORY COLUMNS USING NITRATE, BROMIDE AND CHLORIDE TRACERS

Submitted by
SADEK MOHAMMED YAZID

THESIS SUBMITTED FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN THE FACULTY OF SCIENCE, DEPARTMENT OF AGRICULTURE

UNIVERSITY OF EDINBURGH
1988
I, Sadek Mohammed Yazid, declare that this thesis was composed by myself. My contribution to this work included all the laboratory work for the column experiments, soil and crop sample preparations, chemical and physical analysis and much of the field work. Staff of the Soil Science Department helped with field work and crop and soil analysis.

Signed.
ABSTRACT OF THESIS

SOLUTE LEACHING STUDIES IN CROPPED FIELD PLOTS AND LABORATORY COLUMNS USING NITRATE, BROMIDE AND CHLORIDE TRACERS

A field experiment was carried out, using \( ^{15}N \)-labelled nitrogen fertilizer in a mobile form, to construct a nitrogen mass balance sheet under a potato crop receiving summer rainfall. Nitrate leaching losses were calculated by assuming that all N unaccounted for was lost by leaching.

Laboratory experiments were conducted, using undisturbed soil columns from the same field, using nitrate (\( \text{NO}_3^- \)), bromide (\( \text{Br}^- \)) and chloride (\( \text{Cl}^- \)) tracers, to describe the transport processes in more detail, and in order to obtain information about the dispersion length and the presence or absence of immobile water.

Results of the field work are compared with the leaching predicted using (a) a simple leaching equation and (b) an analytical approach. This comparison shows that in most cases the leaching in the field soil is less than that predicted. The extent of this protection of N against leaching is larger than that observed in the soil columns and in other work with soils of similar texture. The most likely explanation of the very low leaching efficiency of the tracer, recovered compared with model predictions, was attributed to the uptake and subsequent release of \( ^{15}\text{NO}_3^- \)-N fertilizer by roots and soil biomass for osmotic adjustment until the nitrate was diluted by diffusive mixing within the soil or by rainfall.
The poor mass balance obtained in the field experiment was attributed partly or collectively to denitrification due to the cold and wet spring, permanent microbial uptake and rapid leaching beyond the sampling depth. The uncertainty about the amount of microbial uptake of nitrate makes it difficult to attribute fully the poor recovery of tracer, and the rapid loss, to the process of denitrification. Further work is needed to find out which process is most responsible.

Results of column experiments are also compared with model predictions, using the same models which have been used with the field experiments. The comparisons show good agreement with the analytical model, but not with the simple leaching equation approach. The reason for the close agreement with the analytical model was due to the use of the experimentally obtained dispersivity in the model; a good mass balance was obtained in most cases for all tracers used, indicating minimal biological transformation of NO₃⁻-N.
I express my great sincere appreciation to my advisers Dr. K.A. Smith and Dr. A.J.A. Vinten of the Edinburgh School of Agriculture for their advice and guidance. They had the compassion to help whenever I needed it and their comments during my study stimulated much of my thinking and influenced many of my ideas. It was their confidence in my work and their encouragement which made this study possible.

Recognition is also extended to Dr. D. Naysmith for his guidance and help with the field experiments.

I wish to extend my heart-felt thanks to my wife, Aisha, who during the course of my study has always provided me with the rest, relaxation and inspiration, not to mention, the encouragement needed to replenish my energies and dedication to my task.

I would like to sincerely thank all the Technical Staff of the Soil Science Department who were more than willing to help and always did a fine job.

For my father, my sons, Ihab and Awes and to my lovely thirteen-year old daughter, Neeshal, this thesis has been dedicated.
TABLE OF CONTENTS

DECLARATION................................. i
ABSTRACT OF THESIS........................... ii
ACKNOWLEDGEMENT............................ iv
LIST OF TABLES................................. x
LIST OF FIGURES............................... xiii

Chapter

I  INTRODUCTION....................................... 1
II  REVIEW OF LITERATURE........................... 5
  2.1  Introduction................................. 5
  2.2  Role of Nitrogen in Agriculture........... 5
  2.3  Significance of Nitrate Leaching Losses..... 7
      2.3.1  Economic loss........................ 8
      2.3.2  Eutrophication...................... 9
      2.3.3  Health problems.................... 10
  2.4  Factors Affecting Leaching Losses........... 11
      2.4.1  Seasonal and climatic effects....... 11
      2.4.2  Soil type........................... 12
      2.4.3  Land management.................... 16
  2.5  Approaches to Measurement of Leaching...... 20
      2.5.1  Field soil sampling.................. 20
      2.5.2  Lysimeters studies.................... 21
      2.5.3  Tile drain studies................... 21
      2.5.4  Catchment studies.................... 22
      2.5.5  Borehole sampling.................... 23
      2.5.6  Laboratory column studies.......... 23
  2.6  Approaches to Modelling of Leaching...... 24
      2.6.1  Deterministic models............... 25
      2.6.2  Stochastic models.................... 30
      2.6.3  Stochastic mechanistic models........ 31
<table>
<thead>
<tr>
<th>Chapter</th>
<th>MATERIALS AND METHODS</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>III</td>
<td>Site A : Castle Huntly</td>
<td>33</td>
</tr>
<tr>
<td>3.1</td>
<td>Experimental site</td>
<td>33</td>
</tr>
<tr>
<td>3.1.1.1</td>
<td>Location</td>
<td>33</td>
</tr>
<tr>
<td>3.1.1.2</td>
<td>Description</td>
<td>33</td>
</tr>
<tr>
<td>3.1.1.3</td>
<td>Field sampling for NO\text{3} level prior to planting</td>
<td>34</td>
</tr>
<tr>
<td>3.1.1.4</td>
<td>Irrigation planning</td>
<td>34</td>
</tr>
<tr>
<td>3.1.2</td>
<td>Experimental plan and field operations</td>
<td>38</td>
</tr>
<tr>
<td>3.1.2.1</td>
<td>Experimental plan</td>
<td>38</td>
</tr>
<tr>
<td>3.1.2.2</td>
<td>Field operations</td>
<td>38</td>
</tr>
<tr>
<td>3.1.3</td>
<td>Moisture measurement and monitoring</td>
<td>40</td>
</tr>
<tr>
<td>3.1.3.1</td>
<td>Moisture determination at field sampling prior to planting</td>
<td>40</td>
</tr>
<tr>
<td>3.1.4</td>
<td>Laboratory analysis</td>
<td>40</td>
</tr>
<tr>
<td>3.1.4.1</td>
<td>Soil extraction for NO\text{3}--N and NH\text{4}+-N, and chemical analysis</td>
<td>41</td>
</tr>
<tr>
<td>3.1.4.2</td>
<td>Plant total N content analysis</td>
<td>41</td>
</tr>
<tr>
<td>3.1.4.3</td>
<td>Determination of selected soil properties</td>
<td>44</td>
</tr>
<tr>
<td>3.1.4.4</td>
<td>Determination of moisture characteristic curve</td>
<td>44</td>
</tr>
<tr>
<td>3.1.5</td>
<td>Crop harvest</td>
<td>45</td>
</tr>
<tr>
<td>3.2</td>
<td>Site B : Aberlady</td>
<td>45</td>
</tr>
<tr>
<td>3.2.1</td>
<td>Experimental site</td>
<td>45</td>
</tr>
<tr>
<td>3.2.1.1</td>
<td>Location</td>
<td>45</td>
</tr>
<tr>
<td>3.2.1.2</td>
<td>Description</td>
<td>46</td>
</tr>
<tr>
<td>3.2.2</td>
<td>Experimental design and field operations</td>
<td>46</td>
</tr>
<tr>
<td>3.2.2.1</td>
<td>Experimental design</td>
<td>46</td>
</tr>
<tr>
<td>3.2.2.2</td>
<td>Field operations</td>
<td>47</td>
</tr>
<tr>
<td>3.2.2.3</td>
<td>Field sampling procedure for $^{15}$NO\text{3}--N determination</td>
<td>48</td>
</tr>
<tr>
<td>3.2.3</td>
<td>Moisture monitoring with neutron probe</td>
<td>48</td>
</tr>
<tr>
<td>3.2.3.1</td>
<td>Neutron probe calibration</td>
<td>49</td>
</tr>
<tr>
<td>3.2.4</td>
<td>Laboratory analysis</td>
<td>55</td>
</tr>
<tr>
<td>3.2.4.1</td>
<td>Preparation of $^{15}$N--N fertilizer</td>
<td>55</td>
</tr>
<tr>
<td>3.2.4.2</td>
<td>Determination of $^{15}$N--N in the soil profile</td>
<td>55</td>
</tr>
<tr>
<td>3.2.4.2.1</td>
<td>Extraction of $^{15}$NO\text{3}--N from soil samples</td>
<td>55</td>
</tr>
</tbody>
</table>
TABLE OF CONTENTS (continued)

<table>
<thead>
<tr>
<th>Chapter</th>
<th>MATERIALS AND METHODS (cont'd)</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>III</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3.2.4.2.2</td>
<td>Steam distillation of soil extracts</td>
<td>56</td>
</tr>
<tr>
<td>3.2.4.2.3</td>
<td>Isotope ratio analysis</td>
<td>57</td>
</tr>
<tr>
<td>3.2.4.3</td>
<td>Plant total N and ( ^{15}\text{NO}_3^- )-N</td>
<td>58</td>
</tr>
<tr>
<td>3.2.4.4</td>
<td>Determination of selected soil properties</td>
<td>59</td>
</tr>
<tr>
<td>3.2.5</td>
<td>Crop harvest</td>
<td>59</td>
</tr>
<tr>
<td>3.3</td>
<td>Laboratory Column Experiments</td>
<td>59</td>
</tr>
<tr>
<td>3.3.1</td>
<td>Core removal and handling</td>
<td>60</td>
</tr>
<tr>
<td>3.3.2</td>
<td>Sample preparation</td>
<td>60</td>
</tr>
<tr>
<td>3.3.3</td>
<td>The irrigator</td>
<td>60</td>
</tr>
<tr>
<td>3.3.4</td>
<td>Tracer application</td>
<td>66</td>
</tr>
<tr>
<td>3.3.4.1</td>
<td>Saturated flow experiment</td>
<td>66</td>
</tr>
<tr>
<td>3.3.4.2</td>
<td>Unsaturated flow experiment</td>
<td>67</td>
</tr>
<tr>
<td>3.3.5</td>
<td>Leachate collection and chemical analysis</td>
<td>70</td>
</tr>
<tr>
<td>3.3.6</td>
<td>Determination of selected soil properties</td>
<td>71</td>
</tr>
<tr>
<td>3.3.7</td>
<td>Determination of immobile water due to anion exclusion</td>
<td>71</td>
</tr>
<tr>
<td>3.3.8</td>
<td>Hydraulic conductivity determination</td>
<td>73</td>
</tr>
<tr>
<td>IV</td>
<td>WATER BALANCE IN FIELD EXPERIMENTS</td>
<td>74</td>
</tr>
<tr>
<td>4.1</td>
<td>Theory</td>
<td>74</td>
</tr>
<tr>
<td>4.1.1</td>
<td>Water storage</td>
<td>75</td>
</tr>
<tr>
<td>4.1.2</td>
<td>Change in soil water stored</td>
<td>77</td>
</tr>
<tr>
<td>4.1.3</td>
<td>Estimation of evapotranspiration</td>
<td>77</td>
</tr>
<tr>
<td>4.1.4</td>
<td>Estimation of drainage</td>
<td>81</td>
</tr>
<tr>
<td>4.2</td>
<td>Experimental Results</td>
<td>81</td>
</tr>
<tr>
<td>4.2.1</td>
<td>Site A: Castle Huntly. Water balance sheet for the irrigated experiment (1984)</td>
<td>81</td>
</tr>
<tr>
<td>4.2.2</td>
<td>Site B: Aberlady. Water balance sheet for N experiment (1985)</td>
<td>88</td>
</tr>
<tr>
<td>V</td>
<td>NITROGEN MASS BALANCE FROM FIELD EXPERIMENTS</td>
<td>96</td>
</tr>
<tr>
<td>5.1</td>
<td>Introduction</td>
<td>96</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Chapter</td>
<td>Nitrogen Mass Balance from Field Experiments (cont'd)</td>
<td>Page</td>
</tr>
<tr>
<td>---------</td>
<td>-----------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>V Nitrogen Balance Theory..........................</td>
<td>100</td>
<td></td>
</tr>
<tr>
<td>5.2 15N Mass balance sheet............................</td>
<td>102</td>
<td></td>
</tr>
<tr>
<td>5.2.2 NO₃⁻ Displacement from crop root zone..........</td>
<td>104</td>
<td></td>
</tr>
<tr>
<td>5.2.3 Estimation of total NO₃⁻-N losses by leaching from 15N microplots</td>
<td>105</td>
<td></td>
</tr>
<tr>
<td>5.2.4 Estimation of residual NO₃⁻-N (Nₛ(0)) at the start of the Aberlady experiment</td>
<td>106</td>
<td></td>
</tr>
<tr>
<td>5.3 Experimental Results................................</td>
<td>107</td>
<td></td>
</tr>
<tr>
<td>5.3.1 Site A: Castle Huntly, Nitrogen mass balance in the irrigated experiment (1984)</td>
<td>107</td>
<td></td>
</tr>
<tr>
<td>5.3.1.1 Nitrate losses by leaching from the crop root zone</td>
<td>108</td>
<td></td>
</tr>
<tr>
<td>5.3.1.2 Crop uptake of nitrogen........................</td>
<td>113</td>
<td></td>
</tr>
<tr>
<td>5.3.1.3 Nitrogen mass balance sheet for irrigated and unirrigated plots</td>
<td>115</td>
<td></td>
</tr>
<tr>
<td>5.3.2 Site B: Aberlady, Nitrogen mass balance for 15N experiment (1985)</td>
<td>118</td>
<td></td>
</tr>
<tr>
<td>5.3.2.1 Nitrate losses by leaching from the crop root zone</td>
<td>118</td>
<td></td>
</tr>
<tr>
<td>5.3.2.1.1 15NO₃⁻-N losses by leaching from micro-plots</td>
<td>118</td>
<td></td>
</tr>
<tr>
<td>5.3.2.1.2 NO₃⁻-N losses by leaching from controlled plots</td>
<td>121</td>
<td></td>
</tr>
<tr>
<td>5.3.2.2 Crop uptake of soil and fertilizer derived nitrogen</td>
<td>123</td>
<td></td>
</tr>
<tr>
<td>5.3.2.3 15NO₃⁻-N mass balance sheet</td>
<td>125</td>
<td></td>
</tr>
<tr>
<td>5.3.2.4 Mass balance sheet for soil-derived nitrogen</td>
<td>127</td>
<td></td>
</tr>
<tr>
<td>5.3.2.5 Effect of fertilizer addition on mineralization and the uptake of soil-derived nitrogen</td>
<td>128</td>
<td></td>
</tr>
<tr>
<td>VI Theoretical Background to Column Leaching Experiments</td>
<td>130</td>
<td></td>
</tr>
<tr>
<td>6.1 Introduction........................................</td>
<td>130</td>
<td></td>
</tr>
<tr>
<td>6.2 The Principles of Solute Movement in Relation to the Process of NO₃⁻ Leaching</td>
<td>131</td>
<td></td>
</tr>
<tr>
<td>6.2.1 Convection, diffusion and dispersion</td>
<td>131</td>
<td></td>
</tr>
<tr>
<td>Chapter</td>
<td>THEORETICAL BACKGROUND TO COLUMN LEACHING EXPERIMENTS (cont'd)</td>
<td>Page</td>
</tr>
<tr>
<td>---------</td>
<td>-------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>VI</td>
<td>6.2.2 Charge characteristic</td>
<td>135</td>
</tr>
<tr>
<td></td>
<td>6.2.3 Macropore movement</td>
<td>136</td>
</tr>
<tr>
<td></td>
<td>6.2.4 Transformation and plant uptake of nitrogen</td>
<td>137</td>
</tr>
<tr>
<td></td>
<td>6.2.5 Soil variability</td>
<td>138</td>
</tr>
<tr>
<td>VII</td>
<td>RESULTS OF COLUMN LEACHING EXPERIMENTS</td>
<td>139</td>
</tr>
<tr>
<td></td>
<td>7.1 Summary</td>
<td>139</td>
</tr>
<tr>
<td></td>
<td>7.2 Experimental Results</td>
<td>141</td>
</tr>
<tr>
<td></td>
<td>7.2.1 Saturated flow experiment</td>
<td>141</td>
</tr>
<tr>
<td></td>
<td>7.2.2 Unsaturated flow experiment</td>
<td>142</td>
</tr>
<tr>
<td></td>
<td>7.2.3 Shape of the breakthrough curves</td>
<td>144</td>
</tr>
<tr>
<td></td>
<td>7.2.3.1 Parameters for breakthrough curve characterisation</td>
<td>144</td>
</tr>
<tr>
<td></td>
<td>7.2.3.2 Dispersion length determination</td>
<td>146</td>
</tr>
<tr>
<td></td>
<td>7.2.3.3 Saturated flow NO$_3^-$-N BTCs</td>
<td>147</td>
</tr>
<tr>
<td></td>
<td>7.2.3.4 Unsaturated flow</td>
<td>150</td>
</tr>
<tr>
<td></td>
<td>7.2.4 Effect of application rate</td>
<td>156</td>
</tr>
<tr>
<td></td>
<td>7.2.5 Effect of initial moisture content</td>
<td>162</td>
</tr>
<tr>
<td></td>
<td>7.2.6 Effect of time of equilibration before leaching</td>
<td>162</td>
</tr>
<tr>
<td></td>
<td>7.2.7 Effect of replication</td>
<td>166</td>
</tr>
<tr>
<td>VIII</td>
<td>DISCUSSION</td>
<td>169</td>
</tr>
<tr>
<td>IX</td>
<td>SUMMARY AND CONCLUSIONS</td>
<td>176</td>
</tr>
<tr>
<td></td>
<td>BIBLIOGRAPHY</td>
<td>179</td>
</tr>
<tr>
<td></td>
<td>APPENDICES</td>
<td>199</td>
</tr>
<tr>
<td></td>
<td>Appendix A</td>
<td>199</td>
</tr>
</tbody>
</table>
# LIST OF TABLES

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>Potential adverse environmental and health impact of N</td>
<td>9</td>
</tr>
<tr>
<td>2.2</td>
<td>Theoretical leaching depths of nitrate peaks according to textural classes</td>
<td>13</td>
</tr>
<tr>
<td>2.3</td>
<td>Classification of leaching models</td>
<td>24</td>
</tr>
<tr>
<td>3.1</td>
<td>Dates and depth of irrigation water applied during the 1984 cropping season at Castle Huntly</td>
<td>39</td>
</tr>
<tr>
<td>3.2</td>
<td>Per cent damage of potato tubers caused by eelworm during the 1984 cropping season</td>
<td>45</td>
</tr>
<tr>
<td>3.3</td>
<td>Summary of neutron probe calibration data for Aberlady (1985)</td>
<td>54</td>
</tr>
<tr>
<td>3.4</td>
<td>Summary of different nitrate saturated flow treatments (1985)</td>
<td>66</td>
</tr>
<tr>
<td>3.5</td>
<td>Summary of different chloride treatments under unsaturated flow (1986)</td>
<td>69</td>
</tr>
<tr>
<td>3.6</td>
<td>Summary of different bromide treatments under unsaturated flow (1986)</td>
<td>70</td>
</tr>
<tr>
<td>4.1</td>
<td>Crop parameters</td>
<td>80</td>
</tr>
<tr>
<td>4.2</td>
<td>Rainfall, evapotranspiration, crop cover coefficient, change in soil water storage and drainage data for the unirrigated plots during the course of the 1984 experiment at Castle Huntly</td>
<td>83</td>
</tr>
<tr>
<td>4.3</td>
<td>Rainfall, irrigation, evapotranspiration, crop cover coefficient, change in soil water storage and drainage data for the irrigated plots during the course of the 1984 experiment at Castle Huntly</td>
<td>84</td>
</tr>
<tr>
<td>4.4</td>
<td>Rainfall, evapotranspiration, crop cover coefficient change in soil water storage and drainage data for the fertilized treatment during the course of the 1985 experiment at Aberlady</td>
<td>89</td>
</tr>
<tr>
<td>Table</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>-------</td>
<td>-----------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>5.1</td>
<td>Summary of N balance sheet and water budget for potato crop grown in unirrigated plots at Castle Huntly (1984)</td>
<td>109</td>
</tr>
<tr>
<td>5.2</td>
<td>Summary of N balance sheet and water budget for potato crop grown in irrigated plots at Castle Huntly (1984)</td>
<td>111</td>
</tr>
<tr>
<td>5.3</td>
<td>Labelled N balance sheet and water budget for potato crop grown in \textsuperscript{15}N fertilized micro-plots at Aberlady (1985)</td>
<td>119</td>
</tr>
<tr>
<td>5.4</td>
<td>Residual N balance sheet and water budget for potato crop grown in unfertilized plots at Aberlady (1985)</td>
<td>122</td>
</tr>
<tr>
<td>5.5</td>
<td>Total N balance sheet for potato crop grown in \textsuperscript{15}N fertilized micro-plots at Aberlady (1985)</td>
<td>124</td>
</tr>
<tr>
<td>7.1</td>
<td>Summary of different nitrate saturated flow treatments (1985)</td>
<td>142</td>
</tr>
<tr>
<td>7.2</td>
<td>Summary of different chloride treatments under unsaturated flow (1986)</td>
<td>143</td>
</tr>
<tr>
<td>7.3</td>
<td>Summary of different bromide treatments under unsaturated flow (1986)</td>
<td>144</td>
</tr>
<tr>
<td>7.4</td>
<td>Summary of nitrate results from undisturbed saturated columns (1985)</td>
<td>149</td>
</tr>
<tr>
<td>7.5</td>
<td>Summary of chloride results from undisturbed unsaturated columns (1986)</td>
<td>152</td>
</tr>
<tr>
<td>7.6</td>
<td>Summary of bromide results from undisturbed columns (1986)</td>
<td>155</td>
</tr>
<tr>
<td>7.7</td>
<td>Effect of irrigation intensity on nitrate leaching under saturated flow</td>
<td>157</td>
</tr>
<tr>
<td>7.8</td>
<td>Effect of irrigation intensity on chloride leaching under unsaturated flow at higher initial moisture content</td>
<td>157</td>
</tr>
</tbody>
</table>
# LIST OF TABLES (continued)

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>7.9</td>
<td>Effect of irrigation intensity on chloride and bromide leaching under unsaturated flow at lower initial moisture content</td>
<td>153</td>
</tr>
<tr>
<td>7.10</td>
<td>Effect of soil initial moisture content on bromide leaching under unsaturated flow at high flow velocity</td>
<td>164</td>
</tr>
<tr>
<td>7.11</td>
<td>Effect of time of equilibration on chloride and bromide leaching under unsaturated flow.</td>
<td>166</td>
</tr>
<tr>
<td>8.1</td>
<td>Observed and estimated $^{15}\text{NO}_3^{-}$-N losses by leaching from $^{15}\text{N}$ fertilized potato micro-plots during the 1985 growing season at Aberlady</td>
<td>175</td>
</tr>
<tr>
<td>8.2</td>
<td>Range of values for mean water content, effective water content and calculated $\text{NO}_3^{-}$ anion exclusion water content from undisturbed soil columns under saturated and unsaturated flow</td>
<td>175</td>
</tr>
</tbody>
</table>

## Appendix

<table>
<thead>
<tr>
<th>Table</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>List of major symbols and definitions.</td>
<td>199</td>
</tr>
</tbody>
</table>
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>The nitrogen cycle</td>
<td>6</td>
</tr>
<tr>
<td>3.1</td>
<td>Field sampling for NO$_3^-$-N level prior to planting</td>
<td>35</td>
</tr>
<tr>
<td>3.2</td>
<td>Average profile NO$_3^-$-N content in the irrigated plots prior to planting (1984) at Castle Huntly</td>
<td>36</td>
</tr>
<tr>
<td>3.3</td>
<td>Average profile NO$_3^-$-N content in the unirrigated plots prior to planting (1984) at Castle Huntly</td>
<td>37</td>
</tr>
<tr>
<td>3.4</td>
<td>Positions of access tubes for neutron probe moisture measurements in the 1984 field experiment at Castle Huntly</td>
<td>42</td>
</tr>
<tr>
<td>3.5</td>
<td>Positions of access tubes for neutron probe moisture measurements in the 1985 field experiment at Aberlady</td>
<td>50</td>
</tr>
<tr>
<td>3.6</td>
<td>Neutron probe calibration curve for Castle Huntly (1984)</td>
<td>51</td>
</tr>
<tr>
<td>3.7</td>
<td>Neutron probe calibration curve for Aberlady (1985)</td>
<td>52</td>
</tr>
<tr>
<td>3.8</td>
<td>Core removal and handling from the Aberlady (a,b) site for laboratory columns experiments</td>
<td>61</td>
</tr>
<tr>
<td>3.8</td>
<td>Core removal and handling from the Aberlady (c,d) site for laboratory columns experiments</td>
<td>62</td>
</tr>
<tr>
<td>3.9</td>
<td>Experimental set-up for saturated measurements</td>
<td>64</td>
</tr>
<tr>
<td>3.10</td>
<td>Experimental set-up for unsaturated measurements</td>
<td>65</td>
</tr>
<tr>
<td>3.11</td>
<td>Storage of soil cores after addition of (a,b) Cl$^-$ tracer to allow equilibration (unsaturated flow experiment)</td>
<td>68</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>3.12</td>
<td>Breakthrough curves for disturbed soil column leaching experiment for two electrolyte concentrations for experimental measured NO₃⁻ anion exclusion volume from a pulse of NO₃⁻-N leached through disturbed soil column using distilled water and calcium chloride</td>
<td>72</td>
</tr>
<tr>
<td>4.1</td>
<td>Crop cover coefficient during crop growth stages</td>
<td>79</td>
</tr>
<tr>
<td>4.2</td>
<td>Soil water stress factor</td>
<td>79</td>
</tr>
<tr>
<td>4.3</td>
<td>Cumulative rainfall, actual evapotranspiration and drainage for unirrigated plots during the 1984 cropping season at Castle Huntly</td>
<td>86</td>
</tr>
<tr>
<td>4.4</td>
<td>Cumulative rainfall, irrigation, actual evapotranspiration and drainage for irrigated plots during the 1984 cropping season at Castle Huntly</td>
<td>87</td>
</tr>
<tr>
<td>4.5</td>
<td>Cumulative rainfall, actual evapotranspiration and drainage for fertilized and unfertilized treatment during the 1985 cropping season at Aberlady</td>
<td>93</td>
</tr>
<tr>
<td>5.1</td>
<td>Crop uptake of N at different growth stages in the irrigated plots during the 1984 cropping season at Castle Huntly</td>
<td>114</td>
</tr>
<tr>
<td>5.2</td>
<td>Crop uptake of N at different growth stages in the unirrigated plots during the 1984 cropping season at Castle Huntly</td>
<td>116</td>
</tr>
<tr>
<td>6.1</td>
<td>Schematic diagram of various components of (a,b, NO₃⁻ leaching)</td>
<td>133</td>
</tr>
<tr>
<td>7.1</td>
<td>Experimental measure breakthrough curves from a pulse of NO₃⁻-N leached through saturated soil columns at three application rates</td>
<td>148</td>
</tr>
<tr>
<td>7.2</td>
<td>Experimental measured breakthrough curves from a pulse of Cl⁻ leached through unsaturated soil columns at three application rates</td>
<td>151</td>
</tr>
<tr>
<td>Figure</td>
<td>Description</td>
<td>Page</td>
</tr>
<tr>
<td>--------</td>
<td>-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------</td>
<td>------</td>
</tr>
<tr>
<td>7.3</td>
<td>Experimental measured breakthrough curves from a pulse of Br⁻ leached through unsaturated soil columns at three initial soil moisture contents</td>
<td>153</td>
</tr>
<tr>
<td>7.4</td>
<td>Experimental measured breakthrough curves as a function of input volume from a pulse of Br⁻ leached through undisturbed soil columns at three initial soil moisture contents</td>
<td>154</td>
</tr>
<tr>
<td>7.5</td>
<td>Effect of irrigation intensity on the pattern and extent of NO₃⁻ leaching through undisturbed soil columns under saturated flow conditions</td>
<td>159</td>
</tr>
<tr>
<td>7.6</td>
<td>Effect of irrigation intensity on the pattern and extent of Cl⁻ leaching through undisturbed soil columns under unsaturated flow conditions at high initial soil moisture content</td>
<td>160</td>
</tr>
<tr>
<td>7.7</td>
<td>Effect of irrigation intensity on the pattern and extent of solute leaching through undisturbed soil columns under unsaturated flow conditions at low soil moisture content</td>
<td>161</td>
</tr>
<tr>
<td>7.8</td>
<td>Effect of initial soil moisture content at the pattern and extent of Br⁻ leaching through undisturbed soil columns under unsaturated flow conditions</td>
<td>163</td>
</tr>
<tr>
<td>7.9</td>
<td>Effect of time of equilibration time on the pattern and extent of solute leaching through undisturbed soil columns under unsaturated flow conditions</td>
<td>165</td>
</tr>
<tr>
<td>8.1</td>
<td>Comparison of mean observed and predicted ¹⁵NO₃⁻-N distribution in soil following application of Ca¹⁵NO₃ fertilizer to microplots in potatoes at Aberlady (1985)</td>
<td>170</td>
</tr>
<tr>
<td>8.2</td>
<td>Comparison of measured and predicted Cl⁻ pattern and extent of leaching through undisturbed soil column under unsaturated flow conditions</td>
<td>174</td>
</tr>
</tbody>
</table>
CHAPTER I

INTRODUCTION

Systems of agriculture that rely heavily on soil reserves to meet the nitrogen requirements of crops cannot long be effective in producing high yields of crops. Nitrogen fertilizers have become increasingly available for the last five decades, and when used to augment the N supplied by natural processes can increase yields and improve the crop quality. But the poor efficiency with which fertilized nitrogen is used by the crops (50 to 75 percent of the N applied), results in financial losses for farmers and increased amounts of NO$_3^-$--N in surface and ground water. A major concern of present-day farmers is the effective management of N fertilizers for maximum efficiency and minimum pollution of the environment.

One of the keys to more efficient utilization of nitrogen and to minimizing pollution problems is to be able to predict accurately NO$_3^-$--N leaching losses from the crop root zone. For such prediction it is necessary to combine soil nitrogen transformations, plant uptake, and nitrate transport with water flow as described by nitrogen mass balance theory, and the theory of water balance. This is not an easy task, because the other inputs and outputs of the mass balance equation are not easy to measure or to predict due to (i) the variety of sinks and sources of NO$_3^-$--N in the crop root zone (mineralization and nitrification, denitrification, immobilization by soil micro-organisms and crop uptake, etc.), (ii) the uncertainty due to spatial variability about the water passing through the root zone as drainage, (iii) the uncertainty about the efficiency with which NO$_3^-$--N is leached by water passing through the root zone.
In the second field experiment, $^{15}\text{NO}_3^-$-N labelled fertilizer was used as a tracer in order to measure crop uptake of nitrate and the amount retained in the soil during the growing season. A mass balance sheet for $^{15}\text{NO}_3^-$-N was constructed and nitrate loss by leaching was calculated by assuming that all unaccounted for $^{15}\text{NO}_3^-$-N was lost by leaching. The results obtained from this study were tested against the simple leaching equation of Burns (1976). The analytical model of Rose (Rose et al. 1982b) was also used.

Problem (ii) was overcome by a regular soil moisture measurement and by using an approximate water balance method to estimate the drainage. Problem (iii) was approached by column experiments so that the presence of mobile-immobile water could be accurately calculated. Dispersion length was also determined experimentally from the column studies and then introduced to the model of Rose.

With these parameters in hand, the results obtained from the $^{15}$N field experiment and the column studies were compared with model predictions. By these comparisons one could make some evaluation of the efficiency with which $\text{NO}_3^-$-N was leached by water passing through the crop root zone.

The present study was undertaken mainly for the following reasons: firstly, to construct an N mass balance (N budget) which provides a sound basis for estimating N gains, losses and transformations for any agricultural management system. This information was sought by the School of Agriculture, Edinburgh University, as part of a major concern with more efficient utilization of nitrogen by arable crops and minimizing pollution problems. In addition, many marginal areas in Scotland have undergone
an intensification of land use recently, so there is also a need for quantitative data on the effect of this on the release of nitrate and its loss by leaching to drainage water. These losses occur mainly in winter when soils are generally at or above field capacity, but may also occur in summer, especially when high levels of nitrogen have been applied and excess rainfall or irrigation occur. It is with the latter case that this study deals, and it was approached by 1) field soil sampling (see Chapter III, Section 2.5.1) of root zone N distribution in a) irrigated cultivated plots during the 1984 cropping season. b) unirrigated cultivated micro-plots, using $^{15}$N labelled fertilizer, during the 1985 growing season, and 2) measurement of uptake of N by the test crop (Solanum tuberosum L. var. Maris Piper) in both trials.

In the case of the $^{15}$N mass balance, nitrate leaching losses were calculated by assuming that all N unaccounted for N was lost by leaching.

The second objective was to describe the transport processes in more detail, in order to obtain information about the dispersion length and the presence or absence of immobile water. This objective was approached by taking undisturbed soil columns from the field at the Aberlady site (see Chapter III) so that leaching behaviour could be further studied, using miscible displacement techniques. NO$_3^-$ was used with saturated flow, whereas Br$^-$ and Cl$^-$ were used as substitute tracers for assessing the potential movement of NO$_3^-$ under unsaturated flow conditions. Cl$^-$ has been used (Biggar and Nielsen, 1972; Smith, 1972; Smith et al., 1985; White et al., 1984) in this regard, but utility is often limited due to its common occurrence in soils, fertilizer, rocks and precipitation, etc. The merits of Br$^-$ are due to its low natural occurrence (Bowen, 1966; Vinogradov, 1959), and
it is not regarded as toxic to plants (Martin, 1966). Both Cl\(^{-}\) and Br\(^{-}\) serve as microbially inert tracers for NO\(_3\)^{-}.

The results of this experiment may therefore be compared with those obtained from the field observations.

The third objective was to compare the results of model predictions of leaching losses of NO\(_3\)^{-} with the mass balance estimates. To do this, a field water balance must be made to estimate drainage of water below the root zone. For the Burns' model we also need the volumetric field capacity of the soil, which is obtainable from either the moisture characteristic curve or the neutron probe field measurement data. For the Rose model we need the dispersion length, which can be obtained experimentally; the position of the maximum solute concentration (i.e. the distance moved by the solute peak), which is calculated from the estimated drainage; the volumetric field capacity; and also the molecular diffusion of NO\(_3\)^{-}, which is obtainable from the literature.

It was hoped that the results of this study would be of potential value in optimizing the use of N fertilizer when it is applied in the form of NO\(_3\)^{-}-N to the potato crop, both from the standpoint of plant nutrition and environmental quality under Scottish climatic conditions.
CHAPTER II
REVIEW OF LITERATURE

2.1 Introduction

The objectives of this review are:

1) To give a general insight into the importance of nitrate loss from a crop root zone by leaching; the movement of nitrate beyond the rooting depth is important agriculturally because it represents a loss of available N, and movement into ground waters is important environmentally.

2) To provide background information on the major factors which influence the leaching losses.

3) To consider those investigations concerning the relative influence of the soil-water-solute-crop factors on the solute status of soils.

4) To introduce briefly the major approaches that have been used in the prediction of nitrate leaching.

5) To introduce briefly the major approaches that have been taken to study solute leaching.

2.2 Role of Nitrogen in Agriculture

A generalized N cycle is shown in Figure 2.1. This describes the role of the N cycle in agricultural systems, and when specific values are assigned to various flows and pools it can be the basis for the construction of N budgets and simulations. These allow quantification of N losses in any given system and prediction of the long-term effects of various treatments in terms of overall losses.
Figure 2.1 - The nitrogen cycle
or gains of N (Clark, 1981). Plants obtain most of the combined N required for growth from the environment by uptake of simple N compounds, particularly nitrate and ammonium. Soil N is mostly in organic forms which are unavailable for plant uptake. These complex organic compounds are slowly decomposed by heterotrophic microorganisms to ammonia which, in all but the most alkaline soils, is in equilibrium with ammonium ions (Schmidt, 1962). Losses of available mineral N that can occur at this stage include volatilization of ammonia, and chemical fixation of both ammonia and ammonium. Some ammonium is assimilated by soil biomass (immobilization) but generally, in the absence of sufficient carbon and energy supplies, most of the NH$_4^+$ in the rooting zone of well-drained soils is rapidly oxidized to NO$_3^-$ by chemoautotrophic bacteria (nitrification). Thus most crop plants have evolved mechanisms for handling NO$_3^-$ (Olson and Kurtz, 1982). However, there may be a greater energy cost to the plant in using NO$_3^-$ rather than NH$_4^+$ (Miflin, 1980). In the absence of oxygen some microorganisms reduce NO$_3^-$, a process that can result in nitrogen loss from the soil as the gases N$_2$O and N$_2$ (denitrification). Nitrate is also easily leached from the crop root zone as it is not held by the negatively-charged soil colloids. Leguminous plants, by association with N-fixing bacteria, are able to supplement the N from soil organic matter breakdown with N from the atmosphere. Non-leguminous plants must rely on soil mineral N, which may be supplemented by fixed atmospheric N in the form of fertilizers or legume residues.

### 2.3 Significance of Nitrate Leaching Losses

Loss of nitrate from agricultural lands is often the most important channel of N loss from field soils. Losses normally range from 2 to 100 kg N ha$^{-1}$a$^{-1}$ (Wild and
Cameron, 1980a; Hauk and Tanji, 1982). Leached nutrients are always a waste, and may cause environmental problems, nitrate being a particular risk (Gardner, 1965). The solution containing nitrate which passes below the root zone may percolate through porous rocks into an aquifer, or move laterally to rivers through agricultural drains or through systems of natural channels and tissues (Young et al., 1976). Where losses are large enough to cause decreases in crop yield the economic significance is obvious (Cameron and Haynes, 1986). The environmental effects of such losses have recently received the most attention (Fasette, 1973; NRC, 1972; Taylor, 1975, Shuval and Gruener, 1977). The enrichment of lakes with nutrients has many adverse effects on their aesthetic and recreational value, while health problems have been associated with a high nitrate content of drinking water (NRC, 1972, 1978). Table 2.1 summarizes a number of potentially adverse impacts of N on health and the environment.

2.3.1 Economic loss

Leaching losses of NO$_3^-$ are not normally large except when fertilizer input greatly exceeds crop requirement or when the soil is left fallow (Cameron and Haynes, 1986). The amounts of NO$_3^-$ leached from cropland vary greatly (Baker, 1980; Keeney, 1982). However, on intensively managed crop land, the concentration of NO$_3^-$ in leachates seems normally to exceed 10 g N m$^{-3}$ (Baker, 1980; Keeney, 1982). The latter concluded that for many irrigated crops with good agronomic practices and profitable production about 20 g N m$^{-3}$ in drainage effluent may be the lowest achievable. On intensively grazed pasture, leaching losses of N can be significant, due to large concentrations of N deposited in urine patches. Mean concentrations of NO$_3^-$ in the range of 7 to 25 g N m$^{-3}$
have been recorded under such pasture (Baber and Wilson, 1972; Steele et al., 1984).

Table 2.1 - Potential adverse environmental and health impacts of N (after Keeney, 1982).

<table>
<thead>
<tr>
<th>Impact</th>
<th>Causative agent</th>
</tr>
</thead>
<tbody>
<tr>
<td>Human health</td>
<td></td>
</tr>
<tr>
<td>Methemoglobinemia in infants</td>
<td>Excess NO$_3^-$ and NO$_2^-$ in water and food.</td>
</tr>
<tr>
<td>Cancer</td>
<td>Nitrosamines from NO$_2^-$, secondary amines.</td>
</tr>
<tr>
<td>Respiratory illness</td>
<td>Peroxyacyl nitrates, alkyl nitrate, NO$_3^-$ aerosols, NO$_2^-$, vapour in urban atmospheres.</td>
</tr>
<tr>
<td>Animal health</td>
<td></td>
</tr>
<tr>
<td>Environment</td>
<td></td>
</tr>
<tr>
<td>Eutrophication</td>
<td>Excess NO$_3^-$ in feed and water.</td>
</tr>
<tr>
<td></td>
<td>Inorganic and organic N in surface waters.</td>
</tr>
<tr>
<td>Materials and ecosystem damage</td>
<td></td>
</tr>
<tr>
<td></td>
<td>HNO$_3$ aerosols in rainfall.</td>
</tr>
<tr>
<td>Plant toxicity</td>
<td></td>
</tr>
<tr>
<td></td>
<td>High levels of NO$_2^-$ in soils.</td>
</tr>
<tr>
<td>Excessive plant growth</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Excess available N.</td>
</tr>
<tr>
<td>Stratospheric ozone depletion</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Nitrous oxide from nitrification, denitrification, stack emissions.</td>
</tr>
</tbody>
</table>

2.3.2 Eutrophication

The over-enrichment of lakes and estuaries with nutrients such as N and P brings about many generally undesirable changes, including proliferation of algae and aquatic macrophytes, depletion of dissolved oxygen in the bottom water and a decrease in water clarity (Brezonik, 1969). Most low-productivity lakes are commonly believed
to be P- rather than N- limited, while the reverse is often true for eutrophic lakes. Estimates indicate that more than 90 percent of the N entering surface waters originates from non-point sources and that more than 80 per cent is from agricultural lands including livestock feed-lots (NRC, 1978). Many studies have demonstrated that high levels of total N and/or NO$_3^-$ in surface waters are generally related to agricultural activities (Omernick, 1976; Smith et al., 1982). Eutrophication may reduce boat access due to aquatic vegetation, and create health problems such as ear, nose and throat infections (NRC, 1978). It can partially block irrigation and drainage canals, and in arid regions can result in increased water loss from irrigation canals due to evapotranspiration from the floating vegetation.

2.3.3 Health problems

Nitrate per se is relatively non-toxic to humans and domestic animals; acute NO$_3^-$ poisoning in adults requires a single oral ingestion of 1-2 g of NO$_3^-$, far above normal exposure limits (Fassett, 1973; NRC, 1978). The adverse effect of high NO$_3^-$ is actually due to NO$_2^-$; NO$_3^-$ can be reduced to NO$_2^-$ by gastro-intestinal bacteria present in the tract of ruminant animals and in the human infant during the first few months of life (NRC, 1972; Shuval and Gruener, 1977; Taylor, 1975). Nitrite is rapidly absorbed from the stomach into the blood, where it readily oxidizes the iron of hemoglobin to the ferric state, forming methemoglobin. If over 50 per cent of the blood hemoglobin becomes oxidized, death is likely. The large majority of cases of acute NO$_3^-$ toxicity have been reported from households with a private well water supply. The U.S.A. Public Health Service (1962) drinking water standard is 10 g NO$_3^-$-N m$^{-3}$, while the World Health Organization's (1970) recommended level is less than 11.3
g NO$_3$-N m$^{-3}$ and the accepted level is 11.3 to 22.5 g NO$_3$-N m$^{-3}$. However, in the majority of cases of methemoglobinemia the well water was also contaminated with bacteria (International Standing Committee, 1974) and in the reduction of NO$_3^-$ the gastrointestinal microflora are of paramount importance. The actual "safe" level is debatable (Wild, 1977; Wild and Cameron, 1980 b), but it does appear that the use of domestic water supplies containing greater than 20 g NO$_3$-N m$^{-3}$ is likely to increase significantly the number of young infants at risk (NRC, 1978; Burden, 1982). The possibilities of formation of carcinogenic nitrosamines by reaction of ingested amines with NO$_2^-$ in the human stomach is thought to present a further health hazard after exposure to high levels of NO$_3^-$ (Chank, 1975; Crosby and Sawyer, 1976). NO$_3^-$ may affect the cardiac function of man (Malberg et al., 1978). A relation between high NO$_3^-$ concentrations in drinking water and hypertension has been reported (Morton, 1971) but other studies have failed to establish any relationship (Malberg et al., 1978).

2.4 Factors Affecting Leaching Losses

2.4.1 Seasonal and climatic effects

Variations in rainfall distributions and evapotranspiration patterns from year to year and from season to season affect the leaching pattern. The intensity as well as the amount of rainfall is of great importance in determining the pattern and extent of leaching (Wild and Cameron, 1980 a). Summer rainfall usually satisfies the evapotranspiration deficit and leaching is therefore usually minimal, but leaching can occur under intense heavy rainfall due to preferential flow, the amount of loss being dependent on time of fertilizer application (Williams, 1975). A dry summer
can result in the accumulation of soil nitrate due to poor crop uptake, and significantly higher than average leaching losses then occur over the subsequent winter (Garwood and Tyson, 1977). Autumn rainfall can leach residual fertilizer nitrate left after crop harvest or any nitrate released by mineralization when the soil is approaching or has reached field capacity. Total leaching losses of nitrate are characteristically highest during the winter period (Wild and Cameron, 1980a) when a large excess of rainfall over evapotranspiration and a low rate of uptake by crops occurs (Shaw, 1962; Kilmer et al., 1974; Dancer, 1975). An exception is when the soil is frozen (Baker et al., 1975) or when denitrification is the predominant loss process. Williams (1975) stated that spring rainfall determines whether freshly applied fertilizer or newly mineralized nitrate is quickly leached.

2.4.2 Soil type

a. Soil texture and structure. Comparisons of soils of different textures within individual trials are rare (Wild and Cameron, 1980a) but lysimeter (Woldendrop et al., 1965; Kolenbrander, 1969), catchment (Kudeyarov et al., 1981) borehole (Avnimelech and Raveh, 1976) and column studies (Sommerfieldt et al., 1982) have all shown faster rates of nitrate leaching through coarse-textured than through fine-textured soil. Wild and Babiker (1976a) presented a table of calculated depths of leaching that clearly demonstrates the influence of soil texture (Table 2.2).
Table 2.2 Theoretical leaching depths of nitrate peaks according to textural classes

<table>
<thead>
<tr>
<th>Texture class</th>
<th>Volumetric Water content $\theta_v$ ($cm^3/cm^3$)</th>
<th>Depth of nitrate peak (cm) for water input ($Q - cm$)</th>
<th>15</th>
<th>20</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sand</td>
<td>0.09</td>
<td>99 131 194</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Loamy sand</td>
<td>0.25</td>
<td>38 50 73</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sandy loam</td>
<td>0.27</td>
<td>35 46 67</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fine sandy loam</td>
<td>0.34</td>
<td>29 38 54</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Loam</td>
<td>0.34</td>
<td>29 38 54</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clay loam</td>
<td>0.30</td>
<td>23 42 61</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Silty clay loam</td>
<td>0.35</td>
<td>29 37 53</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Clay</td>
<td>0.39</td>
<td>26 33 48</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

---

a. Wild and Babiker (1976 a)
b. Value of $\theta_v$ from Salter and Williams (1965)
c. Calculated from an experimentally based regression equation where the depth of leaching is given by $y = 0.57x + 4.1$ where $x = Q/\theta_v$ and $Q$ is the winter rainfall.

In undisturbed naturally structured soils, especially those with macropores, only partial displacement of resident water and solutes by incoming water and solutes occurs (White, 1985). Recognition of such behaviour, variously described as "channelling", "short-circuiting", "by-passing", "preferential flow", or "partial displacement" (Scotter, 1978; Bouma, 1981; Beven and Germann, 1982; Smetten et al., 1983) is not new (Schumacher, 1864; Lawes et al., 1882) as pointed out by Thomas et al., (1978). Although macropores may comprise only a small fraction of the total soil volume (0.001 to 0.05), they can have a pronounced effect on the rate of infiltration and redistribution of water. Beven and Germann (1982) suggested that rainfall or irrigation between 1 and 10 mm hr$^{-1}$ may be sufficient to initiate macropore flow. White et al., (1984) found that the fractional volume of water participating in solute
transport ranged from 25 per cent of the soil water in a well structured soil (silt loam) to 93 per cent in a recently tilled sandy loam. Cunningham and Cooke (1958), Wild (1972) and Thomas and Phillips (1979) have suggested that when nitrate is held within soil aggregates it will be protected from leaching when by-pass flow occurs. Addiscott and Cox (1976) and Barraclough et al. (1983) have observed that if nitrate fertilizer has been recently applied to the soil, or if soil generated nitrate is held on the outside of aggregates, then by-pass flow causes it to leach faster than it would be by uniform miscible displacement. Shuford et al. (1977) found that nitrate was removed from all depths down to 1 metre in a well drained silt loam following single irrigations with 89 and 178 mm of water. The recovery of nitrate down to 1.35m was also to be found less than that predicted by a convective-dispersive model, suggesting that some nitrate had moved below this depth. Addiscott (1984) concluded that the presence of solute in an immobile phase retards leaching because diffusion between phases never reaches equilibrium. A general conclusion to be drawn from studies on undisturbed soil is that macropores can greatly decrease the time taken for dissolved and suspended matter applied to the surface to reach subsurface drains or ground water (Thomas and Phillips, 1979; Hagedorn et al., 1981; Bouma et al., 1983). The effect of macropores on the quantity of solute leached from soil per millimetre is less easily prescribed. White (1985) stated that whether flow in macropores that by-passes a fraction of the resident water within soil beds increases or decreases the amount of solute leached depends on several locations. These are: the location of the solute, the ratio of macropores to soil matrix flow, and the saturated hydraulic conductivity of the matrix, as well as the antecedent water content of the soil, the contact area between the by-pass flow and relatively static water of
the matrix, and finally the rate of solute diffusion between the mobile and immobile water volumes. In White's view, further research is required on all these aspects.

b. **pH.** The effect of pH on nitrate leaching seems to be small (Hendrick and Welsh, 1927), although from lysimeters Morgan et al. (1942) found a greater loss of nitrate from soil of higher pH. No trials appear to have been reported which compare soils of different organic matter content (Wild and Cameron, 1980a). However, a considerable amount of nitrate leached from agricultural soils can originate from mineralization and nitrification of soil organic N rather than from applied fertilizer N (Kolenbrander, 1981). Low and Armitage (1970) Low (1973) and Guiot (1981) showed that substantial leaching losses of nitrate can occur from unfertilized bare fallow soils.

c. **Soil Organic Matter.** The significance of soil organic matter as a source of nitrate is illustrated by the results of Dowdell et al. (1984), who found no significant difference in the total amount of N leached from fertilized and unfertilized plots cropped with barley. They found from $^{15}$N experiments that over 90 per cent of the total amount leached originated from native soil N and less than 10 per cent was actually from the applied fertilizer. This was attributed to the so-called priming effect, i.e. due to mineralization-immobilization turnover, fertilizer N will be immobilized by microorganisms at the same time that soil organic N will be mineralized and possibly lost.

d. **Charge characteristics of soils.** Because of the predominantly negative change on soil particles, anions such as NO$_3^-$ are partially excluded from the diffuse layer of cations surrounding the particles, therefore a
proportion of soil water does not participate in NO$_3^-$ leaching and the effective pore volume is less (often up to 11 to 20 per cent) than the water content of the soil (Wild, 1981). Nitrate ions therefore travel faster than predicted by the convection theory (Nielsen and Biggar, 1962; Thomas and Swoboda, 1970; Krupp et al., 1972). Soils have significant anion exchange capacity (AEC), resulting in non-specific adsorption of NO$_3^-$ which reduces its rate of leaching (Kingo and Pratt, 1971 a, b; Black and Waring, 1976 c). The effect of adsorption on leaching can be described by adding a retardation factor to the convective-diffusive-dispersive equation (Davidson and Chang, 1972).

2.4.3 Land management

Following ecosystem disturbance such as harvesting, fallowing, cultivating, fire or fertilizing, leaching loss of nitrate is often greatly increased (Khanna, 1981). Agriculture ecosystem tend to be continually disturbed and leaching losses can be large (Wild and Cameron, 1980 a).

a. Cropping. Lack of vegetation for at least part of the year is a key factor stimulating nitrate leaching from cropping systems (Cameron and Haynes, 1986), the magnitude of the loss being dependent on the cropping system. Miller (1906) and Russell and Richards (1920) showed that the average leaching losses were 41.5 kg ha$^{-1}$a$^{-1}$ from a bare fallow lysimeter receiving no fertilizer during the 10 year period 1877-87 and 28 kg ha$^{-1}$a$^{-1}$ during the period 1905-15. Low and Armitage (1970) and Low (1973) found that the greatest leaching from lysimeters (137 kg ha$^{-1}$a$^{-1}$) was under bare fallow, whilst under vigorously growing clover a maximum loss of 30 kg ha$^{-1}$a$^{-1}$ occurred, and under grass the loss was only 2 kg ha$^{-1}$a$^{-1}$. After death and removal of the clover plants, annual leaching
losses were increased to 131 kg ha\(^{-1}\). Cameron and Wild (1980 a) made the following generalization from the summary of Atkins (1976) (unpublished) of results from 57 lysimeter trials located in areas of temperate climate:

"The effect of cropping system is of primary importance, the ratio of amounts of N leached under grass, cereals and bare fallow being 1:6:30. The leaching loss for 100 kg N applied as fertilizer is about 0 to 2 kg under grass, 2 to 10 kg under arable, and 60 to 80 kg under fallow. Leaching losses increase with winter rainfall, but optimum water supplies in the summer can improve crop yield and reduce leaching loss."

Leaching loss increases with size of fertilizer application but the effect of the cropping system remains important. Grassed lysimeters lost over 120 kg N ha\(^{-1}\) by leaching after high applications of fertilizer (500 kg N ha\(^{-1}\)) whereas less than 20 kg N ha\(^{-1}\) occurred from smaller applications (250 kg N ha\(^{-1}\)). (Garwood and Tyson, 1973; Tyson and Garwood, 1974). Comparison of losses from different types of fertilizer show a slight trend for more leaching from nitrate than from ammonium sources (Thies et al., 1977) but differences are small, probably because of rapid nitrification of ammonium (Pratt et al., 1967; Jung and Dressel, 1974). Slow-release N fertilizers only reduced leaching losses under certain crop rotations (Jung and Dressel, 1974). However, Wiklander and Vahtras (1975) showed that leaching loss of N in the first season followed the order urea < (NH\(_4\))\(_2\)SO\(_4\) < Nitro Chalk < Ca(NO\(_3\))\(_2\). Nonetheless, a subsequent experiment over the following growing season (Vahtras and Wiklander, 1977) showed increased leaching from urea due to intensive nitrification of NH\(_4^+\) remaining from the previous season. The extent of NO\(_3^-\) leaching from NH\(_4^+\) based fertilizer will depend on the rate of nitrification
relative to the rate of plant uptake and the period of leaching (Cameron and Haynes, 1986).

**b. Permanent grassland.** Leaching losses of N from upland pasture catchment grazed with sheep can be in the range of 1 to 6 kg ha\(^{-1}\)a\(^{-1}\) (Crisp, 1966; Bargh, 1978) and losses are often less than rainfall inputs (Batey, 1982). Leaching losses under legume pastures can be 8 to 10 times those under all-grass pastures, and in general losses of N from grass-legume pastures also tend to be higher than those from all-grass pastures (Kilmer et al., 1974). Legumes accelerate N leaching losses (Guiot, 1981) because they fix large amounts of N, some of which is released when top growth dies back and/or roots die and nodules slough off (Vallis, 1978). Heavy fertilization can also cause significant leaching of NO\(_3\)\(^-\) below pasture sites (Hood, 1976 a, b), and leaching losses can be relatively large (i.e. 50 to 200 kg N ha\(^{-1}\) a\(^{-1}\)) on intensively managed pastures where high fertilizer rates are combined with high stocking (Horne, 1980; Steele and Shannon, 1982; Ball and Ryden, 1984; Steele et al., 1984). Substantial leaching of NO\(_3\)\(^-\) can occur from unevenly distributed urine patches (O'Connor, 1974; Floate, 1981). In general, extensive pastoral systems lose very little NO\(_3\)\(^-\) by leaching (Kilmer, 1974) since plant uptake and rapid immobilization of NH\(_4\)\(^+\) in the rhizosphere leaves little NO\(_3\)\(^-\) in the soil profile for leaching (Huntjens, 1971 a, b; Huntjens and Albers, 1978). Losses from pastures are considerably lower than from arable sites receiving the same fertilizer inputs (Kolenbrander, 1973; Kilmer, 1974). Shallow-rooted grasses with their less efficient extraction of soil NO\(_3\)\(^-\) and water allow higher losses of fertilizer N than do those with deep rooting system (Kilmer, 1974). The effect of grazing animals on leaching losses was observed by Ball and Ryden (1984); the losses were 140 to 190 kg N ha\(^{-1}\) a\(^{-1}\) below an intensively
grazed, fertilized, ryegrass pasture in the U.K., while losses from a similar cut sward were only 35 to 40 kg N ha\(^{-1}\) a\(^{-1}\).

c. Forests. Nitrate losses by leaching were reported to be very low (Likens et al., 1977; Henderson et al., 1978; Gosz, 1981; Melillo, 1981). Losses from coniferous forests are 0.5 to 1.5 kg N ha\(^{-1}\) a\(^{-1}\) (Gosz, 1981) and for deciduous forests 3 to 4 kg N ha\(^{-1}\) a\(^{-1}\) (Melillo, 1981). The amount of N lost by leaching is often less than the input from rainfall. Removal of vegetation by clear-cutting can result in increasing leaching losses (Vitousek, 1981; Fredriksen et al., 1975). The burning of forest has also been shown to increase leaching losses of \(\text{NO}_3^-\) (Lewis, 1974; Stark, 1977).

d. Irrigation. In many cases, irrigation has been reported to increase leaching losses of \(\text{NO}_3^-\) due to excess water moving through the crop root zone (Bauder and Schneider, 1979; Timmons and Dylla, 1981). For partial and full replenishment of maize Dylla (1981) found that annual \(\text{NO}_3^-\) losses by leaching increased from 17 to 53 per cent in comparison to non-irrigated maize. The method of irrigation can greatly affect the amount of \(\text{NO}_3^-\) leached (Viets et al., 1967). Furrow irrigation generally removes nutrients from directly below the furrow, while with sprinkler and flood irrigation the downward movement of \(\text{NO}_3^-\) is more uniform, due to the more extensive volume of soil that is leached.

e. Non-agricultural activities. In a study of a number of catchments in England and Wales, Owens (1970) reported that the proportion of total N from sewage effluent was generally small (less than 17 per cent) except in
industrial areas, and the remainder was from other sources such as land drainage.

2.5 Approaches to Measurement of Leaching

A number of approaches have been taken to study solute leaching. The information needed on nitrate leaching is the concentration of nitrate in solution that moves out of the range of plant roots and the loss in kg ha\(^{-1}\), the former because it represents the degree of pollution hazard, and the latter because it is an economic loss to the farmer and is an important part of the nitrogen balance sheet (Wild and Cameron, 1980a). The main methods of measuring nitrate leaching are:

2.5.1 Field soil sampling

The profile distribution of nitrate can be measured by soil sampling and extraction of the soil samples with a salt solution (Bremner, 1965). Alternatively, porous ceramic caps may be used to extract the soil solution (Hansen and Harris, 1975). To calculate the amount of the nitrate loss (kg ha\(^{-1}\)) the water flux must also be known. The required water flux can be calculated from a water balance equation or from the rate of change in water content of the soil. The calculated nitrate loss is liable to be in error if solutions for analysis are taken at fixed time intervals (Wild and Cameron, 1980a). The major constraints are that large numbers of measurements of both water flux and concentration are needed to be representative and that deep samples may be difficult to obtain, as in stony soils. Spatial variability of NO\(_3\)\(^-\) results in large variability in results of both soil solution NO\(_3\)\(^-\) levels (Nielsen et al., 1979) or extracted NH\(_4\)\(^+\) and NO\(_3\)\(^-\) levels (Broadbent and Carlton, 1978, Cameron and Wild, 1984; MacDuff and White, 1984).
2.5.2 Lysimeter studies

Lysimeters offer advantages because they give quantitative measurements of leaching losses from a defined soil volume, and they generally avoid large variations associated with field studies. Three principal types are known: (a) either walled-in undisturbed soil blocks or monoliths fitted into boxes; (b) tanks filled with loose soil; and (c) field tension lysimeters based on the placement of a suction plate below the soil surface (i.e. they have no walls). The first two types may suffer from container edge effects, resulting in increased aeration and preferential flow pathways (Wild and Cameron, 1980 a). Filled lysimeters do not retain the original soil structure and the settling time for the replaced soil is uncertain. Field lysimeters have also been used in N balance studies (Chichester, 1977; Dinchev and Badzov, 1969; Zamyatina et al., 1973). They offer the advantages of the confined microplot along with the capacity to estimate N leaching. The main disadvantages are high cost, lack of direct data on gaseous N loss, and restricted soil sampling. The permanent installation of lysimeters also allows long-term studies so that adequate allowance can be made for climatic variations (Legg and Meisinger, 1982).

2.5.3 Tile drain studies

In the majority of leaching loss studies by this method, water samples were collected one at a time rather than on a volume flow basis, so the sampling did not provide a reliable indicator of the amounts of nitrate loss (Thomas and Barfield, 1974).

Cooke and Williams (1970) stated that although useful comparisons have resulted from intermittent sampling of
drain effluents, the method is not suitable for assessing field leaching losses. There is a need for proportional water sampling (Bostock and Riely, 1976; Hood, 1976 a). The proportion can be calculated from a water balance equation, but there can be no certainty that the solution collected by the drain is representative of the whole because tiles usually intercept only part of the water flow down the profile.

2.5.4 Catchment studies

The advantages of catchment studies is that they avoid the variability problems associated with soil sampling. This is because collection of water draining from strictly confined catchment areas can provide an integrated measure of the leaching loss. This method is restricted to areas which have an impermeable sub-stratum. In large catchments there are usually errors in measuring inputs and outputs, and identifying the source of nitrogen, especially where the intensity of management varies. Bingham et al. (1971) reported that about 45 per cent of the applied N was estimated to be leached per annum. Porter (1975) found that NO\textsubscript{3}\textsuperscript{-} in drainage water accounted for over 35 per cent of the total nitrogen output from the watershed (omitting gaseous loss), the rest being as agricultural produce and stream particulate N. In contrast to these large losses, Bargh (1978) showed only a small proportional loss of N by stream flow (5 kg ha\textsuperscript{-1}a\textsuperscript{-1}) in New Zealand from an input of 35 kg ha\textsuperscript{-1}a\textsuperscript{-1}. These large variations in relationships between losses and soil management reported in the literature are due to differences in experimental conditions (Burwell et al., 1976).
2.5.5 Borehole sampling

In agricultural investigations movement below a depth of 1 or 2 metres is rarely monitored, but insofar as it affects the quality of drinking water, movement through unsaturated zones of the major aquifers is also important. Deep borehole samples taken from the chalk and permotriassic sandstones show a relationship between concentrations of nitrate in the interstitial water and land use history (Young et al. (1976) Young and Grey, 1978). The highest nitrate concentrations were found beneath fertilized arable land (15 to 50 mg Nl\(^{-1}\) or higher), and the lowest beneath unfertilized permanent grassland (less than 3 mg Nl\(^{-1}\)).

2.5.6 Laboratory column studies

Complete cores of undisturbed soil taken in the field can be leached in the laboratory, where application rate and initial moisture content can be controlled and monitored under both saturated and unsaturated flow conditions. Most studies in laboratories have been conducted on columns of repacked soil and other porous materials such as pumice, sand and porcelain (e.g. Passioura and Rose, 1971). The experiments involve the successive miscible displacement of one fluid by another through the column of material. The effluent is analysed to produce a breakthrough curve (i.e. effluent solution concentration versus time or cumulative drainage volume). The study of such curves has been the basis for the development of most current theories of leaching (Cameron and Haynes, 1986).
2.6 Approaches to Modelling of Leaching

Many workers have attempted to model and predict nitrate leaching with various degrees of success. The ability to predict nitrate leaching has obvious applications to the prediction of fertilizer N requirements for cropping systems. In recent years there has been a variety of approaches to describing solute leaching in field soils. Leaching models have been reviewed by Gardner (1955), Biggar and Nielsen (1967), Frissel and Poelstra (1967), Boast (1973), Gupta et al. (1979) and Wild and Cameron (1980 a). Approaches to modelling solute movement have been detailed by Nielsen et al. (1982) and Addiscott and Wagenet (1985). Leaching models also represent an important component of larger models that simulate the complete N cycle (Tanji and Gupta, 1978; Tanji, 1982). Table 2.3 summarizes the classification of leaching models (Addiscott and Wagenet, 1985). The purpose

Table 2.3 A classification of leaching models (Addiscott and Wagenet, 1985)

I. Deterministic models

A. Mechanistic (usually based on rate parameters)
   1. Analytical* (e.g. Nielsen & Biggar, 1962; Genuchten & Wierenga, 1976).
   2. Numerical* (e.g. Childs & Hanks, 1977; Robbins et al., 1980).

B. Functional (usually based on capacity parameter)
   1. Partially analytical (e.g. De Smedt & Wierenga, 1978; Rose et al., 1982 a, b).
   2. Layer and simple approach (e.g. Bressler, 1967; Tanji et al., 1972; Burns, 1974; Addiscott, 1977).

II. Stochastic models

A. Mechanistic (e.g. Dagan & Bressler, 1979; Amoozegar-Frad et al., 1982).
B. Non-mechanistic (transfer function) (Jury, 1982; Jury et al., 1982).

* Refers to the solution of the flow equations.
of this section is to introduce briefly the major approaches that have been used, which are:

2.6.1 Deterministic models

They presume that a system or process operates such that the occurrence of a given set of events leads to a uniquely definable outcome. The analytical and numerical (mechanistic) solutions to the convective-dispersion-diffusive flow equation are numerous (Kirkham and Powers, 1972; Bresler, 1973; Kirda et al., 1973; De Smedt and Wierenga, 1978; Gupta et al., 1979). These models were accurate in the description of laboratory breakthrough curves, but less appropriate and difficult to use for field situations. The problem is mainly associated with obtaining the apparent diffusion coefficient \( E \) according to the following equation:

\[
E = D_s + mU
\]  

(2.1)

where \( D_s \) is the effective diffusion coefficient in soil \((\text{cm}^2 \text{day}^{-1})\), and the term \( mU \) is the mechanical dispersion which remains unknown for unsaturated soils (Nielsen and Biggar, 1981). No direct method of calculating dispersivity has yet been devised, thus its value must be obtained experimentally. Once obtained, the models give accurate descriptions (Rose et al., 1982 a, b). Good agreement between model prediction and \( ^{15}\text{NO}_3 \)-leaching pattern from lysimeter studies was reported by Rose et al. (1982 b), and good agreement was also obtained in a field tracer leaching experiment by Cameron and Wild (1982 b).

The simplest model of leaching is of one solution displacing another from the soil pore with uniform displacement and no mixing, or "Piston flow", so called by
analogy with a piston displacing a fluid from a cylinder. It is expressed by an early equation (Rouselle, 1913) which was also derived by Levin (1964) by making simplifications and approximations in chromatographic theory:

\[ Z_p = \frac{Q}{\theta_v} \] (2.2)

where \( Z_p \) is the depth of the front of displacing solution (cm), \( Q \) is the quantity (cm) of displacing solution and \( \theta_v \) the volumetric water content. This approach should work best in sandy soils. Rao et al. (1976) found it to give a good estimate of the position of the solute front, but not its spread. Wild and Babiker (1976a) found that it tended to overestimate nitrate movement and suggested that this was because it ignored the effects of soil aggregation.

Partially analytical models: these models were designed to simulate the movement of a pulse of solute, and they also deal with successive pulses of solute by treating each one separately and summing their effects. However, they have important limitations in simulating solute leaching in heterogeneous profiles, or when profiles contain solute to depths at the start of the leaching period (Addiscott and Wagenet, 1985). They probably have potential as both research and management models, but with limitations in each case. These models are based on simplifying the theory governing solute movement. The position of the solute peak is computed by ignoring the effects of dispersion and diffusion, and then imposing around this peak the computed effects of these factors. Removing the dispersion term from the convection dispersion equation (Wagenet, 1983) resulted in piston flow, i.e.
\[ \frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad (2.3) \]

The effects of diffusion and dispersion on an assumed initially rectangular pulse was described by Rose et al. (1982 b)

\[ C = C_0/2 \left( \text{erfc} \frac{Z - a}{2(D_0t + ma)^{1/2}} - \text{erfc} \frac{Z - B}{2(D_0t + mB)^{1/2}} \right) \quad (2.4) \]

where \( m \) is the dispersivity and \( B = (a - \Delta F) \), \( \Delta F \) being the thickness of the pulse as it leaves the soil surface. Rose et al. (1982 a) and De Smedt and Wierenga (1978) show that during the infiltration and redistribution of an increment \( Q \) cm of water, the distance \( a \) (cm) moved by the solute peak is given by

\[ a = Q/\theta_{vfc} \quad (2.5) \]

where \( \theta_{vfc} \) is the water content at field capacity. These models, though partially analytical, are essentially capacity models, as solute displacement is calculated using \( \theta_{vfc} \), and not rate of movement (Addiscott and Wagenet, 1985).

Layer models and other simple approaches: chromatographic theory is now used much less widely than the approach listed in Table 2.3 (Addiscott and Wagenet, 1985), partly because its main relevance is to solutes that undergo exchange or adsorption during transport, whereas much recent leaching work has been concerned with nitrate and other non-adsorbed solutes (Addiscott and Wagenet, 1985). Empirical models have been developed that are not based directly on the classical flow equation but on observed quantitative relationships among variables (Cameron and Haynes, 1986). These models used simple chromatographic theory to simulate partial displacement of solute from
field soils (Thomas et al., 1978). There is also a number of simple models which divide the soil into horizontal layers. Most are based on mass conservation in respect of both solute and water. Two early examples of this kind of model are those of Bresler (1967) and Tanji et al. (1972). Another simple model was developed independently by Terkeltoub and Babcock (1971) and Burns (1972). In this, rainfall or irrigation is applied to the top layer of the soil, causing a temporary increase in its water content. The incoming water and salts are assumed to mix with water and salts already present in this layer. If the new water content of the layer exceeds field capacity, the surplus water and the salts it contains are transferred to the next layer where the procedure is repeated. This continues down the profile until a layer is encountered which is either the bottom layer or in which incoming water does not cause the water content to exceed field capacity. Burns (1974) extended the above-mentioned model to include the effect of evaporation, using the evaporative limit concept. The minimum water content, and a storage maximum (field capacity) are used to characterize each layer. The required loss of water is taken from the top layer unless this brings the water content below the evaporative limit, in which case the demand is met from the second or subsequent layers. Water loss from the second or subsequent layers is assumed to occur by capillary rise. Burns obtained good simulations of chloride movement, slightly less accurate simulations for nitrate, but rather poorer simulations of change in water content. Cameron and Wild (1982) did not get such good simulations of chloride movement with Burns' model as they did with that of Rose et al. (1982 a, b). Burns' model has been shown to account successfully for nitrate leaching in some sandy soils (Burns, 1975) but has been found to be less appropriate for more coarsely structured soil because of
the assumption of instantaneous total equilibrium of water and solute in each layer (Cameron and Wild, 1982 b). The model can also be used in the form of a simple equation for the fractional loss \( f \) of a non-adsorbed solute below \( h \) cm depth during a percolation of \( P \) cm (Burns, 1975).

\[
f = \left( \frac{P}{P + \theta_{vfc}} \right)^h
\]

This equation gave satisfactory agreement with simplified data collected from the literature. Burns' model and equations are primarily management tools; and he has demonstrated their potential by showing how the variability in yield response data could be reduced by plotting yield against the amount of N applied calculated to have remained in the profile after rainfall, using the above equation, rather than simply against the rate of N applied (Burns, 1980).

Leaching in soil is affected by mobile and immobile water phases due to the influence of soil structure (soil pore size variations) (Addiscott, 1977). The immobile (retained) phase represents the water held in small pores and "dead-end" pores that are considered not to contribute to flow but that are accessible to solute only by diffusion. The mobile phase represents the pore system that is involved in mass flow and thus only this phase can be displaced. The division between the two phases is at a tension of 2 bar. Rainfall causes piston flow in the mobile phase during which solute may move just from one layer to the next or, if the fall is large, through several layers. When piston flow ceases, solute movement between the phases occurs to equalize the concentrations in the soil water.
2.6.2 Stochastic models

These models presuppose that soil properties vary spatially so that solute and water movement also vary. These models have evolved with the recognition of problems caused by variability for deterministic models. Spatial and temporal variation in field soil properties is sufficient to render estimates of means highly unreliable. Acknowledgement of the mean behaviour of a field may be less important in some cases than that of its statistical or spatial variation (Nielsen et al., 1983). Therefore, geostatistical methods of data analysis have been introduced into the analysis of solute movement, and applications have allowed considerable progress in spatial interpolation, spatial averaging and design of a better sampling scheme (Nielsen et al., 1982). These models can be broadly divided into (Addiscott and Wagenet, 1985)

a) approaches in which allowance is made for spatial variability in existing mechanistic models; and b) approaches focussed on the variability of solute and water transfer which take no account of mechanism.

Non-mechanistic stochastic models: these models were suggested for soils by Raats (1978), and used by Jury (1982). This approach measures the distribution of solute travel times from the soil surface to some reference depth. A distribution function of the form

\[ P_L (I) = \int_0^I f_L (I) \, dI \]  

(2.7)

is constructed in which \( f_L (I) \) represents the probability density function summarizing the probability \( P_L \) that a solute added at the soil surface will arrive at depth \( L \) as the quantity of water applied at the surface increases from \( I \) to \( (I + dI) \). In general \( f_L (I) \) is proving to be log-normally distributed (Biggar and Nielsen, 1976; Van
de Pol et al., 1977). Field comparisons have shown good agreement between measured and predicted bromide concentrations (Jury et al., 1982), and indicate that this model could be useful as a stochastically-based management model for solute movement.

2.6.3 Stochastic-mechanistic models

In this type of model randomly-distributed input values are used in a mechanistic model to produce a distribution of output values. The analytical solution of the classical flow equation for steady-state was used by Amoozegar-Fard et al. (1982), either in a deterministic way, with mean values for pore water velocity (U) and the diffusion coefficient (D), to produce mean concentration profiles, or stochastically, using random U and D values to generate distributions of concentration profiles. There were substantial differences between the simulations from the two approaches. The variability in D proved much less important than that in U, particularly at greater soil depths; i.e. it was the variability in convective, rather than diffusive processes that was of overriding importance in producing solute fluxes. Similar conclusions have been shown by Dagan and Bresler (1979), and Bresler and Dagan (1979, 1981).

Addiscott and Wagenet (1985) summarized their conclusion from a review of modelling approaches to solute leaching as follows:

1) Analytical solutions of the mechanistically-based convection-dispersion equation are soundly based and have been validated in carefully controlled laboratory experiments, but their deterministic nature and rigid boundary conditions limit their use
to experiments designed around them. They are principally research models.

2) Numerical models based on the above mentioned equation are more flexible than the analytical ones, but their deterministic nature makes them difficult to use due to spatial variability of soil hydraulic properties. They too tend to be used for research purposes.

3) Stochastic models developed to accommodate the variability of hydraulic properties have proved useful for assessing the impact of this variability. The simpler models of this kind should, when further developed, be useful for management as well as research.

4) The simpler, less mechanistic, functional models are useful for management.

5) Few solute transport models have been exhaustively tested under field conditions. There is a need for quantitative criteria for validating models universally, and these should be established and used to compare the abilities of the various types of models to simulate the results of field experiments.
CHAPTER III

MATERIALS AND METHODS

3.1 Site A : Castle Huntly

3.1.1 Experimental Site

3.1.1.1 Location
The field research was conducted at the Horticulture Unit of The Edinburgh School of Agriculture located at Castle Huntly (NG299297), about 6 miles west of the city of Dundee, Scotland, in the summer of 1984.

3.1.1.2 Description
The experiment was conducted on a soil developed on a reddish brown sandy loam belonging to the Kippen association. The soil shows no signs of imperfect drainage except at the very base of the slope where there are signs of temporary waterlogging at depths over 50cm. The plot area had almost zero slope in all directions. The bulk density and field capacity of the surface soil are approximately 1.3 g cm$^{-3}$ and 35 per cent by weight ($\theta_w$), respectively. The volumetric water content ($\theta_v$) of the surface soil at field capacity is 46 percent. The average annual precipitation at the Field Research Farm is 68.3 cm and annual potential evaporation is 55.6 cm (personal communication from the Met. Office). During the 1984 growing season (2 April to 22 August) rainfall was 10.0 cm and potential evaporation was 42.0 cm. The average maximum temperature was 16.8°C during the course of the experiment.
3.1.1.3 Field sampling for NO$_3^-$-N levels prior to planting.

The variability of the experimental site at Castle Huntly due to previous cropping was a problem. Small areas of heavily fertilized vegetables had led to large variation in available nutrients. Field sampling for NO$_3^-$-N indicated that the site could be divided into plots with different initial available N levels, and this was used as a basis for different N treatments. Three levels of NO$_3^-$-N were obtained from the chemical analyses of samples taken with a mechanical auger at 20 cm intervals up to 60 cm soil depth approximately six weeks prior to planting (Figure 3.1). Initial soil NO$_3^-$-N levels were classified as the standard, medium and low levels according to standard requirements (160 kg ha$^{-1}$) of the test crop (Maris Piper potatoes) used in the experiment. The standard and medium levels were the result of recent fertilization, and the low level was due to previous crop removal. The available N levels in the 0-60 cm soil depth at sampling are shown in Figures 3.2 and 3.3 for irrigated and unirrigated plots respectively prior to planting and were classified as:

a. Standard level: i.e. 150 kg ha$^{-1}$ and greater, named NS.
b. Medium level: i.e. greater than 100 kg ha$^{-1}$ but less than 150 kg ha$^{-1}$, named NM.
c. Low level: i.e. less than 100 kg ha$^{-1}$, named NL.

3.1.1.4 Irrigation planning

The irrigation treatment was scheduled using weekly MORECS data for the appropriate grid square number (45). The following steps were applied:

i. 30 cm in diameter

ii. Estimated from contour map as an area-weighted mean within each plot at 20 cm intervals up to 60 cm soil depth
Figure 3.1—Field sampling for NO$_3^-$-N prior to planting at Castle Huntly

Sampling date 2/4/84
Sampling depth 60 cm
Contours in Kg ha$^{-1}$
Scale 1:250
Figure 3.2 - Interpolated profile NO$_3^-$-N content in the irrigated plots prior to planting (1984) at Castle Huntly
Figure 3.3 - Interpolated profile $\text{NO}_3^-$-N content in the unirrigated plots prior to planting (1984) at Castle Huntly
a. Selection of the likely soil moisture deficit (SMD) for main crop potatoes based on the site soil texture. The site was therefore classified as Class B1, and the available water content was assumed equal to 20% by volume. The recommended water per application, critical SMD and the initial SMD were: 3, 5 and 3 cm respectively.

b. The water balance sheet was started on the first day of April by assuming zero SMD.

c. Subtraction of weekly value of rainfall from weekly water loss and then adding or subtracting the results of SMD from the previous week.

d. Irrigation, therefore, was applied as the recommended amount as above, when the planned deficit was reached.

3.1.2 Experimental plan and field operations

3.1.2.1 Experimental design
The main variables consisted of three different initial soil NO₃⁻-N levels and two different irrigation regimes with no replication. Field plots 4.0 m x 4.0 m were used.

3.1.2.2 Field operations
A basal dressing of P and K fertilizer was applied shortly before planting. Rates were 160 and 240 kg ha⁻¹ of P₂O₅ and K₂O. No nitrogen fertilizer was applied as sufficient N was already present in the soil profile. (see Figures 3.2 and 3.3). The plots were planted by hand in mid-May, 1984. Each plot was planted with six rows at 76 cm spacing, after ridges had been made by a ridging machine. the average ridge height was approximately 10 cm. Planted
Alleys approximately the same size as the plot were left between each treatment to prevent the influence of one treatment on another. Water was applied into irrigated plots using a sprinkler irrigation system. The system was calibrated prior to planting so that time and amount of irrigation was estimated depending on the size of the plot and the allowable soil moisture deficit. The irrigation system used was sensitive to wind when calibrated, but wind was unimportant in most cases at times of irrigation application during the season. The system consisted of a rubber hose (2.54 cm in diameter) connected to an adjacent water source (a standpipe) at one end. Two sprinklers (nozzle diameter 0.4 cm) were connected to the other end through a T junction so that two plots were irrigated simultaneously; the third plot was irrigated separately after irrigation application had ceased in the other two plots. The discharge from the water source was adjusted to give approximately 1.5 cm h⁻¹ irrigation depth to each plot. The dates and amounts of irrigation water applied are given in Table 3.1.

Table 3.1 Dates and depth of irrigation water applied during the 1984 cropping season at Castle Huntly.

<table>
<thead>
<tr>
<th>Date</th>
<th>Plot 2 (cm)</th>
<th>Plot 4 (cm)</th>
<th>Plot 6 (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>13/7/84</td>
<td>4.22 (2.29) *</td>
<td>4.29 (0.53)</td>
<td>4.28 (0.33)</td>
</tr>
<tr>
<td>25/7/84</td>
<td>3.33 (0.76)</td>
<td>2.20 (0.44)</td>
<td>2.90 (0.26)</td>
</tr>
<tr>
<td>1/8/84</td>
<td>1.47 (0.33)</td>
<td>1.38 (0.35)</td>
<td>1.48 (0.19)</td>
</tr>
<tr>
<td>10/8/84</td>
<td>2.24 (0.38)</td>
<td>1.80 (0.13)</td>
<td>2.12 (0.50)</td>
</tr>
<tr>
<td>15/8/84</td>
<td>2.29 (0.32)</td>
<td>1.70 (0.19)</td>
<td>1.66 (0.25)</td>
</tr>
<tr>
<td>22/8/84</td>
<td>1.89 (0.30)</td>
<td>1.92 (0.23)</td>
<td>2.34 (0.62)</td>
</tr>
</tbody>
</table>

(* Figures in brackets represent standard error (s.e)

The amounts of irrigation water received by each plot were measured using five plastic graduated cylinders 11 cm in
diameter. Each cylinder was placed in a row immediately before irrigation application started, and then the amount of irrigation water received was calculated by averaging the amount of water collected in the cylinders at the end of each irrigation application in each plot. A dense cover of weeds occurred because no herbicide was applied prior to planting. This was removed by hand on two occasions (11/7/84 and 25/7/84). This weed removal will have influenced the subsequent N balance significantly.

3.1.3 Moisture measurements and monitoring

3.1.3.1 Moisture determination prior to planting
Soil water content was determined gravimetrically prior to planting. Samples were taken using a mechanical auger at 20 cm intervals to a depth of 60 cm mainly for $\text{NO}_3^-\text{-N}$ and $\text{NH}_4^+\text{-N}$ analysis. The results showed that the soil was near field capacity water content at the time of sampling.

3.1.3.2 Moisture monitoring with neutron probe*
Soil water content during the cropping season was measured approximately weekly with the neutron probe (9 sets of readings were taken approximately weekly) in the ridge from 6/7/84 until 22/8/84) at 5 cm and then at 10 cm intervals to a 75 cm soil depth (65 cm below the ridge), and at 10 cm intervals to a 90 cm soil depth below the furrow. The experiment involved six access tubes with no replication, one access tube being placed in the centre of the ridge of the third row of each plot, for all treatments. The experiment also involved twelve tubes with two replicates, an access tube being placed in the furrow adjacent to the third ridge in each plot (Figure

* The neutron probe used in the experiment was the "Wallingford" probe, with a 50 m Ci americium-beryllium source.
3.4. Neutron probe readings were taken immediately before irrigation applications. On one occasion (1/8/84) Neutron probe readings were taken immediately after irrigation had ceased in the irrigated plots, followed by another set of readings after 2 days (3/8/84), so that the field capacity of the soil profile could be determined and compared with that obtained from the soil moisture characteristic curve determination. Calibration of neutron probe will be presented later with Site B.

3.1.4 Laboratory analysis

3.1.4.1 Soil extraction for \( \text{NO}_3^-\) and \( \text{NH}_4^+\) analysis
Soil samples were collected from each plot on three occasions (13/7, 25/7 and 22/8/84) during the course of the experiment. The samples were taken from the ridge, and then at 20 cm intervals to 40 cm below the ridge using a 6.7 cm diameter soil corer designed to take intact cores. Samples were taken to a laboratory and immediately sieved using a 2 mm sieve. \( \text{NO}_3^-\) was extracted from the soil by shaking with 1M KCl for 1 hour, the extract was filtered and \( \text{NO}_3^-\) and \( \text{NH}_4^+\) in the extract were determined in duplicate samples according to Henriksen and Selmer-Olsen (1970).

3.1.4.2 Plant total N analysis
Two plants were taken from each plot on three occasions as with soil samples during the growing season. Plant tubers, shoot and roots were washed with water. The weights of fresh and dry tubers, shoots and roots were determined. The dry weight of the whole plant was obtained by drying the fresh parts of the plants at 105°C for 48 hours. The dry matter of the plant was coarsely milled using a general laboratory purpose mill and then finely milled with a ball mill.
Figure 3.4 - Positions of access tubes for neutron probe moisture measurements in the 1984 field experiment at Castle Huntly
Total N was determined, in duplicate, in the different parts of the plant using an automatic nitrogen analyser (Carlo Erba ANA 1400 N analyser). The samples were weighed into a tin container and, using the automatic sampler, introduced into a reactor, which is maintained at 1000°C. Both container and sample melt and the tin primes a violent reaction at about 1700°C. Under these conditions, even thermally resistant materials are completely oxidised. The combustion products are carried by a constant flow of helium gas through an oxidation catalyst (NiO) maintained at 1000°C. Nickel oxide is used because of its chemical-physical characteristics: it inhibits the formation of nitrogen oxides, is suitable for high temperature operation and does not attack the quartz reaction tube. It also does not absorb nitrogen and therefore does not affect the chromatographic aspect of the system. A layer of silvered cobalt oxide positioned at the bottom of the combustion tube completes the oxidation and retains interfering substances produced during the combustion of halogenated substances.

The mixture of $N_2$, $N_xO_y$, $CO_2$ and $H_2O$ passes through the reduction reactor filled with reduced copper stored at 730°C. At this temperature the nitrogen oxides are reduced to elemental nitrogen which then together with the carbon dioxide and water pass through two absorbent filters. The first filter consists of magnesium perchlorate (anhydrous) which absorbs $H_2O$; while the second filter consists of soda-lime which retains the $CO_2$. The elemental nitrogen enters the chromatographic column and, together with the carrier gas, flows through a thermal conductivity detector, which provides an electrical signal proportional to the concentration of nitrogen present. By calibrating the instrument under the same conditions with a standard sample, a direct print
out of micrograms of nitrogen present in the sample is obtained.

3.1.4.3 Determination of selected soil properties
Particle size distribution on the <2 mm soil material was determined by the pipette method (Black et al., 1965). The sand fractions were separated into two fractions by sieving the coarse sand grains before the finer grains were separated into size fractions by sedimentation. Particle size fractions were expressed as a percentage of the total <2 mm soil material. The following treatment was applied to the soil samples to obtain a satisfactory dispersion of the soil particles: preoxidation to remove the organic matter using 6 percent hydrogen peroxide, followed by addition of sodium hexametaphosphate \((\text{NaP}_2\text{O}_7)_6\) (5 percent solution) to replace polyvalent cations and \(\text{H}^+\) ions to prevent flocculation. It has been found that sodium hexametaphosphate is very effective, because it forms soluble co-ordination compounds with calcium and other troublesome ions.

In addition to particle size distribution, the following determinations were also made on the soil samples using procedures as outlined in the reference mentioned above: pH, organic matter, available phosphorus, available potassium, bulk density.

3.1.4.4 Determination of soil moisture characteristic curve
Undisturbed soil samples were taken from the soil surface using a 7.3 x 7.3 cm metal ring. A smaller undisturbed sample was obtained by pushing gently a smaller 4 x 2 cm metal ring into the original sample and it was then saturated with water. A soil moisture retention curve (soil moisture characteristic curve) was obtained by taking the saturated soil sample and determining the moisture content as increasing matric tension was applied.
Data pairs were plotted and the moisture retention curve was obtained. A tension table was used to determine soil water content at low water tension (-5 to -10 kPa). A tension of -5 kPa was used for the field capacity estimation in this experiment. At higher tension, a pressure membrane was used (-15 to -1.5 x 10^3) kPa. Permanent wilting point was determined at a suction of (-1.5 x 10^3) kPa.

3.1.5 Crop harvest
Crop yields were not obtained due to the early end of the experiment (22/8/84). Damaged plant tubers were found in all plots during the third week of July, caused by cutworm. The degree of damage increased in most of the plots (Table 3.2) later in the season therefore a decision was made to end the experiment prematurely.

Table 3.2 Per cent damage of potato tubers caused by cutworm during the 1984 cropping season

<table>
<thead>
<tr>
<th>Plot No.</th>
<th>11/7/84</th>
<th>25/7/84</th>
<th>22/8/84</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0</td>
<td>11.5</td>
<td>56.0</td>
</tr>
<tr>
<td>2</td>
<td>0</td>
<td>9.1</td>
<td>17.0</td>
</tr>
<tr>
<td>3</td>
<td>0</td>
<td>23.0</td>
<td>36.0</td>
</tr>
<tr>
<td>4</td>
<td>0</td>
<td>6.3</td>
<td>68.0</td>
</tr>
<tr>
<td>5</td>
<td>0</td>
<td>50.0</td>
<td>44.0</td>
</tr>
<tr>
<td>6</td>
<td>0</td>
<td>23.5</td>
<td>27.0</td>
</tr>
</tbody>
</table>

3.2 Site B: Aberlady

3.2.1 Experimental site

3.2.1.1 Location
The field research was conducted at Luffness Mains Farm (private), near Aberlady, (NG348679) located about eighteen miles north east of Edinburgh, Scotland in the summer of 1985.
3.2.1.2 Description
The experiment was conducted on a brown forest soil of fine sandy loam belonging to the Dreghorn series (raised from beach deposits derived mainly from carboniferous sediments). The Dreghorn series includes many of the most intensively farmed and valuable soils in Scotland. Typical crops grown on them included early and main crop potatoes, leeks and brussel sprouts as well as carrots, cauliflower and strawberries. The site at Luffness Mains showed no signs of imperfect drainage except at depths over 50 cm due to occasional rises in water table. The field capacity values were found, by observation of the weekly field soil moisture data, to be 15, 20 and 25 percent for soil depth 0 to 20, 20 to 40 and 40 to 60 cm, respectively. The latter value of the field capacity for 40 to 60 cm may over-estimate true field capacity because this depth was probably within the capillary fringe of the water table after occasional rain storms.

The bulk density values were 1.1, 1.4 and 1.5 cm$^{-3}$ in the ridge, and 0 to 20 cm and 20 to 40 cm below the ridge, respectively. The average annual precipitation is 61.6 cm (personal communication with Met Office) and during the 1985 growing season (1 April to 22 September) was 47.1, the potential evaporation was 36 cm. The average temperature during the course of the experiment was 9.6°C. The plot area had almost zero slope in all directions.

3.2.2 Experimental plan and field operations

3.2.2.1 Experimental design
The main variables consisted of two different soil nitrogen levels and three different irrigation regimes replicated four times, the unfertilized plots ($N_0$) are considered as the controls). The experimental treatments were arranged according to a randomized block design.
The control field plots were 3 m x 3 m and the $^{15}$N micro-plots were 3 m x 2 m, located within larger main plots.

The proposed levels of irrigation to be imposed on the test crop (Maris Piper potatoes) were not applied as planned because little or no moisture deficits occurred due to the above-average rainfall during the growing season. Thus the experiment was considered as a study of rainfall effect rather than irrigation effect on nitrate leaching from the crop root zone. The lack of irrigation application resulted in a large number of replicates of the fertilized treatment.

3.2.2.2 Field operations

"Temic" compound for eel worm protection was applied on two occasions; the first application was approximately three weeks before planting, whereas the second was a month after planting. The rates were 25 and 40 kg ha$^{-1}$ respectively. There were no signs of eel worm attack throughout the cropping season. The recommended application of phosphorus and potassium for a potato crop was broadcast by hand over the site area. Rates were 160 and 240 kg ha$^{-1}$ of P$_{2}$O$_{5}$ and K$_{2}$O, respectively. Nitrogen fertilizer was applied separately, shortly before planting. $^{15}$N-labelled material was broadcast by hand over 2 m x 3 m micro-plots located within larger main plots at a rate equivalent to 160 kg ha$^{-1}$. The remainder of each main plot was similarly treated with unlabelled N fertilizer. The applications of N, P and K fertilizer were performed before ridging. The plots were planted with four rows at 88 cm spacing. The ridge average height was approximately 10 cm. An alley was left between each treatment to prevent the influence of one treatment on another.
3.2.2.3 Field sampling procedure for $^{15}$N determination

Soil samples were collected on three occasions (14/6, 3/7 and 15/8/85) from the micro-plots as well as from the control plots. In three micro-plots two samples were taken and in the fourth three samples were taken. Samples from the ridge were taken by mixing the whole cross section of the ridge in the field and subsampling, whilst samples below the ridge were taken using a stainless steel tube with a cutting edge and split inner sleeve (internal diameters of the tube and sleeve were 7.2 and 6.6 cm respectively). The soil cores were then cut into 20 cm segments, sealed in polythene bags labelled with micro-plot and plot number and soil depth and stored in a freezer at -15°C until analysis of NO$_3^-$, NH$_4^+$ and isotopic abundance of $^{15}$N. Low temperatures have long been used for the storage of fresh soil samples for inorganic nitrogen analysis. Gasser (1958) found that -10°C was adequate to prevent change in nitrate and ammonium contents. Allen and Grimshaw (1962), however, suggested that this was not satisfactory. Goodlass (1978) found that a temperature of 5°C appears to have been low enough to prevent changes in nitrate content after storage for eight weeks.

3.2.3 Moisture monitoring with neutron probe

Soil water content during the course of the experiment was measured approximately weekly with the neutron probe, where nineteen sets of readings were taken from 15/5/85 until 25/9/85. The experiment involved 16 tubes in four treatments replicated four times. One access tube was placed in the ridge of the second row from the outside of each micro-plot for all $^{15}$N treatment in four replications, one access tube was placed in the centre of each control plot (Figure 3.5). The neutron probe readings were taken at 5 cm, 10 cm and then at 10 cm
intervals to a 80 cm soil depth below the ridge (no access tubes were placed in the furrow in this experiment.

3.2.3.1 Neutron probe calibration
Figures 3.6 and 3.7 show the calibration curves for the Castle Huntly and Aberlady sites, respectively. The objective behind the calibration procedure is to obtain a valid regression analysis of volumetric moisture content and neutron probe count rate so that the soil water content can be estimated from measured values of count rate as follows:

\[ MVF = MN + C \]  
(3.1)

where \( MVF \) is volumetric soil moisture content (per cent)  
\( N \) is measured count rate \( cs^{-1} \)
\( M \) and \( C \) are the gradient and intercept of the calibration equation

The count rates should be corrected for the effect of dry bulk density (Grecen and Schralle 1976) using the following equation

\[ N' = N \left( \frac{BS}{BD} \right)^{0.5} \]  
(3.2)

where \( N' \) is bulk density corrected count rate \( cs^{-1} \)
\( BS \) is standard dry bulk density \( g \ cm^{-3} \)
\( BD \) is actual dry bulk density \( g \ cm^{-3} \)

The total random error is made up of four components which are:
Figure 3.5 - Positions of access tubes for neutron probe moisture measurements in the 1985 field experiment at Aberlady
Figure 3.6 - Neutron probe calibration curve for Castle Huntly (1984)
Figure 3.7 - Neutron probe calibration curve for Aberlady (1985)
Figure 3.7 - Neutron probe calibration curve for Aberlady (1985)
a. Nuclear counting error: it is usually very small and is due to the random nature of the disintegrations in the radioactive source, and should be much less than 1% MVF (Bell, 1976).

\[ NE = (N/t)^{0.5} \]  

where \( t \) is count time (s)

b. Error from regression analysis: in general, estimates of the change in moisture content are much more accurate than estimates of absolute moisture content. The first is an estimate of the accuracy of the gradient of the regression, whereas the second is an estimate of the accuracy of the intercept of the regression.

c. Error due to placement: this error can be very serious and relates to the assumption that observations are made at a particular depth whereas in fact the source has been positioned at a slightly different depth. The effect of this error is most severe under two conditions, firstly when the source is near to the soil surface and secondly when there is a marked step change in either water content or dry bulk density within the profile. Within a soil with no large changes in moisture content down the profile the effect of this error term becomes negligible the deeper the observations are made down the soil profile. Estimates can be made for this term but they involve large assumptions. First one has to assess the accuracy of the depth gauge on the neutron probe. This reads to ±1 cm; however, it is possible to estimate position to within ±0.25 cm.

The second factor is the estimate of tube height. On a level site the estimate will be very good, but on an uneven or sloping site the accuracy of this term will be reduced. When determining the tube height, at least five
observations should be made to assess the variability of this term. The third factor is the slippage of the cable as the source is lowered down the access tube (a biased error term). In view of difficulties in calculating this term, it is more usual to take great care while taking readings with neutron probe and ignore this term.

d. Site variability error: This is the natural variability of the site and is estimated by the standard error of the mean of replicate observations within a treatment (at least three replicates of each treatment are required).

Table 3.3 Summary of calibration data for Aberlady (1985)

| Soil series: | Dreghorn |
| Texture:     | Sandy loam |
| Crop:        | Potatoes |
| \( N_w \):   | 876.9 |

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Count rate (N)</th>
<th>Bulk density (BD)</th>
<th>Corrected count rate (N')</th>
<th>Surface correction (C)</th>
<th>( N' C / N_w )</th>
<th>Measured MVF (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>131</td>
<td>1.106</td>
<td>136.4</td>
<td>1.936</td>
<td>0.302</td>
<td>19.6</td>
</tr>
<tr>
<td>10</td>
<td>217</td>
<td>1.106</td>
<td>226.0</td>
<td>1.317</td>
<td>0.314</td>
<td>19.6</td>
</tr>
<tr>
<td>15</td>
<td>274</td>
<td>1.270</td>
<td>266.3</td>
<td>1.078</td>
<td>0.323</td>
<td>22.8</td>
</tr>
<tr>
<td>20</td>
<td>318</td>
<td>1.430</td>
<td>291.3</td>
<td>1.015</td>
<td>0.336</td>
<td>26.0</td>
</tr>
<tr>
<td>30</td>
<td>339</td>
<td>1.510</td>
<td>302.2</td>
<td></td>
<td>0.345</td>
<td>27.3</td>
</tr>
<tr>
<td>40</td>
<td>359</td>
<td>1.540</td>
<td>316.9</td>
<td></td>
<td>0.361</td>
<td>27.0</td>
</tr>
<tr>
<td>50</td>
<td>338</td>
<td>1.580</td>
<td>294.6</td>
<td></td>
<td>0.356</td>
<td>27.6</td>
</tr>
<tr>
<td>60</td>
<td>352</td>
<td>1.570</td>
<td>307.7</td>
<td></td>
<td>0.351</td>
<td>31.3</td>
</tr>
<tr>
<td>70</td>
<td>382</td>
<td>1.550</td>
<td>336.1</td>
<td></td>
<td>0.383</td>
<td>36.7</td>
</tr>
<tr>
<td>80</td>
<td>425</td>
<td>1.500</td>
<td>380.1</td>
<td></td>
<td>0.433</td>
<td>35.8</td>
</tr>
<tr>
<td>90</td>
<td>448</td>
<td>1.520</td>
<td>398.1</td>
<td></td>
<td>0.454</td>
<td>35.5</td>
</tr>
</tbody>
</table>

General regression:  

\[
\text{MVF}>20 = 147.06* n - 24.414 \quad (r = 0.877) \\
\text{MVF20} = 140.82* n - 21.401 \\
\text{MVF10} = 116.77* n - 5.88 \\
\text{MVF7.5} = 122.76* n - 2.974 \\
\text{MVF5} = 146.198*n - 0.07
\]

N.B. The 7.5 cm curve was obtained by interpolating correction factors from between 5 cm and 10 cm curves.
3.2.4 Laboratory analysis

3.2.4.1 Preparation of $^{15}$N fertilizer preparation

$^{15}$N labelled calcium nitrate containing 2.0 atom percent excess $^{15}$N (i.e. about six times the natural abundance) was used. $^{15}$N was prepared by mixing, in aqueous solution, calcium nitrate containing 5 atom per cent $^{15}$N (BOC Prochem, London, UK) with a calculated quantity of the same salt but of normal isotopic composition, recrystallising, grinding to a powder and mixing again. Sub-samples were taken for isotopic analysis to confirm the actual enrichment achieved and its uniformity; results were satisfactory.

3.2.4.2 Determination of $^{15}$N content of $\text{NO}_3^-$ in the soil profile

The standard method for the determination of the $^{15}$N content of ammonium and nitrate in soil (Bremner, 1965) was modified by Smith et al. (1984) to allow its application to soil samples up to ca. 500 g in weight. This made it possible to obtain sufficient nitrogen for isotopic analysis even at the very low concentration of inorganic N found in the soil profile (root zone) towards the end of the growing season when most of the tracer had been taken up by the plants. A constant length of time was adopted by Smith et al. (1984) for the distillation stage, and they found that the incomplete recovery of ammonia from samples containing large amounts of nitrate had no effect on isotopic composition. Quantitative measurement of total ammonium and nitrate in soil extracts was carried out by continuous flow.

3.2.4.2.1 Extraction of $^{15}$NO$_3^-$-N from the soil

Soil cores were thawed and finely chopped with a knife, stones were removed and discarded and the soil was
weighed. Sub-samples (20 g) were placed in an oven at 105°C for moisture determination. The remainder of the soil was shaken for one hour at room temperature with two litres of 1M KCl solution. The soil/KCl suspensions were then filtered under suction, and the soil in filter funnels washed with 500 ml 1M KCl, which were then added to the corresponding extracts and mixed thoroughly. 20 ml aliquots were taken for colorimetric determination of NO$_3^-$-N and NH$_4^+$-N by continuous flow analysis as mentioned earlier. The volume of the remaining extract was concentrated to about 400 ml by evaporation under infrared lamps, prior to steam distillation of NH$_3$ for isotopic abundance measurements.

3.2.4.2.2 Steam distillation of soil extracts
The steam distillation was carried out with a modified version of the standard apparatus described by Bremner (1965), using a 1 litre round-bottomed flask to accommodate 400 ml of the concentrated soil extract and heating it with an electrical heating mantle. Magnesium oxide was added to liberate ammonia from NH$_4^+$. When the contents of the flask reached boiling point the mantle was switched off and steam was allowed to enter the flask. The distillate was collected in a flask containing 10 ml of 2 per cent boric acid/indicator solution. At the end of the distillation period (6 minutes), ethanol was added to the reaction flask and distillation resumed for an equal length of time to prevent any cross-contamination (memory effect), arising from successively distilling samples of high and low $^{15}$N content in the same apparatus.

A second receiving flask containing 10 ml of 2 per cent boric acid/indicator solution was placed under the condenser. The reaction flask was disconnected from the distillation unit, Devarda's alloy was added to reduce
\( \text{NO}_3^- \) to \( \text{NH}_4^+ \) and the flask was immediately reconnected. The distillation procedure was then repeated.

The contents of the first receiving flask were discarded because too little N was present as \( \text{NH}_4^+ \) to permit isotopic measurements. However, the quantities of \( \text{NO}_3^- \)-N present in soils fertilized with nitrate are generally much higher, and in these circumstances error in estimating of fertilizer-derived mineral nitrogen based on \( ^{15}_N \) determinations of nitrate fraction alone would not be seriously in error (Smith et al, 1984).

The contents of the second receiving flask were titrated with standard sulphuric acid in order to estimate the amount of \( \text{NO}_3^- \) from the second distillation. The neutralized distillate was then acidified with 0.35 ml of 0.5 M sulphuric acid and evaporated down to 2-3 ml for \( ^{15}_N \) measurement by mass spectrometry (determination done by Mr Robert S. Howard). Acidifying the distillate is absolutely necessary where complete loss of N can occur when \( (\text{NH}_4)_3\text{BO}_3 \) is taken to dryness. The method of evaporating the distillate should promote a steady evaporation without spattering, without risk of cross contamination or contamination from ambient ammonia.

3.2.4.2.3 Isotope-ratio analysis
Isotope-ratio analysis of sample N involves a three step procedure:

i) conversion of sample N to \( \text{NH}_4^+ \)-N by means mentioned above,

ii) oxidation of \( \text{NH}_4^+ \)-N to \( \text{N}_2 \), and

iii) determination of the isotopic composition of \( \text{N}_2 \).

\( ^{15}_N \) was determined in distillates from soil extracts by an automated system combining a Carlo Erba ANA 1400 N analyser and a VG Isogas 622 mass spectrometer. Sample N
was converted directly to $N_2$ by dry Dumas combustion (see section 3.2.4.2.2). After conversion of combined $N$ to $N_2$, the gas is introduced into the mass spectrometer via a 2 m-long stainless steel capillary tube for determination of its isotopic composition. In the mass spectrometer the $N_2$ molecules are ionized by exposure to a hot filament. The resultant molecular ions are then caused to travel through a magnetic field where the three molecular species of $N_2$: $^{14}N - ^{14}N$, $^{14}N - ^{15}N$ and $^{15}N - ^{15}N$ are separated. Care must be taken to minimize contamination by other charged particles having the same mass and charge as the $N_2$ molecules.

The percentage of $NO_3^- - N$ (or $NH_4^+ - N$) present which was derived from fertilizer (per cent NDFF) was calculated from the relationship:

$$\text{per cent NDFF} = \frac{N_S - N_O}{N_f - N_O} \times 100 \quad (3.4)$$

Where $N_S = \text{atom per cent } ^{15}N \text{ in } NO_3^- \text{ (or } NH_4^+) \text{ in extract of soil from fertilized microplot}$

$N_O = \text{atom per cent } ^{15}N \text{ in } NO_3^- \text{ (or } NH_4^+) \text{ in extract of soil from unfertilized control plot}$

$N_f = \text{atom per cent } ^{15}N \text{ in added fertilizer}$

Results were calculated assuming the soil bulk density in the ridge to be 1.1 g cm$^{-3}$, and 1.4 and 1.6 in the 0 - 20 and 20 - 40 cm depths below the ridge, respectively.

3.2.4.2 Plant total N and $^{15}N$ determinations

One plant was taken from each microplot in all replicates as well as from the control plots on three dates (14/6, 3/7 and 15/8/85) during the growing season and then treated as for the Castle Huntly samples for total N
analysis. The $^{15}$N plant content was determined using the same system as for the soil.

3.2.4.4 Determination of selected soil properties
Particle size distribution, bulk density and the moisture characteristic curve, as well as $\text{NO}_3^-\text{-N}$ and $\text{NH}_4^+\text{-N}$ content, were measured on soil samples using the procedures outlined earlier for the 1984 experiment.

3.2.5 Crop harvest
Potatoes were harvested on 2nd October from two separate rows 1.0 m long in each plot. The outside rows were discarded. The fresh weights of tubers were obtained so that absolute yields in kg ha$^{-1}$ would be calculated.

3.3 Laboratory Column Experiments
From the field experiment at Aberlady (which was on a non-cracking soil), results suggested that nitrate ions may be protected from leaching due to the presence of immobile water. It was decided therefore to carry out laboratory experiments under both saturated and unsaturated water flow conditions in undisturbed soil column in order to investigate the presence or absence of immobile water and to get information about the dispersion length in the soil. Under laboratory conditions, application of the irrigation solution can be closely controlled, and water spread evenly, and the soil water potential and flow rate from samples may be monitored easily. Large additions of nitrate and other tracers (chloride and bromide) were made in order to measure leaching.
3.3.1 Core removal and handling

Intact soil cores, 15 cm in diameter and 25 cm in depth, were removed from the Aberlady site early in autumn 1985 and 1986, respectively, by using a hydraulic sampling system (Figure 3.8 a,b,c and d), and used for further solute leaching studies under saturated and unsaturated water flow, respectively. Each soil core was labelled and sealed into a plastic bag, taking care not to compact the soil surface in any way. This procedure produced a relatively undisturbed soil core fitting tightly into the PVC cylinder. Smaller undisturbed soil samples were collected from around each soil core with a 7.5 cm diameter soil corer to a depth of 40 cm for texture, bulk density, gravimetric moisture content and for other physical soil properties determinations such as porosity and volumetric moisture content. The results obtained were used to estimate bulk density, porosity, initial moisture content and water filled porosity of the soil columns. The results indicated that the soil in the columns was at field capacity at the sampling dates in both years.

3.3.2 Sample preparation

In both experiments, the cores were stored at room temperature. To prepare for an experiment the base was cut level with the bottom of the cylinder by chipping away soil to give an unsmeared surface. The cores were then 25 cm high with a diameter of 15 to 15.5 cm and a volume of 4420 to 4720 cm$^3$. Any space between soil and cylinder was blocked with bentonite slurry distributed all over the core edges, after which the cylinder was reweighed. The sample was then positioned near or beneath the irrigator in saturated and unsaturated flow experiments, respectively.
Figure 3.8 - Core removal and handling from the Aberlady site for laboratory columns experiments.
Figure 3.8 - Core removal and handling from the Aberlady site for laboratory columns experiments
In the saturated flow experiment before an experimental run, the columns were saturated slowly from the base of the soil upwards by means of a small increment in the water head to avoid soil structure damage, using distilled water or 0.005M CaCl$_2$. In two cases gypsum was applied either to the surface or to the base of the soil column in order to restrict the flow rate. Filter paper was also used to restrict loss of sediment from columns but it tended to restrict flow, giving variable flow rates in some experiments. Residual nitrate was leached before an experimental run from all saturated soil columns.

In the unsaturated flow experiment, three tensiometers were installed horizontally through the sides of the cylinder. The tensiometers were located 4, 13 and 21 cm below the soil surface. They were connected to a mercury manometer by stiff polythene tubing. The tensiometers were sealed into the core within rubber bungs, and time was allowed for the tensiometers to equilibrate. Prior to an experimental run, sand was placed at the bottom of each core.

3.3.3 The irrigator

Prime considerations in constructing the irrigator were that it should be cheap, simple and capable of applying irrigation water evenly and maintaining a constant head. Mariotte bottle (Figure 3.9) and peristaltic pump (Figure 3.10) were used for saturated and unsaturated flow, respectively.

In the unsaturated flow experiment, a reservoir containing the irrigation solution of 0.005 M CaSO$_4$ was connected to the peristaltic pump so that irrigation solution could be
Figure 3.9 - Experimental set-up for saturated measurements
Figure 3.10 - Experimental set-up for unsaturated measurements
applied to the soil column with different application rates depending on the size of the delivery tube, and so that three soil columns could be irrigated simultaneously. Three application rates were used: 0.05, 0.27 and 1.12 cm h⁻¹, classified as low, medium and high flow rate respectively for chloride. One application rate was used in all experimental runs with bromide.

### 3.3.4 Tracer application

#### 3.3.4.1 Saturated flow experiment

A pulse of 100 cm³ of solution containing 2600 g m⁻³ of KNO₃ was applied to the soil surface and then was followed by distilled water or 0.005 M CaCl₂ solution applied at a constant head of approximately 10 cm. A summary of the treatment flow rates is given in Table 3.4.

Table 3.4 Summary of different NO₃⁻ saturated flow treatments (1985)

<table>
<thead>
<tr>
<th>Treatment</th>
<th>No. of cores</th>
<th>Q</th>
<th>θ_{iv}</th>
</tr>
</thead>
<tbody>
<tr>
<td>LNO₃</td>
<td>2</td>
<td>0.05 (0.00) *</td>
<td>0.47 (0.03)</td>
</tr>
<tr>
<td>NNO₃</td>
<td>2</td>
<td>0.51 (0.06)</td>
<td>0.49 (0.005)</td>
</tr>
<tr>
<td>HNO₃</td>
<td>2</td>
<td>3.60 (0.90)</td>
<td>0.46 (0.04)</td>
</tr>
</tbody>
</table>

Remarks
- A) Soil columns were initially saturated slowly by applying water from the bottom of each core.
- B) Residual NO₃⁻-N was leached before an experimental run.
- C) Gypsum crust at either soil surface or base, to restrict the inflow or the outflow producing LNO₃ treatment.

( )* Figures in brackets represent standard error (s.e).

Δ only the high rate
3.3.4.2 Unsaturated flow experiment

A pulse of 100 cm$^3$ of CaCl$_2$ solution containing 3400 - 3700 g Cl$^-$/m$^3$ was applied at the soil surface and this was treated as follows:

a. Followed immediately by 0.005 M CaSO$_4$ irrigation solution.

b. Irrigation solution applied after allowing a waiting period of approximately two months for chloride redistribution in the soil column (under the field moisture condition found at sampling). The moist condition was retained by covering the soil cores (Figure 3.11a).

c. Irrigation solution applied after a waiting period of approximately two months under evaporative conditions at room temperature. The long waiting period for evaporation was due to low room temperature (Figure 3.11b).

d. Irrigation applied immediately after tracer application and disappearance from the soil surface. This was applied after each first run of any other treatment had finished and effluent had ceased, after irrigation application for the first run was stopped. Then the core was weighed to determine the initial moisture content of the soil column for the next run.

A summary of the different Cl$^-$ treatments is given in Table 3.5.
b. Under moist conditions

Figure 3.11 - Storage of soil cores after addition of Cl⁻ tracer to allow equilibration (unsaturated flow experiment).

a. Under evaporative conditions
Table 3.5 Summary of different Cl\textsuperscript{−} treatments under unsaturated flow

<table>
<thead>
<tr>
<th>Treatment</th>
<th>No. of cores</th>
<th>$Q$ \textsuperscript{−1} cm\textsuperscript{3} cm\textsuperscript{−3}</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L\textsubscript{Cl}</td>
<td>2</td>
<td>0.07 (0.00)</td>
<td>0.24 (0.02)</td>
</tr>
<tr>
<td>M\textsubscript{Cl}</td>
<td>2</td>
<td>0.27 (0.00)</td>
<td>0.18 (0.00)</td>
</tr>
<tr>
<td>H\textsubscript{Cl}</td>
<td>1</td>
<td>1.10 (NA)</td>
<td>0.21 (NA)</td>
</tr>
<tr>
<td>B</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M\textsubscript{Cl}</td>
<td>2</td>
<td>0.29 (0.01)</td>
<td>0.17 (0.01)</td>
</tr>
<tr>
<td>H\textsubscript{Cl}</td>
<td>2</td>
<td>1.01 (0.05)</td>
<td>0.17 (0.00)</td>
</tr>
<tr>
<td>C</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>M\textsubscript{Cl}</td>
<td>2</td>
<td>0.25 (0.00)</td>
<td>0.23 (0.01)</td>
</tr>
<tr>
<td>H\textsubscript{Cl}</td>
<td>2</td>
<td>0.95 (0.00)</td>
<td>0.23 (0.01)</td>
</tr>
<tr>
<td>A\textsuperscript{+}</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>L\textsubscript{Cl}</td>
<td>2</td>
<td>0.08 (0.01)</td>
<td>0.37 (0.00)</td>
</tr>
<tr>
<td>M\textsubscript{Cl}</td>
<td>2</td>
<td>0.28 (0.00)</td>
<td>0.28 (0.03)</td>
</tr>
<tr>
<td>H\textsubscript{Cl}</td>
<td>3</td>
<td>1.12 (0.14)</td>
<td>0.34 (0.03)</td>
</tr>
</tbody>
</table>

(A) Figures in brackets represent standard error (s.e)

Bromide addition was not originally planned in this experiment, but results from the first experimental run with Cl\textsuperscript{−} showed a 30 - 70% excess, indicating that an additional source of Cl\textsuperscript{−} was present in the soil. Subsequent chemical analysis showed appreciable Cl\textsuperscript{−} in the
bentonite used as the core sealant. Therefore it was decided to use Br\textsuperscript{-} instead of Cl\textsuperscript{-} due to its very low concentration in soils.

Thus Br\textsuperscript{-} was added in the following procedure:

a. A pulse of 100 cm\textsuperscript{3} of CaBr\textsubscript{2} \cdot 2H\textsubscript{2}O containing 950 Br\textsuperscript{-} gm\textsuperscript{-}3 was added to the soil surface followed immediately by 0.005 M CaSO\textsubscript{4} irrigation solution to either initially dry or moist soil in the column.

b. A second experimental run was made by applying the same tracer and irrigation solution that was applied for the first run immediately following completion of the first run. A summary for the different Br\textsuperscript{-} treatments is given in Table 3.6.

Table 3.6 Summary of Br\textsuperscript{-} treatments under unsaturated flow

<table>
<thead>
<tr>
<th>Treatment</th>
<th>No of Cores</th>
<th>Q cmh\textsuperscript{-}1</th>
<th>(\theta_{iv}) cm\textsuperscript{-}3</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-HBr</td>
<td>2</td>
<td>1.06 (0.00)</td>
<td>0.16 (0.01)</td>
<td>(D)treatment: irrigation was applied immediately after tracer application. Soil columns allowed to dry first under evaporative conditions at room temperature.</td>
</tr>
<tr>
<td>A-HBr</td>
<td>2</td>
<td>0.85 (0.00)</td>
<td>0.24 (0.00)</td>
<td>(A)treatment: as with Cl\textsuperscript{-} tracer</td>
</tr>
<tr>
<td>A\textsuperscript{+}-HBr</td>
<td>4</td>
<td>0.94 (0.07)</td>
<td>0.36 (0.01)</td>
<td>(A\textsuperscript{+})treatment: as with Cl\textsuperscript{-} tracer</td>
</tr>
</tbody>
</table>

( ) Figures in brackets represent standard error (s.e)

3.3.5 Leachate collection and chemical analysis

Leachates from the columns were collected using automatic fraction collectors and the aliquots were kept in a
refrigerator until analysed. NO$_3^-$-N was determined as for the field experiment. Ion-selective electrodes were used for measurement of [Br$^-$] and [Cl$^-$]. Relative concentrations of $C_{ex}/C_{app}$ were plotted against $V_{ex}/V_0$ to get the breakthrough curves (BTCs) for the different treatments.

3.3.6 Determination of selected soil properties.

Soil columns were weighed at the start and at the end of each run to determine the initial and final moisture content of the soil column. A waiting period was included at the end of each run for drainage to cease, before the weight was taken. All the soil in the column was then dried at 105°C and calculations were made for bulk density, total porosity and pore volume and water filled porosity.

3.3.7 Determination of immobile water volume due to anion exclusion

The fraction of soil water from which the anions were excluded was obtained from a knowledge of the anion breakthrough curves and the total amount of water in the column. This was demonstrated by sieving and repacking soil from one column and measuring the breakthrough curve from the disturbed soil column (Figure 3.12). The column was leached exhaustively with distilled water before applying a pulse of 100 cm$^3$ KNO$_3$ solution, the peak position occurred at 0.93 pore volumes. When 0.1 M CaCl$_2$ was used for pre-treatment and leaching on the same column the peak occurred at 1.06 pore volume. This difference represented the volume of water which did not participate in flow due to anion exclusion (i.e. immobile water). The phenomenon occurs because of electrostatic repulsion; non specifically adsorbed anions such as NO$_3^-$, Cl$^-$, Br$^-$
Figure 3.12 - Breakthrough curves for disturbed soil column leaching experiment for two electrolyte concentrations for experimental measured NO$_3^-$ anion exclusion volume from a pulse of NO$_3^-$-N leached through disturbed soil column using distilled water and calcium chloride.
Figure 3.12 - Breakthrough curves for disturbed soil column leaching experiment for two electrolyte concentrations for experimental measured NO$_3^-$ anion exclusion volume from a pulse of NO$_3^-$-N leached through disturbed soil column using distilled water and calcium chloride.
are excluded from the area close to the soil surfaces. Thus the effective pore volume is less than the average water content of the soil during the process of transport.

3.3.8. Hydraulic conductivity determination

A simple measurement was made to determine the saturated hydraulic conductivity in the saturated flow experiment and $K_{sat}$ was calculated from the following equation:

$$K_{sat} = \frac{Q \cdot X}{A \cdot H}$$  \hspace{1cm} (3.5)
CHAPTER IV
WATER BALANCE IN FIELD EXPERIMENTS

4.1 Theory

Water needed by crops is obtained from the soil, to which water is added either naturally through rainfall or artificially through irrigation, or both. The amount of water held by soil in the range between the field capacity and the wilting point is generally taken as that available to plants. The water over and above the field capacity in deep, well drained soils often drains so rapidly that little of it can be taken up by plants. Under impeded drainage, poor aeration may reduce availability of water to plants and, if prolonged, the plants may wilt and die. As the available moisture range represents the water reservoir for the plants, its size determines to an appreciable degree the frequency of irrigation needed. The water requirement of crops is the quantity of water required by a crop in a given period of time for their normal growth under field conditions. It includes evapotranspiration and other economically unavoidable losses, and since the major part of the water required by the crop has to be obtained from the soil, the amount that a soil can retain in the root zone and the frequency of rewetting are very significant. The retained volume of water represents the balance between gains and losses of the water added to or lost from the soil under consideration.

The movement of water in the field can be characterized as a continuous cyclic, repetitive sequence of processes, without beginning or end (Hillel, 1980). The cycle begins with the entry of water into the soil by the process of infiltration, continues with a temporary storage of water in the soil, and ends with its removal.
from the soil by drainage, evaporation, or plant uptake. The water balance is merely a detailed statement of the law of conservation of matter, which states simply that matter can neither be created nor destroyed, but can only change from one state or location to another, since water is not normally decomposed, or produced in the soil. The water content of a soil profile of finite volume cannot increase without addition from outside, nor can it diminish unless transported to the atmosphere by evaporation or to deeper zones by drainage.

In the analysis of the water balance, rainfall, change in water storage and drainage below the root zone are estimated on the assumption that run off is zero over the period of examination. In periods of zero precipitation or irrigation, change in stored water is attributed to water use by plants. The water balance equation utilizes the principle that the change in water content of the soil is represented by differences between the water which has been added (by rainfall or irrigation) and the amount which has been lost (by evapotranspiration from the soil, crop and by drainage).

4.1.1 Water storage

In its simplest form, the water balance merely states that in a given volume of soil, the difference between the amount of water added, \( W_{in} \), and the amount of water withdrawn, \( W_{out} \), during a certain period is equal to the change in water content \( \Delta W \) during the same period.

\[
\Delta W = W_{in} - W_{out} \quad (4.1)
\]

When gains exceed losses, the water content change is positive; and conversely, when losses exceed gains, \( \Delta W \) is negative.
Of the water infiltrated, some evaporates directly from the soil surface, some is taken up by plants for growth or transpiration, some may drain downwards beyond the root zone, whereas the remainder accumulates within the root zone and adds to soil moisture storage.

The root zone water balance is expressed in integral form (Hillel, 1980):

\[
\text{change in storage} = (\text{gains}) - (\text{losses})
\]

\[
(AS + AV) = (R + I + C) - (P + D + E + T)
\]  

(4.2)

where $\Delta S$ is change in root zone soil moisture storage

$\Delta V$ is increment of water incorporated in the plants

$P$ is run-off

$C$ is upward capillary flow into the root zone

$R$ is rainfall

$D$ is downward movement drainage out of the root zone

$E$ is direct evaporation from the soil surface

$T$ is transpiration by plants.

$I$ is irrigation (if any)

All quantities are expressed in terms of volume of water per unit area (equivalent depth units) during the period considered. The amount of run off generally is small in agricultural fields and particularly in irrigated soils so that in this study $P$ is neglected.

The neutron meter was used to measure the water content as a function of depth down a profile at intervals during the experiments (Chapter III). From these results it was possible to derive a wide range of soil water variables which include change in soil water stored, storage capacity of the profile available water capacity and soil water deficit. Rainfall and irrigation were measured as indicated previously (Chapter III).
4.1.2 Change in stored soil water

The simplest measurement is the change in soil water stored in a given depth of soil. This is widely used in catchment hydrology and field water balance studies. The difference in volumetric water content between successive measurements is integrated over suitable intervals to a given depth of the profile to yield the change $S$ in the amount of water stored to that depth (Holmes 1960; Van Bavel et al., 1968 a,b; Bowman and King, 1965; Sartz, 1972), i.e. by solving

$$
\Delta S = \sum_{j=1}^{j=n} (\theta_{i+1,j} - \theta_{i,j}) (Z_{j+1} - Z_j) (4.3)
$$

where $\theta_{i,j}$ is the mean volumetric water content at time $i$ of zone $j$ at a depth from $Z_i$ to $Z_{j+1}$ and $n$ is the number of zones.

4.1.3 Estimation of evapotranspiration

During the growth season the largest composite term in the losses is generally the evapotranspiration (which is the potential evapotranspiration "designated ETp" representing the climatic demand for water) (Hillel, 1980). Potential evapotranspiration (ETp) from a well watered field depends on the energy supplied to the surface by solar radiation, which is a climatic characteristic of each location and varies little from year to year (Van Bavel and Hillel, 1976). However, it is often assumed that ETp depends entirely on the external climatic inputs and is independent of the transient properties of the field itself.
Actual evapotranspiration ($ET_a$) is a fraction of $ET_p$ depending on the degree and density of plant canopy coverage of the surface, as well as on moisture and root distribution. $ET_a$ from a well-watered stand of a close growing crop will generally approach $ET_p$ during the active growth stage but may be below it during the early growth stage, prior to full canopy coverage and again toward the end of the growing seasonal, as the mature plant begins to dry out (Hillel and Guron, 1973).

The actual evapotranspiration $ET_a$ is estimated using the following equation.

$$ET_{ai} = ET_{pi} [K_c K_s + K_w (0.9 - K_c)]$$

(4.4)

Where $ET_{pi}$ is the potential evapotranspiration of a short cut grass crop adequately supplied with water on day 1 (cm).

$K_c$ is a crop coefficient related to percent crop cover on day 1 as obtained from Table 4.1 corresponding to Fig. 4.1 (Parkes, 1987) and is assumed to develop linearly throughout the crop development state of growth. Initially, maximum and harvest crop coefficients are 0.20, 1.05 and 0.70, respectively.

$ET_{pi}$ is set to equal weekly $ET_p/7$.

$K_w$ is a coefficient set equal to 0.8, 0.5 and 0.3 for the first, second and third day, respectively, following rain or irrigation.

$K_s$ is a soil water stress factor and is set to equal unity when no significant soil moisture occurs. In this analysis it was assumed that no significant deficits occurred at any time during the summer. (Figure 4.2) (Parkes, 1987)
Figure 4.1 - Crop cover coefficient during crop growth stages (Parkes, 1987)

Figure 4.2 - Soil water stress factor (Parkes, 1987)
Potential evapotranspiration is estimated from temperature, vapour pressure, wind-run and sunshine hour data, using the Penman equation (1963).

The change in soil moisture storage can be written as follows, assuming change of plant water content to be relatively unimportant and since ETa is the actual evapotranspiration, by rewriting (4.2):

$$\Delta S_i = (P_i + I_i) - (D_i + ET_{ai})$$  \hspace{1cm} (4.5)

Table 4.1 Crop parameters (Parkes, 1987)

<table>
<thead>
<tr>
<th>Crop</th>
<th>Min rooting depth</th>
<th>Max rooting depth</th>
<th>Initial Kc</th>
<th>Max. Kc</th>
<th>Harvest Kc</th>
<th>Crop growth stage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potatoes</td>
<td>0.15</td>
<td>0.60</td>
<td>0.21</td>
<td>1.05</td>
<td>0.70</td>
<td>30</td>
</tr>
<tr>
<td>Cereals</td>
<td>0.15</td>
<td>0.76</td>
<td>0.23</td>
<td>1.05</td>
<td>0.30</td>
<td>15</td>
</tr>
<tr>
<td>Lettuce</td>
<td>0.08</td>
<td>0.40</td>
<td>0.21</td>
<td>0.95</td>
<td>0.85</td>
<td>20</td>
</tr>
<tr>
<td>Grass</td>
<td>0.92</td>
<td>0.92</td>
<td>0.25</td>
<td>1.00</td>
<td>1.00</td>
<td>1</td>
</tr>
<tr>
<td>Crucifers</td>
<td>0.08</td>
<td>0.45</td>
<td>0.21</td>
<td>0.95</td>
<td>0.85</td>
<td>20</td>
</tr>
<tr>
<td>Carrots</td>
<td>0.15</td>
<td>0.80</td>
<td>0.21</td>
<td>1.05</td>
<td>0.50</td>
<td>20</td>
</tr>
<tr>
<td>Raspberries</td>
<td>0.50</td>
<td>0.60</td>
<td>0.21</td>
<td>1.05</td>
<td>0.75</td>
<td>15</td>
</tr>
<tr>
<td>Peas</td>
<td>0.15</td>
<td>0.92</td>
<td>0.21</td>
<td>1.05</td>
<td>0.95</td>
<td>20</td>
</tr>
</tbody>
</table>

During the emergence and early growth stage of a row crop there is little plant material. Thus, evaporation from the soil surface dominates evapotranspiration and $K_c$ is small. As the plants grow and cover more of the soil, transpiration begins to dominate evapotranspiration and both evapotranspiration and $K_c$ increase.

In the early growth stages of row crops such as potatoes, where there is considerable exposed soil, irrigation or rainfall will wet the soil, and the crop coefficient will
increase abruptly. The value of $K_c$ does, however, decrease in just a few days as the soil dries. Because this increase is short-term, it is usually ignored and the values of $K_c$ that are used to calculate the actual evapotranspiration are those applied when the soil surface between rows is relatively dry, but there is adequate water in the root zone. Crop cover is assumed to develop linearly throughout the crop development stage of the growth.

4.1.4 Estimation of drainage

Another essential item of the field-water balance is the drainage out of the root zone. When rain or irrigation raises the soil water storage above the field capacity, then the excess storage capacity either drains immediately or represents run-off (Parkes, 1987). Since run-off loss is negligible in good management agricultural fields, if rainfall and irrigation (if any) are measured, $ET_a$ can be estimated from Equation (4.4), therefore by rearranging Equation (4.5):

$$D_i = (R_i + I_i) - (ET_a + \Delta S_i) \quad (4.6)$$

4.2 Experimental Results

4.2.1 Site A : Castle Huntly. Water balance sheet for the irrigated experiment (1984)

During the course of the experiment considerable drainage losses from the crop root zone were predicted, using the water balance equation. These drainage losses occurred despite the fact that the summer of 1984 was drier than the average, but losses were higher from the irrigated plots later in the season. The average annual rainfall for the site is 68.1 cm over a 30 year period (1941 to
1970), whereas the total rainfall during the experiment was only 10 cm. Cumulative rainfall, evapotranspiration, and drainage totals, as well as the crop cover coefficient and the change in water storage for each interval during the course of the experiment are given in Tables 4.2 and 4.3 for unirrigated and irrigated plots, respectively.

The appreciable drainage from all plots (54 to 64 percent of the total) during the period 2/4 to 5/7/84 is due to: A) periods of rainfall occurring in this period (6.5 cm), and the soil profile being at or above its field capacity moisture water content due to previous winter rainfall (30 cm); B) Zero or small plant uptake of water occurring because of the prolonged period prior to emergence (10/6/84) due to late planting, so that the soil surface was left bare for approximately 9 weeks. Thus water was only extracted from the top few centimetres of the soil profile.

Later in the season, during active vegetative growth (5/7 to 10/8/84) and during maturation towards the end of the experiments (10/8 to 22/8/84), a period of moderate rainfall occurred (3.5 cm), but no drainage was observed from unirrigated plots, possibly due to the water deficit resulting from increased plant uptake. Plants in these plots may have suffered from water stress during the month of August where rainfall was only 0.5 cm, unless they extracted water from below the root zone (sampling depth).

In irrigated plots, the drainage loss was only 17, 26 and 20 per cent from the standard, moderate and low nitrogen level treatments respectively, during active vegetative growth and maturation. This is probably due to increased plant uptake, as the crop water requirement increased during this period, provided that water availability to plants was not limiting. Thus $K_c$ increased and
The table below presents data for the 1994 experiment at Castle Henry. It illustrates water storage and drainage data for the unirrigated plots during the course of the experiment. The table covers evaporation, crop cover, andCoefficient change in soil water storage and due to upward water movement by capillarity due to evaporation, crop growth, and rainfall. Evapotranspiration is determined using a modified energy balance approach. The data is presented in a tabular format with columns for different periods and variables.
Table 4.3 Rainfall, irrigation, evapotranspiration, crop cover coefficient, change in soil water storage and drainage data for the irrigated plots during the course of the 1984 experiment at Castle Huntly.

<table>
<thead>
<tr>
<th>Interval</th>
<th>R (cm)</th>
<th>I (cm)</th>
<th>ETp (cm)</th>
<th>Kc</th>
<th>ETa (cm)</th>
<th>ΔS (cm)</th>
<th>D+ (cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>NL</td>
<td>NM</td>
<td>NS</td>
<td></td>
<td>NL</td>
<td>NM</td>
<td>NS</td>
</tr>
<tr>
<td>2/4 - 5/7</td>
<td>6.5</td>
<td>-</td>
<td>-</td>
<td>26.9</td>
<td>0.20</td>
<td>4.7</td>
<td>-2.2</td>
</tr>
<tr>
<td>5/7 - 11/7</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
<td>2.1</td>
<td>0.32</td>
<td>0.4</td>
<td>-0.3</td>
</tr>
<tr>
<td>11/7 - 25/7</td>
<td>1.0</td>
<td>4.3</td>
<td>4.3</td>
<td>4.2</td>
<td>4.7</td>
<td>0.56</td>
<td>2.1</td>
</tr>
<tr>
<td>25/7 - 1/8</td>
<td>2.0</td>
<td>2.2</td>
<td>2.9</td>
<td>3.3</td>
<td>2.3</td>
<td>0.68</td>
<td>1.6</td>
</tr>
<tr>
<td>1/8 - 3/8</td>
<td>0.1</td>
<td>1.4</td>
<td>1.5</td>
<td>1.5</td>
<td>0.8</td>
<td>0.74</td>
<td>0.6</td>
</tr>
<tr>
<td>3/8 - 10/8</td>
<td>0.2</td>
<td>-</td>
<td>-</td>
<td>1.1</td>
<td>0.86</td>
<td>1.1</td>
<td>-0.9</td>
</tr>
<tr>
<td>10/8 - 15/8</td>
<td>0.0</td>
<td>1.8</td>
<td>1.9</td>
<td>2.6</td>
<td>1.8</td>
<td>0.95</td>
<td>1.6</td>
</tr>
<tr>
<td>15/8 - 22/8</td>
<td>0.1</td>
<td>1.7</td>
<td>1.7</td>
<td>2.3</td>
<td>2.0</td>
<td>0.95</td>
<td>1.6</td>
</tr>
<tr>
<td>Entire Season</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2/4 - 22/8</td>
<td>10.0</td>
<td>11.4</td>
<td>12.3</td>
<td>13.9</td>
<td>41.7</td>
<td>-</td>
<td>13.7</td>
</tr>
</tbody>
</table>

* Calculated by solving water balance Equation (4.6)
* Upward water movement by capillarity due to evaporation, crop extraction of soil water below the sampling depth or due to experimental measurement error.
approached unity (ETa ETp 1.8 cm) as the crop approached maturity when full cover was reached (9/8/84). It can be concluded that plant uptake of water was a major factor in preventing drainage losses during this period.

Figure 4.3 shows that drainage losses from the unirrigated plots were negligible throughout the growing season because of increased plant uptake of water due to the season being drier than the average. The moderate rainfall which occurred did not bring up the soil moisture content to field capacity, and the soil water storage increments were used up by the plants. ETa generally was greater than the amount of precipitation during the entire season. Figure 4.4 shows the effect of rainfall and irrigation on the amount of water loss by drainage below the root zone. Generally, the greater the quantity applied by irrigation the higher were the drainage losses. Drainage losses were higher from the irrigated plots than the unirrigated. The loss of similar amounts of water by drainage from all plots during the early course of the experiment (3/4 to 11/7/84) was due to rainfall and not because of irrigation, which did not start until 13/7/84. This may indicate that the soil profile does not suffer from texture and structure heterogeneity (spatial variability) and hence water and solute may move uniformly within the crop root zone.

The reliability of these results may be subject to errors in estimating drainage losses from the water balance equation due to:
A) Occurrence of dense weeds on all plots for a prolonged period during the growing season up to 25/7/84
Figure 4.3 - Cumulative rainfall, actual evapotranspiration and drainage for unirrigated plots during the 1984 cropping season at Castle Huntly
Figure 4.4 - Cumulative rainfall, irrigation, actual evapotranspiration and drainage for irrigated plots during the 1984 cropping season at Castle Huntly
the number of weeds on irrigated and high N plots could be expected to be greater than on unirrigated and low N plots. This would result in under-estimating the actual evapotranspiration (ET\textsubscript{a}) consequently overestimation drainage losses. Weeds may also affect the crop cover coefficient, resulting in a higher K\textsubscript{c}.

B) Errors associated with the use of neutron probe for estimating the change in soil water storage (Chapter III).

C) The lack of replication in this study makes it impossible to estimate the variability in drainage.

4.2.2 Site B: Aberlady. Water balance sheet for \textsuperscript{15}N experiment (1985)

During the course of the experiment considerable drainage losses from the crop root zone were predicted from the water balance equation. Drainage losses were highest prior to emergence when plant uptake of water had not yet occurred, as well as during the early growth stages when plant uptake was relatively small. These drainage losses occurred because the summer of 1985 was wetter than the average. Average annual rainfall over a 30 year period (1941 to 1970) is 60.0 cm (see Chapter III), whereas the total rainfall during the experiment amounted to 47.1 cm. Cumulative rainfall, evapotranspiration and drainage totals as well as the crop cover coefficient and the change in water storage for each interval during the growing season are given in Table 4.4. The appreciable drainage during the period 2/4 to 3/7/85 was attributed to A) the low water holding capacity of the soil (θ\textsubscript{vfc} = 0.15 - 0.25 cm\textsuperscript{3}cm\textsuperscript{-3}); B) the soil profile being at or above field capacity moisture content during the early course of the experiment due to previous winter rainfall, C) late crop emergence, possibly because of the
<table>
<thead>
<tr>
<th>Interval</th>
<th>R</th>
<th>ET&lt;sub&gt;p&lt;/sub&gt;</th>
<th>K&lt;sub&gt;c&lt;/sub&gt;</th>
<th>ET&lt;sub&gt;a&lt;/sub&gt;</th>
<th>ΔS</th>
<th>D*</th>
</tr>
</thead>
<tbody>
<tr>
<td>3/4 -15/5</td>
<td>5.4</td>
<td>7.0</td>
<td>0.10</td>
<td>2.1</td>
<td>0.5 (110.0)</td>
<td>2.8</td>
</tr>
<tr>
<td>15/5-22/5</td>
<td>2.1</td>
<td>1.0</td>
<td>0.10</td>
<td>0.4</td>
<td>1.5 (9.8)</td>
<td>0.2</td>
</tr>
<tr>
<td>22/5-29/5</td>
<td>1.8</td>
<td>1.6</td>
<td>0.10</td>
<td>0.5</td>
<td>-0.7 (129.0)</td>
<td>2.0</td>
</tr>
<tr>
<td>29/5-5/6</td>
<td>0.0</td>
<td>2.4</td>
<td>0.10</td>
<td>0.2</td>
<td>-1.5 (7.8)</td>
<td>1.3</td>
</tr>
<tr>
<td>5/6 -12/6</td>
<td>1.9</td>
<td>1.4</td>
<td>0.20</td>
<td>0.5</td>
<td>0.7 (2.7)</td>
<td>0.7</td>
</tr>
<tr>
<td>12/6-19/6</td>
<td>1.7</td>
<td>1.7</td>
<td>0.20</td>
<td>0.5</td>
<td>-0.5 (16.1)</td>
<td>1.7</td>
</tr>
<tr>
<td>19/6-26/6</td>
<td>1.3</td>
<td>1.4</td>
<td>0.32</td>
<td>0.6</td>
<td>0.0 (82.45)</td>
<td>0.7</td>
</tr>
<tr>
<td>26/6-5/7</td>
<td>1.4</td>
<td>1.8</td>
<td>0.44</td>
<td>0.9</td>
<td>-1.8 (6.1)</td>
<td>2.3</td>
</tr>
<tr>
<td>5/7 -10/7</td>
<td>0.6</td>
<td>1.7</td>
<td>0.56</td>
<td>0.7</td>
<td>-0.4 (338.9)</td>
<td>0.3</td>
</tr>
<tr>
<td>10/7-17/7</td>
<td>2.4</td>
<td>1.9</td>
<td>0.68</td>
<td>1.1</td>
<td>2.2 (43.7)</td>
<td>-0.9</td>
</tr>
<tr>
<td>17/7-24/7</td>
<td>2.6</td>
<td>1.9</td>
<td>0.80</td>
<td>1.3</td>
<td>1.3 (43.1)</td>
<td>0.0</td>
</tr>
<tr>
<td>24/7-1/8</td>
<td>7.3</td>
<td>1.1</td>
<td>0.92</td>
<td>1.4</td>
<td>2.5 (29.9)</td>
<td>3.4</td>
</tr>
<tr>
<td>1/8 -9/8</td>
<td>0.7</td>
<td>1.8</td>
<td>1.05</td>
<td>1.8</td>
<td>-2.3 (12.1)</td>
<td>1.2</td>
</tr>
<tr>
<td>9/8 -16/8</td>
<td>3.8</td>
<td>1.8</td>
<td>1.00</td>
<td>1.4</td>
<td>3.0 (14.1)</td>
<td>-0.6</td>
</tr>
<tr>
<td>16/8-30/8</td>
<td>2.4</td>
<td>3.1</td>
<td>0.85</td>
<td>2.6</td>
<td>-3.0 (21.8)</td>
<td>2.8</td>
</tr>
<tr>
<td>30/8-6/9</td>
<td>2.0</td>
<td>1.2</td>
<td>0.80</td>
<td>0.9</td>
<td>0.9 (31.8)</td>
<td>0.2</td>
</tr>
<tr>
<td>6/9 -13/9</td>
<td>0.9</td>
<td>1.0</td>
<td>0.75</td>
<td>0.8</td>
<td>0.3 (275.7)</td>
<td>-0.2</td>
</tr>
<tr>
<td>13/9-18/9</td>
<td>0.3</td>
<td>1.5</td>
<td>0.70</td>
<td>0.7</td>
<td>-1.4 (55.4)</td>
<td>1.0</td>
</tr>
<tr>
<td>18/9-25/9</td>
<td>8.9</td>
<td>0.7</td>
<td>0.60</td>
<td>0.6</td>
<td>9.7 (494)</td>
<td>-1.4</td>
</tr>
<tr>
<td>Entire Season</td>
<td></td>
<td></td>
<td></td>
<td>19.0</td>
<td>11.0</td>
<td>20.6</td>
</tr>
</tbody>
</table>

* Mean of 9 samples; calculated by solving water balance Equation (4.6)
( ) Figures in brackets represent coefficient of variation (percent)
+ Upward water movement by capillarity due to rising in water table as a result of storm occurrence.
physiological age of the seed (Wurr DCE, 1978); and (D) because the soil temperatures were lower than average. Drainage losses during this period amounted to 67 to 85 percent of the total amount of rainfall (15.5 cm). The period of seedling emergence is characterized by high respiration rates and biochemical activity, thus it follows that the rate of seedling emergence is conditioned by the temperature regime and aeration status. The effect of temperature on seedling emergence is especially striking as has been shown by several workers (Glendenning, 1942; Willis et al, 1957). Furthermore, the surface zone of wet soil does not warm up readily in springtime, owing to greater thermal inertia and downward conduction and loss of latent heat by higher evaporation. Consequently germination and early seedling growth are retarded (Hillel, 1980).

Later, during the active vegetative growth stages (5/7 to 15/8/84), heavier rainfall occurred (17.0 cm), but the drainage loss was only 16 percent. This was probably due to increased plant uptake of water, because water availability was not limiting. $K_c$ increased and approached unity and $ET_a$ approximately equalled $ET_p$ as the crop approached maturity (1.85 cm vs 1.80 cm for $ET_a$ and $ET_p$ respectively when full cover was reached). The influence of plant cover on evapotranspiration has been recognized by most investigators and it is particularly important for row crops that start out from a bare soil and approach 100 per cent cover at maturity. Two principal factors associated with degree of crop cover can be expected to influence the evapotranspiration. The first is related to reflection. Reflection of light from bare soil, especially wet soil, is usually lower than that from a dense crop. The second factor is related to the relative ease with which water is evaporated from a bare soil compared with transpiration from a crop.
Evaporation from most bare soils decreases rapidly 1 or 2 days after rainfall or irrigation. The flow of water in the soil to the soil surface rapidly becomes less than the potential evaporation. Under the same conditions transpiration may not be limited as much as 2 weeks later (Hillel, 1980). In this experiment the soil water content was sufficient to maintain transpiration but evaporation from the soil to the same extent. As a result, transpiration was dominant over evaporation and increased as the percentage crop cover $K_c$ increased. The evapotranspiration was higher in this experiment because of the prolonged period during which the soil surface was wet (Tanner and Lemon, 1962). The extent and depth of rooting determines the volume of soil from which plants can extract water. Evapotranspiration is greater the more extensive and deep the rooting characteristic of the plant, provided soil water is limiting in the upper part of the soil profile. Viets (1962) stated that where fertilizers are needed and water is available deeper in the profile fertilization in general increases the extent and depth of rooting and thereby evapotranspiration, under semi-arid conditions. Rooting depth would be expected to have much less influence on evapotranspiration under humid conditions. Occasional rises in water table occurred during this period (10/7 to 17/7; 9/8 to 16/8 in Table 4.4) and were observed from the weekly neutron probe measurement of soil moisture content, because periods of heavier rainfall occurred and because the soil profile was at or above field capacity (Table 4.4). The 40 to 60 cm soil depth was within the capillary fringe of the water table, which remained occasionally within the rooting depth of the test crop. The water table may have contributed an additional reserve and restricted water movement below the root zone and hence may have partly reduced the drainage losses during this period. A rising water table may have an adverse effect on plant growth
through its effect of oxygen availability to roots ($O_2$ deficit) and excess of $CO_2$. Respiration is the first process to react to low $O_2$ or high $CO_2$ concentrations. Lack of oxygen stops the process of ion uptake very rapidly and continued anaerobic conditions lead to loss of ions from the root (Hopkins, 1956). This has a considerable implication for root growth in waterlogged soils, where the availability of $O_2$ may depend upon transport down the air filled spaces in the root itself (Luxmore et al., 1970). Other effects are on microbial activity. As the rate of decomposition of soil organic matter decreases under anaerobic conditions, the liberation of mineral $N$ also diminishes. The existing $NO_3$ in the soil may be reduced to $N_2O$ or $N_2$ gas which is then lost from the soil.

In this experiment, no observations were made of root growth, to see if waterlogging injury had occurred. However, there were no obvious signs of injury to the plant tops.

Later in the season (maturity to end of experiment) heavy rainfall continued. The largest amount of rainfall (8.85 cm) occurred during the final week of sampling out of a total during this period (16/8 to 25/9/84) of 14.3 cm. Inspite of the heavy rainfall, the drainage loss was only 16 per cent. Again, the likely explanation of the low drainage losses was the plant uptake and the rising water table, as mentioned earlier for the vegetative growth stages.

The most important factor affecting water transport through the soil profile is the homogeneity of soil texture and structure. This is shown in Figure 4.5. No significant differences in drainage losses were observed between fertilized and non-fertilized plots. This
Figure 4.5 - Cumulative rainfall, actual evapotranspiration and drainage for fertilized and unfertilized treatment during the 1985 cropping season at Aberlady
eased the study of water and solute movement through the soil profile. The figure also shows that appreciable amounts of rainfall had drained from both treatments early in the season; the amount of water lost by drainage represents the largest component of the water balance. The small occasional soil moisture deficits observed (neutron probe data) in the ridge had no effect on the crop at earlier growth stages because of the low demand for water by the crop. Late in the season, the small deficits also had no effect, due to deeper root penetration in the soil profile which remained at or above field capacity throughout the cropping season.

The above results can be briefly summarised as follows:

1. The largest water losses by drainage (85 per cent of the totals) were observed during the early part of the experiment when plant demand for water was minimal and the soil surface was mainly bare ($K_c$ was only 0.20) for a prolonged period of time due to late emergence. The heavy rainfall which occurred during this period (15.5 cm) and the low water holding capacity (0.20 cm$^3$ cm$^{-3}$) of the soil were also major factors producing these large losses.

2. As crop uptake of water increased, drainage losses decreased to 16 per cent indicating that crop removal of available water was a major factor in reducing drainage losses. Water uptake increased during active vegetative growth and during maturation due to increased transpiration as the crop grew and consequently $K_c$ increased. Similar losses were observed for the final growth period towards the end of the experiments.
Continuation of heavy rainfall caused occasional rises in the water table which restricted downward movement of a newly added water and hence drainage losses were reduced, but the rising water table also had an adverse effect on the plant growth through its effect on plant respiration and nutrient availability to the crop. Though the test crop (potatoes) is classified as a crop highly tolerant to high ground water level, quality of tubers was found to be influenced by the flood which occurred shortly before harvest, when soil surface was within the capillary fringe. Neutron probe data for this week (18/9 to 25/9/85) showed high soil water content (23.1 ± 6.0; 31.8 ± 11.4) in the top 5 and 10 cm of the soil profile, respectively. Mackerron and Jefferies (1985) found that when tubers were flooded for 120 hours under field conditions 60 to 69 per cent were rotted.
5.1 Introduction

Mass balance investigations are a natural approach in studying environmental aspects of the agricultural N cycle because they emphasize a basic principle that everything is interconnected in nature. The final N balance sheet is the product of many physical, chemical and biological processes, all interacting with the environment and each other over time. The main use of nitrogen balances has been in estimating the net N losses, or the unaccounted for N, in a given agricultural production system. To estimate accurately the net N losses and to ascribe this loss to a certain process, an account must be made of all of the other major N transformations. The term "N budget" is defined as the application of mass conservation principles so that N is conserved in the various transformations and biological processes of the system. Nitrogen budgets constructed for field and experimental plots have clearly shown that the major mechanisms by which N is removed from soils are crop uptake, leaching and gaseous losses. Erosion losses are usually small compared with the above outputs. The magnitude of leaching losses will vary depending on the soil NO$_3^-$-N content, water content, rooting depth, water addition and pattern of water movement. Nitrogen losses via denitrification also vary greatly depending on NO$_3^-$-N level, available carbon, temperature, and oxygen and moisture status.

In temperate arable soils, the three main loss processes mentioned above, i.e. crop uptake, leaching and denitrification are all important. Leaching losses must
be measured indirectly if drainage from a soil cannot be easily measured (sampled). A simple approach, which can be applied at any site and requires no instrumentation in the field, is to measure the total nitrate content of the soil profile before and after leaching is expected to occur, and regard any decrease as leaching. However, this method has important limitations because account must be taken of any crop uptake and of mineralization of organic N in soil or crop residues occurring between sampling times. If nitrate is transformed by immobilization or lost by denitrification, leaching will be overestimated, but when soil temperatures are low these processes should be minimal and an approximate estimate of leaching loss may be obtained.

An important component of soil N balances is the net mineralization of organic N. In most studies this has been estimated by growing a crop that receives no fertilizer N or organic amendments. This approach is useful as long as other inputs, such as precipitation and irrigation are measured and as long as losses through leaching and denitrification are minimal. If these requirements are met, the N uptake of control plots can be used to estimate N mineralization plus residual N, provided the crop assimilation capacity has not been exceeded. Soils differ widely in their ability to mobilize organic N, due to environmental effects such as moisture regime and temperature under different crop management and cropping systems. At very high moisture contents the rate of biological activity and decomposition decreases through lack of oxygen, and leaching losses of nitrate will make it less available to soil microorganisms. The majority of soil fungi and actinomycetes are aerobes as are many of the bacteria. Under anaerobic conditions, decomposition is dependent on anaerobic
bacteria, which are less efficient than aerobic organisms (Yoshida 1975; Campbell, 1978; Patrick, 1982).

There are two well-known methods of measuring nitrogen loss. The first is non-isotopic fertilizer experiments, in which several rates of nitrogen fertilizer are applied to a crop; these have commonly been used to deduce the efficiency with which fertilizer nitrogen is used. Such experiments give a useful indication of the extent to which nitrogen fertilizer is used by a crop, but give no information on the fate of the fertilizer nitrogen not taken up. The second is $^{15}$N labelled fertilizer experiments. The major benefit from using $^{15}$N is that the quantity of fertilizer derived N retained in soil can also be measured, therefore it is possible to calculate the overall quantity of fertilizer N retained in the crop, soil system and, by difference, the amount lost. Although the $^{15}$N balance method is invaluable in determining the quantity of fertilizer N lost from a system it gives no direct information on the cause of loss.

Nitrate leaching is often the most important channel of N loss from field soil in cultivated agricultural lands. Losses normally range from 2 to 100 kg ha$^{-1}$ a$^{-1}$ (Wild and Cameron, 1980a; Hauk and Tanji, 1982).

The $\text{NO}_3^-$ originates from inorganic fertilizer and from mineralization of soil organic matter, crop residues and animal residues. Ammonium from fertilizer and organic source undergoes nitrification, which is defined as the process whereby $\text{NH}_4^+$ is oxidized via $\text{NO}_2^-$ to $\text{NO}_3^-$. The reactions are mediated in soil by two small groups of chemoautotrophic bacteria. One group, the $\text{NH}_4^+$ oxidizers, initiates the process with the formation of $\text{NO}_2^-$, while the second group, the $\text{NO}_2^-$ oxidizers,
completes the process by converting $\text{NO}_2^-$ to $\text{NO}_3^-$ promptly as it is formed. In most agricultural soils this process is very fast. When a high fertilizer rate is used in combination with heavy irrigation or rainfall on light-textured soils, leaching losses of $\text{NO}_3^-$ can be significant.

In most arable and calcareous soils, the predominant form of mineralized N is $\text{NO}_3^-$, since under most conditions $\text{NH}_4^+$ is rapidly nitrified to $\text{NO}_3^-$ and this ion is therefore considered to be the major form of N used by most higher plants. In acid soils nitrification is often, although not always, inhibited (Ellenberg, 1977; Havill et al., 1974; Osborne and Whittington, 1981). This had led to the assumption that $\text{NH}_4^+$ rather than $\text{NO}_3^-$ is the predominant form of available N absorbed by plants in acid soils (Ingestad, 1970, 1971, 1973, 1976, 1979; Gingon and Rorison, 1972; Krajina et al., 1973; Wittshire, 1973; Havill et al., 1974). However, Jansson (1958) discussed the fate of $\text{NH}_4^+$ which reaches the soil by natural means i.e. dissolved in precipitation and by adsorption from the air (Egner, 1955), or artificially added as a fertilizer. No differentiation was made between these natural and artificial $\text{NH}_4^+$ sources. He pointed out that adding $\text{NH}_4^+$-N fertilizer to the soil will suddenly increase the $\text{NH}_4^+$ pool. Part of the added ions will arrive at adsorption points in which they immediately become fixed. This part may be considerable. When the extractable $\text{NH}_4^+$ pool has disappeared (via nitrification), part of the fixed $\text{NH}_4^+$ may be released and become nitrified.

The non-fixed, biologically available part of the added $\text{NH}_4^+$-N will be liable to the following processes, arranged in descending order of importance:
If the $\text{NH}_4^+$ addition is considerable, all three processes will begin and proceed simultaneously for a limited period of time, until the surplus is used up, and during this period the fertilizer nitrogen may be diluted by the mineralization outflow from the organic part of the nitrogen cycle. If immobilization demand is strong, the main part of the non-fixed $\text{NH}_4^+\text{-N}$ will be immobilized and only a small part will be available to the nitrifiers and the plants. In addition, when the $\text{NH}_4^+$ pool is used up, the accumulated $\text{NO}_3^-$ may be drawn into the immobilization process and plants will be unsuccessful in competing for it. On the other hand, if the immobilization demand is met before the $\text{NH}_4^+$ pool is emptied, the rest will be nitrified and become available to plants in the form of $\text{NO}_3^-$. 

Nitrogen budgets have been constructed for many different agricultural systems utilizing both conventional and $^{15}\text{N}$ tracer techniques (Allison 1966; Hauk, 1971, 1973; Zamyatina, 1971; Broadbent and Carlton, 1978; Keeney, 1982a; Legg and Meisinger, 1982). Since the final $\text{N}$ balance sheet is the product of many physical, chemical and biological processes interacting with one another over time, the fate of $\text{N}$ applied varies widely, depending on soils, crops, cropping systems, and environmental factors.

### 5.2 Nitrogen Balance Theory

In the absence of significant biological $\text{N}$ fixation, most transformations, gains and losses in soil $\text{N}$ involve mineral $\text{N}$ ($\text{NH}_4^+$ and $\text{NO}_3^-$ ions). Wild and Cameron (1980) therefore wrote an equation quantifying the $\text{N}$ balance for
a prescribed area and time interval in the form given in equation (5.1)

In a field experiment, several terms in equation (5.1) are difficult to measure accurately, so various assumptions have to be made to simplify the N balance (Legg and Meisinger, 1982).

\[
N_s(0)+N_p(0)+N_{min}(t)+N_R(t)=N_s(t)+N_p(t)+N_s(0)_L+N_{min}(t)_L+N_D(t)+N_r(t) \tag{5.1}
\]

where

- \(N_s(0)\) is the initial soil NO\(_3^-\)--N content, including NO\(_3^-\)--N fertilizer;
- \(N_p(0)\) is the NO\(_3^-\)--N originating from plant seed;
- \(N_{min}(t)\) is the net NO\(_3^-\)--N mineralized from soil organic nitrogen between time (0) and time (t);
- \(N_R(t)\) is the rainfall NO\(_3^-\)--N added to the soil profile;
- \(N_s(t)\) is the NO\(_3^-\)--N remaining in the effective root zone after time interval (t) has passed since fertilizer application;
- \(N_p(t)\) is the NO\(_3^-\)--N taken up by the test crop at time (t);
- \(N_s(0)_L\) is the NO\(_3^-\)--N lost by leaching due to excess rainfall and/or irrigation at time (t);
- \(N_{min}(t)_L\) is the NO\(_3^-\)--N originating from soil organic nitrogen losses by leaching at time (t);
- \(N_D(t)\) is the NO\(_3^-\)--N losses by denitrification;
- \(N_r(t)\) is the NO\(_3^-\)--N losses by runoff.

In both experiments, losses by denitrification or run-off and gains from rainfall and/or irrigation application were not measured and nitrification of NH\(_4^+\) was assumed to be fast. An error term (E) which includes the unmeasured
components may be introduced into Equation (5.1), which on rearrangement gives

\[ N_s(0)_L = [N_s(0) + N_p(0)] - [N_s(t) + N_p(t)] + [N_{\text{min}}(t) - N_{\text{min}}(t)_L] + E \]  

(5.2)

If the other inputs and outputs are known the equation can be used to calculate leaching loss of NO\textsubscript{3}\textsuperscript{−}-N by difference. This would be useful if the other inputs and outputs are easy to measure or to predict (Wild and Cameron, 1980 a), but the extensive literature on mineral N budgets in soil shows this is usually not so (Allison, 1955, 1966, 1973; Bartholomew and Clark, 1965; Veitz and Hageman, 1971, Bartholomew, 1972; Russell, 1973; Neilson and MacDonald, 1978). In this project Equation (5.2) was evaluated by using \textsuperscript{15}N tracer techniques and unfertilized plot treatments, and by estimating mineralization separately.

In both experiments (Castle Huntly and Aberlady), \( N_s(0)_L \) was also estimated separately, using Burns' leaching equation (Burns, 1976), but no allowance for plant uptake of N or for biological transformation was made.

5.2.1 \textsuperscript{15}N Mass balance sheet

By using nitrogen fertilizer labelled with \textsuperscript{15}N it is possible to measure the portion of fertilizer N recovered in a crop as well as the quantity remaining in the root zone, assuming that \textsuperscript{15}N does not take part in mineralization/immobilization reactions. Thus it is also possible to calculate the overall quantity of fertilizer N retained in the crop-soil system and hence, by difference, the amount lost by leaching and/or gaseous loss as ammonia
(volatilization) or dinitrogen and nitrous oxide (denitrification). Similarly, $^{15}N_{R}(t)$ and $^{15}N_{F}(t)$ are usually small under good field management conditions. Therefore Equation (5.2) can be written as follows:

$$^{15}N_{D}(t) = ^{15}N_{S}(0) + ^{15}N_{D}(0) - ^{15}N_{S}(t) - ^{15}N_{D}(t) - ^{15}N_{S}(0)_L + E (5.3)$$

where $^{15}N_{S}(0)_L$ is estimated separately from Burns' equation (Burns, 1976), and $E$ is an error term. The largest sources of error are often associated with the estimation of soil mass per unit volume, crop dry matter and the spatial variability of $N$ because many $N$ transformations are linked with water movement or soil water content.

The addition of labelled inorganic fertilizer $N$ to the soil will result in some immobilization of labelled $N$ and some mineralization of non-labelled native soil $N$. Applications of inorganic fertilizer $N$ have been reported to stimulate, depress, or have no effect on mineralization of native soil organic $N$ (Gadet and Soubies, 1965; Broadbent, 1970). An apparent increase in mineralization of native soil $N$ following addition of $^{15}N$ labelled fertilizer $N$ has been observed under laboratory, greenhouse, and field conditions (Legg and Stanford, 1967; Saphozhnikov et al, 1969; Broadbent and Nakashima, 1971; Westerman and Kurtz, 1973; Westerman and Tucker, 1974). The use of $^{15}N$-labelled fertilizer makes it possible to measure the $N$ uptake by plants from the fertilizer. The quantity of fertilizer-derived $N$ retained in the soil can also be measured. Thus it is possible to calculate the amounts of soil-derived $N$ taken up by the crop and that retained in the soil. Since leaching losses of nitrate can be estimated separately from Burns' leaching equation (5.5) by assuming similar quantities of residual nitrate are present in fertilized and unfertilized treatments at
the beginning of the experiment and that nitrification of
\( \text{NH}_4^+ \) to \( \text{NO}_3^- \) is fast, the term \( N_{\text{min}}(t) - N_{\text{min}}(t)_L \) can be
estimated by rearranging Equation (5.2):

\[
14N_{\text{min}}(t) - 14N_{\text{min}}(t)_L = 14N_S(t) + 14N_P(t) - 14N_S(0)
- 14N_P(0) + 14N_S(0)_L - E
\]

\[ (5.4) \]

5.2.2 Nitrate displacement from the crop root zone

The amount of nitrate displaced from the potential root
zone of the potato crop during the course of the
experiments was calculated. For the Castle Huntly
experiment, and the control plots (unfertilized) in the
Aberlady study, a simple chromatographic equation was
used, which assumes that nitrate is uniformly distributed
within the soil profile when leaching occurs (Burns,
1975). It was assumed that \( ^{15}N \)-labelled fertilizer in
the latter study was mixed only with the top 10 cm of the
soil in the ridge. The equation is:

\[
L = \frac{Ah}{50} \left( \frac{D}{D + \theta_{vf.c}} \right)^{h-\frac{1}{2}}w
\]

\[ (5.5) \]

where

- \( h \) is the effective rooting depth (cm);
- \( A \) is the amount of residual \( \text{NO}_3^- \)-N present in the
top 50 cm of the soil profile, and/or the
amount of \( \text{NO}_3^- \)-N added as fertilizer (kg ha\(^{-1} \));
- \( D \) is the accumulated drainage (cm);
- \( w \) is the soil depth to which \( \text{NO}_3^- \)-N is mixed (cm);
- \( \theta_{vf.c} \) is the volumetric moisture content of the soil
at field capacity (cm\(^3\) cm\(^{-3}\)).

For the Castle Huntly site, the volumetric moisture
content of the soil at field capacity (0.46 cm\(^3\) cm\(^{-3}\)) was
determined from the moisture characteristic curve, while
for the Aberlady experiment it was estimated from the neutron probe data of the moisture monitoring measurement (0.15-0.25 cm$^3$ cm$^{-3}$). An average of 0.20 cm$^3$ cm$^{-3}$ was taken for the Aberlady site. Drainage loss below the root zone was also estimated by solving the water balance equation.

5.2.3 Estimation of total NO$_3$-N losses by leaching from $^{15}$N microplots

The estimation of the total nitrate losses from the fertilized treatment was done by two different methods, which are:

1. The "sum" method, which simply states that the total nitrate losses ($T_{N_S}(0)_L$) from the fertilized treatment is the sum of estimated nitrate lost from fertilizer ($^{15}N_S(0)_L$) and that lost from soil-derived N ($^{14}N_S(0)_L$), which gives

$$T_{N_S}(0)_L = ^{15}N_S(0)_L + ^{14}N_S(0)_L$$  \hspace{1cm} (5.6)

The estimated nitrate loss from soil-derived N in the fertilized treatment, $^{14}N_S(0)_L$, was assumed to be equal to that lost from the control treatment. This follows from the assumption that, at the start of the experiment, there were equal amounts of residual nitrate -N present in the root zone of both fertilized and control treatments, and since similar water losses by drainage from both treatments were observed. Estimates of leaching of both fertilizer and soil-derived N were made by using Burns' equation (5.5).

2. The difference method, which comprises two separate steps:
A) Estimation of the net mineralization \( \left( N_{\text{min}}(t) - N_{\text{min}}(t)_L \right) \) in the fertilized treatment from Equation (5.4) using the estimated value of \( N_S(0)_L \) obtained from the control treatment as above.

B) Solution of Equation (5.2) to obtain the amount of total loss of nitrate by leaching.

The difference method has been used in Table 5.5 to obtain the total N balance sheet.

5.2.4 Estimation of residual \( \text{NO}_3^- - \text{N} \) \( (N_S(0)) \) at the start of the Aberlady experiment (1985)

Residual \( \text{NO}_3^- - \text{N} \) present in the root zone prior to fertilization and planting was not determined. Therefore it was estimated from the measured \( \text{NO}_3^- - \text{N} \) present in the root zone \( (N_S(t)) \) at the first sampling date, which was approximately at crop emergence. This was done as follows. Rearrangement of Equation (5.2) gives (in the absence of crop uptake):

\[
N_S(0) = N_S(t) - \left[ N_{\text{min}}(t) - N_{\text{min}}(t)_L \right] - N_S(0)_L \quad (5.7)
\]

Mineralization over the period from planting to first sampling state was estimated using the results of previous study of \( \text{NO}_3^- - \text{N} \) mineralization in the same soil (Elmes, 1985). The assumed temperature was 9.6°C. The leaching loss of mineralized \( \text{NO}_3^- - \text{N} \) \( (N_{\text{min}}(t)_L) \) was predicted using Burns' Equation (5.5) assuming uniform rain distribution and constant mineralization rate during three equal intervals of the period of interest. Residual leaching loss \( (N_S(0)_L) \) was also estimated using Equation (5.5). This gave a value of 80 kg ha\(^{-1}\) for \( N_S(0) \) at Aberlady.
5.3 Experimental Results

5.3.1 Site A : Castle Huntly. Nitrogen mass balance in the irrigated experiment

The reliability of the nitrogen mass balance results which are presented in this section should be treated with caution, because A) the lack of replication in this study makes it impossible to estimate the variability in nitrogen balance (Equation 5.2) components such as crop uptake of N, estimated NO$_3$-N losses by leaching and NO$_3$-N retained in the soil and hence the unaccounted for N component; B) the presence of dense weeds on all the experimental plots, for a prolonged period during the cropping season, may also have influenced the fate of N, through their removal of nitrogen and water from the crop root zone. However, the nitrogen balance in the Castle Huntly plots was influenced by two major climatic factors: the above-average temperature during the cropping season, and the fact that the season was drier than average. These two factors are important through their effects on nitrogen availability as well as on water availability. The rate of mineralization is generally highest at soil water contents near to field capacity. Nitrogen mineralization tends to be impeded in wet soils with moisture contents exceeding field capacity. At the dry end of the range, between a tension of 15 bars and air dryness, nitrogen mineralization continues to decline gradually. Bacterial activity is also sensitive to soil moisture, and most biological reactions are influenced by temperature, therefore it is consistent that mineralization is also affected in this experiment by these environmental factors. The existence of a moisture-temperature interaction indicates that these factors should not be considered independent.
The variability of the experimental site was a problem due to previous cropping, with small areas of heavily fertilized vegetables which had led to large variations in available nutrients. Field sampling for \( \text{NO}_3^- \)-N indicated that the site could be divided into plots with different available N levels, and this was used as a basis for different treatments (see Chapter III).

5.3.1.1 Nitrate losses by leaching from the crop root zone

Throughout the entire course of the experiment, negligible nitrate losses by leaching from the crop root zone were predicted from the unirrigated plots, using Burns' model (Equation 5.5). The estimated nitrate losses were minimal, because: A) the summer of 1984 was drier than the average (i.e. evapotranspiration exceeded rainfall) and nitrate was taken up by the crop; B) the water holding capacity of the soil was relatively high (0.46 \( \text{cm}^3 \text{ cm}^{-3} \)); C) removal of water by weeds from the crop root zone made it less available for drainage losses.

During the early part of the experiment (2/4 to 11/7/84) only a small fraction of the initial nitrate present in the root zone was lost by leaching. The predicted losses were 3, 6 and 2 per cent from low, moderate and standard N level plots, respectively (Table 5.1). Leaching losses occurred because the soil profile was at or near field capacity due to previous winter rainfall (30 cm), the soil was bare for a prolonged period of time due to late planting, and plant uptake of water and nitrate was relatively small so that most of the nitrate in the soil solution was readily available for leaching when periods of rainfall occurred (6.6 cm). The differences in the leaching losses were due to differences in the drainage losses of water among the plots which, though small, are indicative of spatial variability in water movement or
Table 5.1 Summary of N balance sheet and water budget for potato crop grown in unirrigated plots at Castle Huntly (1984)

<table>
<thead>
<tr>
<th>Plot No</th>
<th>Initial N Level</th>
<th>Date</th>
<th>( N_{s(0)+n_{p(0)}} )</th>
<th>( N_s(t) )</th>
<th>( (N_p(t) )</th>
<th>( N_{s(0)L} )</th>
<th>( N_{min(t)}-N_{min(t)} ) _L</th>
<th>E</th>
<th>D</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>NL</td>
<td>2/4/84</td>
<td>53.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+24.7</td>
<td>3.6</td>
<td>6.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>11/7/84</td>
<td>51.6</td>
<td>24.7</td>
<td>1.4</td>
<td>+28.1</td>
<td>3.6</td>
<td>6.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>*25/7/84</td>
<td>43.8</td>
<td>37.3</td>
<td>0.0</td>
<td>+67.5</td>
<td>3.6</td>
<td>6.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>22/8/84</td>
<td>43.9</td>
<td>76.6</td>
<td>0.0</td>
<td>-</td>
<td>3.6</td>
<td>6.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>NM</td>
<td>2/4/84</td>
<td>131.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>+35.6</td>
<td>4.6</td>
<td>6.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>11/7/84</td>
<td>68.2</td>
<td>19.8</td>
<td>7.4</td>
<td>-74.6</td>
<td>4.6</td>
<td>6.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>*25/7/84</td>
<td>40.6</td>
<td>15.8</td>
<td>0.0</td>
<td>-12.7</td>
<td>4.6</td>
<td>6.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>22/8/84</td>
<td>67.2</td>
<td>76.5</td>
<td>0.0</td>
<td>-</td>
<td>4.6</td>
<td>6.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1</td>
<td>NS</td>
<td>2/4/84</td>
<td>175.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-31.6</td>
<td>3.1</td>
<td>6.6</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>11/7/84</td>
<td>116.3</td>
<td>24.3</td>
<td>2.8</td>
<td>-40.4</td>
<td>3.1</td>
<td>6.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>*25/7/84</td>
<td>77.8</td>
<td>56.8</td>
<td>0.0</td>
<td>-25.0</td>
<td>3.1</td>
<td>6.6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>22/8/84</td>
<td>81.8</td>
<td>68.2</td>
<td>0.0</td>
<td>-</td>
<td>3.1</td>
<td>6.6</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*weeds removed
water content due to spatial variability in soil structure between the plots.

During the period 11/7 to 25/7/84, rainfall was only 1.0 cm. No further leaching losses were suggested by Burns' model, because such a small amount of rainfall did not bring the soil to its field capacity, and drainage losses did not occur. Crop and weed removal of water continued, utilizing the soil water from below the sampling depth, or water which was available through upward movement by capillarity.

Later in the season (25/7 to 22/8/84) during maturation (weeds having been removed from all plots at the start of this period), there was a much higher demand for water by the crop. The rainfall was 2.4 cm but no leaching losses were predicted, for the same reasons mentioned above.

Higher nitrate losses by leaching from the crop root zone of the irrigated plots were predicted (Table 5.2), due to higher drainage. The irrigation applied brought up the soil to its field capacity and irrigation plus rainfall exceeded the crop water requirement (i.e. evapotranspiration). Throughout the entire season, the predicted nitrate losses amounted to 17, 21 and 23 percent of the total initially present at the start of the experiment (2/4/84) from low, moderate and standard N level plots respectively. Reasons for these differences were as for the unirrigated plots.

During the early course of the experiment (2/4 to 11/7/84) when irrigation application was not yet started, a similar trend of nitrate losses was observed. Reasons for
Table 5.2 Summary of N balance sheet and water budget for potato crop grown in irrigated plots at Castle Huntly (1984)

<table>
<thead>
<tr>
<th>Plot No</th>
<th>Initial N Level</th>
<th>Date</th>
<th>$N_s(0)+N_p(0)$</th>
<th>$N_s(t)$</th>
<th>$(N_p(t)$</th>
<th>$N_s(0)_L$</th>
<th>$N_{min(t)}-N_{min(t)}_L$</th>
<th>E</th>
<th>D</th>
<th>I+R</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>NL</td>
<td>2/4/84</td>
<td>50.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>11/7/84</td>
<td>80.6</td>
<td>7.0</td>
<td>1.9</td>
<td>+39.5</td>
<td>4.0</td>
<td>6.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>*25/7/84</td>
<td>48.1</td>
<td>12.6</td>
<td>3.6</td>
<td>+14.3</td>
<td>5.0</td>
<td>10.9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>22/8/84</td>
<td>85.7</td>
<td>51.2</td>
<td>8.7</td>
<td>+95.6</td>
<td>7.7</td>
<td>21.4</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>6</td>
<td>NM</td>
<td>2/4/84</td>
<td>145.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>11/7/84</td>
<td>53.8</td>
<td>25.9</td>
<td>3.9</td>
<td>-61.4</td>
<td>3.6</td>
<td>6.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>*25/7/84</td>
<td>62.7</td>
<td>35.3</td>
<td>20.2</td>
<td>-26.8</td>
<td>6.8</td>
<td>10.9</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>22/8/84</td>
<td>61.1</td>
<td>153.0</td>
<td>31.1</td>
<td>+100.2</td>
<td>9.5</td>
<td>22.3</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>NS</td>
<td>2/4/84</td>
<td>163.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>11/7/84</td>
<td>51.8</td>
<td>14.5</td>
<td>0.0</td>
<td>-96.7</td>
<td>0.0</td>
<td>6.6</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>*25/7/84</td>
<td>40.2</td>
<td>25.9</td>
<td>5.8</td>
<td>-91.1</td>
<td>3.9</td>
<td>10.8</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td></td>
<td>22/8/84</td>
<td>35.0</td>
<td>44.8</td>
<td>41.6</td>
<td>-41.6</td>
<td>9.1</td>
<td>23.9</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

* weeds removed
minimal losses were as for un-irrigated plots. No leaching loss from the NS plot was suggested by Burns' model. This was attributed to a more dense weed to be in this plot due to higher nitrate availability. Spatial variability in water movement may have exerted an influence on the extent of the leaching losses.

Later in the season (11/7 to 25/7/84), 4.2 cm of irrigation water was applied to each plot to meet fully the soil moisture deficit developed; rainfall was 1.0 cm. Nitrate losses were 4, 11 and 4 per cent of the totals from low, moderate and standard N level plots, respectively. These losses occurred because no room was left for rain when irrigation was applied.

Late in the season (25/7 to 22/8/84) the estimated leaching losses were higher. Four irrigations were applied, the totals were 7.1, 8.0 and 9.3 cm for low, moderate and standard N level plots, respectively. Rainfall was 2.4 cm during this period. Generally, nitrate losses were the highest of any period throughout the entire season. This is because A) larger water movement due to irrigation and rainfall effect resulted in a higher drainage loss, B) weeds were removed from all plots at the start of this period, C) crop uptake of water decreased after full crop cover was reached (9/8/84).

The above results may be summarized as follows:

1. Large water movement and high NO$_3^-$ concentration are prerequisites for leaching to occur from the crop root zone.
2. Spring rainfall readily leached the nitrate from the bare soil, when the soil was near or at field capacity due to the previous winter rainfall.

3. Summer rainfall did not satisfy the evapotranspiration deficit and therefore leaching did not occur in un-irrigated plots.

4. Summer irrigation was used to satisfy the evapotranspiration deficit, but no room was left for retention of rainfall which resulted in excess water and therefore in leaching.

5. Removal of water by crop and weeds minimized the leaching losses.

6. The dry summer resulted in the accumulation of soil nitrate due to small water movement and poor crop uptake of nitrate.

7. Percentage leaching losses were variable for the same irrigation regime because spatial variability in water movement was large among the plots.

5.3.1.2 Crop uptake of nitrogen

Figure 5.1 shows N uptake by the crop in irrigated plots at different growth stages. The increments were small throughout the growing season possibly due to weed removal. In early growth stages N uptake was small in all plots because roots were mainly in the surface layer. The smallest uptake was from the low N level plot and the highest was from the moderate N level plot. Uptake from the standard N level plot was suppressed by the relatively more dense weeds present in the plot. Later in the season, during the active growth stages the uptake was poor and the increments were small in all plots. The
Figure 5.1 - Crop uptake of N at different growth stages in the irrigated plots during the 1984 cropping season at Castle Huntly
possible reasons for this are: A) leaching due to irrigation, although Burns' model suggested that leaching was very small; B) immobilization of N by soil biomass, although net mineralization occurred in NL plot; C) weed removal of N. It seems the most likely effect was due to weed removal of N. This was verified later in the growing season (25/7-22/8/84) after weeds had been removed from the plots. Crop uptake of N was increased in all plots and the highest uptake was from the NM plot (118 kg ha⁻¹) because soil derived N was not removed by weeds during this stage. N uptake also increased sharply in the NL plot.

A similar trend was observed in unirrigated plots. This can be seen in Figure 5.2. The crop uptake of N was higher from unirrigated plots than irrigated plots particularly in the NL and NS treatments possibly because A) higher amounts of N were removed by a more dense weed population in the irrigated plots. B) leaching also occurred from the irrigated plots during the late period of growth (25/7 to 22/8/84); or C) NO₃⁻ in the lower depths of the rooting zone was the source of N for the crop during the above mentioned period when the surface soil dried out in the unirrigated plots.

5.3.1.3 Nitrogen mass balance sheet for unirrigated and irrigated plots
Results are summarized in Tables 5.1 and 5.2 for unirrigated and irrigated plots, respectively. Unaccounted for N was estimated from nitrogen balance Equation (5.2) by difference, and included immobilization of mineral N by soil biomass, N removal by dense weeds, mineralization of soil organic N, denitrification and accumulated errors. When the difference is negative, this may be because net immobilization occurs, whereas a positive difference may be due to net mineralization, if
Figure 5.2 - Crop uptake of N at different growth stages in the unirrigated plots during the 1984 cropping season at Castle Huntly.
other components of unaccounted for N are small. The main points to be noted from these results are:

1. Unaccounted for N was negative in the high N level plots, irrespective of irrigation treatment, throughout the entire course of the experiment, but it was higher in the irrigated treatment, probably due to the denser weed cover present.

2. Unaccounted for N was negative in the moderate N level plots, irrespective of irrigation treatment, for most of the growing season, but it was more negative in the unirrigated plot because poorer plant uptake of N occurred.

3. Unaccounted for N was positive in the moderate N level plots, irrespective of irrigation treatment, during the final part of the experiment, due to weed removal from both plots, but it was higher with irrigated plots because irrigation stimulated mineralization.

4. Unaccounted for N was positive in the low N level plots, irrespective of irrigation treatment, throughout the entire season, but it was higher in the irrigated plot due to higher mineralization.

5. Crop uptake of N generally was poor in unirrigated plots due to the dry summer but it was poorer in irrigated plots due to denser weeds present on these plots.
5.3.2 Site B: Aberlady. Nitrogen mass balance for $^{15}\text{N}$ experiment

During the summer of 1985, a field experiment was conducted at the Aberlady site using $^{15}\text{N}$-labelled calcium nitrate fertilizer on micro-plots. The purpose was to compile a $^{15}\text{N}$ mass balance sheet for the experimental micro-plots, and to investigate the major mechanisms by which $^{15}\text{N}$ was transformed or removed from the soil. In addition, another budget sheet was compiled for the controls, to investigate gains to the soil N-pool, or losses by which residual and soil-derived N were removed from the crop root zone.

Crop uptake of $^{15}\text{N}$, as well as that retained in the soil, was measured on three occasions during the growing season. Water loss by drainage was predicted from the components of the water balance equation (see Chapter IV); and labelled nitrate loss by leaching was estimated separately from Burns' leaching equation (5.5). Some measurements (prediction of water loss and nitrate losses by leaching) were also performed on the controls.

5.3.2.1 Nitrate losses by leaching from the crop root zone

Losses of nitrate by leaching below the crop root zone from fertilized and control treatments occurred because the season was wetter than the average, the soil water holding capacity was low, and the soil profile was at or above its field capacity throughout the course of the experiment.

5.3.2.1.1 $^{15}\text{NO}_3^-\text{-N}$ losses by leaching from microplots

Cumulative $^{15}\text{NO}_3^-\text{-N}$ losses by leaching for each interval are given in Table 5.3. The estimated loss of labelled nitrate by leaching amounted to 29 per cent of the total amount of $^{15}\text{NO}_3^-\text{-N}$ labelled fertilizer applied (160 kg ha$^{-1}$).
Table 5.3  Labeled N balance sheet and water budget for potato crop grown in 15N fertilized micro-plots at Aberlady (1985)

<table>
<thead>
<tr>
<th>Date</th>
<th>15Ns(0)+15Np(0)</th>
<th>15Ns(t)*</th>
<th>15Np(t)**</th>
<th>15Ns(0)_L+</th>
<th>E</th>
<th>D</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>3/4/85</td>
<td>160.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14/6/85</td>
<td>89.1</td>
<td>4.7</td>
<td>46.9</td>
<td>-19.3</td>
<td>7.3</td>
<td></td>
<td>12.3</td>
</tr>
<tr>
<td>3/7/85</td>
<td>50.1</td>
<td>31.8</td>
<td>71.4</td>
<td>-6.7</td>
<td>11.1</td>
<td></td>
<td>15.5</td>
</tr>
<tr>
<td>15/8/85</td>
<td>6.3</td>
<td>82.5</td>
<td>84.8</td>
<td>+13.6</td>
<td>14.3</td>
<td></td>
<td>32.8</td>
</tr>
</tbody>
</table>

* Geometric mean  
** Arithmetic mean  
+ Estimated from Equation (5.5)  
( ) Figures in brackets represent standard error (s.e)  

a Geometric mean + l.s.e  
b Geometric mean - l.s.e

Sample size = 9
during the early course of the experiment, up to emergence (3/4 to 14/6/85).

This large loss occurred because of the heavy rainfall (12.3 cm), and little plant uptake of $^{15}\text{NO}_3^{-}$-N and water due to late emergence.

Later, during the initial growth stage (14/6 to 3/7/85), there was less rainfall (3.2 cm), and estimated labelled nitrate loss by leaching was 16 per cent of the total amount applied. This was due to increased plant uptake of $^{15}\text{NO}_3^{-}$-N and water which minimized water loss by drainage and hence reduced nitrate loss by leaching. During the active vegetative growth (3/7 to 15/8/85), leaching loss of nitrate was only 8 per cent despite heavy rainfall (17.0 cm) during this period. This is because crop demand for water and nitrogen was large, so plant uptake of labelled nitrate made it less available for leaching. Moreover, plant uptake of water reduced its loss by drainage and hence labelled nitrate loss by leaching was reduced. Occasional rises in the water table caused by occasional rain storms may also have reduced water loss by drainage through its restriction on water movement below the root zone, and consequently reduced nitrate loss by leaching. During maturation (15/8 to 25/9/85) the estimated loss of labelled nitrate not shown (see Table 4.4) was lowest (8 per cent). This is because the crop requirement of $\text{NO}_3^{-}$-N and water remained relatively high during this period, and because of occasional rises in the water table caused by very heavy rain storm (8.9 cm) during the final week of the experiment (18/9 to 25/9/85).

Burns' equation predicted that 53 per cent of the fertilizer derived nitrogen (NDFF) was lost by leaching.
below the crop root zone during the entire course of the experiment.

5.3.2.1.2 \(\text{NO}_3^-\)N losses by leaching from control plots

Predicted nitrate loss by leaching was also large from the control plots (Table 5.4) and the relative estimated loss was higher than the loss from the fertilized plots during the early course of the experiment (3/4 to 14/6/85) (51 vs 29 per cent of the total). This is due to the assumption that the residual \(\text{NO}_3^-\)N in the soil profile was mixed uniformly with the soil to a greater depth (50 cm) than the mixing depth for the fertilizer (10 cm). The estimated loss during this period was 51 per cent of the estimated total amount of \(\text{NO}_3^-\)N present in the crop root zone at the start of the experiment (80 kg ha\(^{-1}\)). The reasons which led to this large predicted loss were given above with the \(^{15}\text{N}\) results. Contributing to the large loss of nitrate is the fact that roots had not yet reached their maximum depth (50 cm), so plant uptake of N and water was only from part of the zone initially containing the nitrate.

During the early stages of growth, 14 per cent of the residual \(\text{NO}_3^-\)N was predicted to be lost by leaching. As with the \(^{15}\text{N}\) results, the increased plant uptake of N and water during this period and the occasional rises in the water table were major factors in protecting nitrate from leaching loss. During the active growth stages (3/7 to 15/8/85) and maturation (15/8 to 25/9/85) the nitrate leaching losses were only 8 and 0 per cent, respectively. The reasons leading to this loss were given above in relation to the \(^{15}\text{N}\) micro-plots.
Table 5.4 Residual N balance sheet and water budget for potato crop grown in unfertilized plots at Aberlady (1985)

<table>
<thead>
<tr>
<th>Date</th>
<th>(N_s(0)+N_p(0))</th>
<th>(N_s(t)^*)</th>
<th>(N_p(t)^{**})</th>
<th>(N_s(0)_L^+)</th>
<th>(N_{\min}(t)-N_{\min}(t)_L^+)</th>
<th>D</th>
<th>R</th>
</tr>
</thead>
<tbody>
<tr>
<td>3/4/85</td>
<td>80.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>14/6/85</td>
<td>61.7</td>
<td>75.0(^a)</td>
<td>11.0 (0.42)</td>
<td>40.7</td>
<td>+33.4</td>
<td>7.3</td>
<td>12.3</td>
</tr>
<tr>
<td>3/7/85</td>
<td>46.8</td>
<td>56.2</td>
<td>59.8 (5.9)</td>
<td>51.1</td>
<td>+77.7</td>
<td>11.1</td>
<td>15.5</td>
</tr>
<tr>
<td>15/8/85</td>
<td>17.4</td>
<td>22.4</td>
<td>102.5 (16.4)</td>
<td>57.2</td>
<td>+97.1</td>
<td>14.3</td>
<td>32.8</td>
</tr>
</tbody>
</table>

* Geometric mean
** Arithmetic mean
+ Estimated from Equation (5.5)
( ) Figures in brackets represent standard errors (s.e)

a Geometric mean + 1 s.e
b Geometric mean - 1 s.e

Sample size = 4
Burns' leaching equation estimated that 72 per cent of the residual NO$_3^-$-N was lost by leaching below the crop root zone of the unfertilized plots during the entire course of the experiment.

The assumption of zero crop uptake, implicit in applying Burns' leaching equation, is more accurate during the early course of the experiment and during the early growth stages when plant uptake of NO$_3^-$-N is relatively small, and microbial activity is minimal. However, when microbial activity causing mineralization, nitrification or denitrification and plant uptake of NO$_3^-$-N occur, all of these processes can cause changes in the observed nitrate distribution.

5.3.2.2 Crop uptake of soil and fertilizer-derived nitrogen

Before losses of fertilizer N can be calculated, the amount taken up by the crop must be known. Unambiguous measurements of uptake by plants are only obtained in experiments where the fertilizer is 'labelled' by isotope and its uptake is measured. Relatively few such experiments have been done, most estimates of uptake being based on experiments with unlabelled fertilizer which may be subject to considerable error. The use of $^{15}$N-labelled fertilizer, and the application of the principle of isotope dilution, make it possible to assess the relative contributions to N uptake by plants from the soil N pool and the fertilizer N, respectively. In most arable soils, the predominant form of mineralized N is NO$_3^-$ and this ion is generally considered to be the major form of N used by most higher plants (Ellenburgh, 1977; Havel et al, 1974; Osborne and Whittington, 1981).
Table 5.5 Total N balance sheet for potato crop grown in $^{15}$N fertilized micro-plots at Aberlady (1985)

<table>
<thead>
<tr>
<th>Date</th>
<th>$T_{NS}(0)$</th>
<th>$^{14}N_{NS}(0)$</th>
<th>$T_{NS}(t)*$</th>
<th>$^{14}N_{NS}(t)*$</th>
<th>$T_{NP}(t)**$</th>
<th>$^{14}N_{NP}(t)**$</th>
<th>$T_{NS}(0)_L$</th>
<th>$N_{min(t)}-N_{min(t)}_L$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3/4/85</td>
<td>240.0</td>
<td>80.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>14/6/85</td>
<td>165.9</td>
<td>148.9</td>
<td>148.9</td>
<td>76.8</td>
<td>107.9</td>
<td>54.0</td>
<td>14.8 (1.8)</td>
<td>10.1 (2.1)</td>
</tr>
<tr>
<td>3/7/85</td>
<td>125.0</td>
<td>109.6</td>
<td>144.5</td>
<td>74.9</td>
<td>120.2</td>
<td>46.6</td>
<td>65.8 (10.6)</td>
<td>35.0 (12.9)</td>
</tr>
<tr>
<td>15/8/85</td>
<td>49.0</td>
<td>33.3</td>
<td>71.9</td>
<td>42.7</td>
<td>96.4</td>
<td>18.9</td>
<td>152.5 (16.9)</td>
<td>70.0 (19.5)</td>
</tr>
</tbody>
</table>

* Geometric mean
** Arithmetic mean
+ Estimated by difference from Equation (5.2)
$\times$ Estimated by difference from Equation (5.4)
( ) Figures in brackets represent standard error (s.e)

a Geometric mean + 1 s.e
b Geometric mean - 1 s.e
Table 5.5  Total N balance sheet for potato crop grown in $^{15}$N fertilized micro-plots at Aberlady (1985)

<table>
<thead>
<tr>
<th>Date</th>
<th>$T_{N}(0)$</th>
<th>$^{14}T_{N}(0)$</th>
<th>$T_{N}(t)$</th>
<th>$^{14}T_{N}(t)$</th>
<th>$T_{N}(t)$</th>
<th>$^{14}T_{N}(t)$</th>
<th>$T_{N}(t)$</th>
<th>$^{14}T_{N}(t)$</th>
<th>$T_{N}(t)$</th>
<th>$^{14}T_{N}(t)$</th>
<th>$T_{N}(t)$</th>
<th>$^{14}T_{N}(t)$</th>
<th>$T_{N}(t)$</th>
<th>$^{14}T_{N}(t)$</th>
<th>$N_{min}(t)-N_{min}(t)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3/4/85</td>
<td>240.0</td>
<td>80.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>14/6/85</td>
<td>165.9</td>
<td>134.9</td>
<td>84.8</td>
<td>107.9</td>
<td>14.8</td>
<td>10.1</td>
<td>106.9</td>
<td>47.6</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3/7/85</td>
<td>125.0</td>
<td>144.5</td>
<td>74.9</td>
<td>120.2</td>
<td>65.8</td>
<td>35.0</td>
<td>129.2</td>
<td>81.0</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15/8/85</td>
<td>49.0</td>
<td>71.9</td>
<td>42.7</td>
<td>96.4</td>
<td>152.5</td>
<td>70.0</td>
<td>128.4</td>
<td>84.9</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Geometric mean  
** Arithmetic mean  
+ Estimated by difference from Equation (5.2)  
x Estimated by difference from Equation (5.4)  
( ) Figures in brackets represent standard error (s.e)

a Geometric mean + 1 s.e  
b Geometric mean - 1 s.e
Table 5.5 shows the uptake of soil and fertilizer-derived N on the fertilized micro-plots. The amounts of NO$_3^-$-N taken up by the crop plants either from soil-derived N or fertilizer N were small at emergence but were higher from soil-derived N. Crop uptake increased with time during the growing season irrespective of the source of available N. Similar amounts of soil- and fertilizer-derived N were taken up during the early growth stages (14/6 to 3/7/85), while greater N uptake by the crop was from fertilizer N later in the season (3/7 to 15/8/85), at which the highest crop uptake of N occurred, due to higher crop demand for N. In general, Table 5.5 shows that similar amounts of soil-derived N and fertilizer N were taken up almost equally by the crop throughout the entire season.

A comparison between the means for the fertilized plots (Table 5.5), and the unfertilized plots (Table 5.4) shows a greater uptake of soil-derived N on the unfertilized plots, except at emergence, where similar amounts of soil- and fertilizer-derived N were taken up by the crop. In the unfertilized plots the highest N uptake was during the early growth stages, while it was during the later stages with the fertilized plots. Generally it seems that the plants in the unfertilized plots used the soil-derived N more efficiently, and fertilization with N had depressed soil-derived N uptake by the crop.

5.3.2.3 $^{15}$NO$_3^-$-N Mass balance sheet
The recovery of $^{15}$N from the soil and crop in the four micro-plots used in the potato field at Aberlady is given in Table 5.3. The values for the soil were very variable, thus a geometric mean was taken of the 9 results. Values for crop uptake were more consistent, so an arithmetic mean was used.
Nitrate leaching losses were estimated by Burns equation (5.5). The resulting deficit in $^{15}$N balance may be attributed entirely to denitrification (not measured) because:

a) $\text{NO}_3^-$-N is not readily taken up by the soil microorganisms (biomass), $\text{NH}_4^+$-N being the preferred form of nitrogen (Legg and Stanford, 1967).

B) Under wet conditions in spring after fertilizer application, the most likely loss is due to denitrification. The loss has been reported to be large and rapid (Legg and Meisinger, 1982). Rates of loss up to 3 kg ha$^{-1}$ day$^{-1}$ on a sandy soil near Aberdeen were observed for the same period (Batey and Killham, 1986).

Denitrification losses from soil-plant systems have usually been obtained by the difference between N additions and recoveries, where leaching losses were measured or controlled. In this study, leaching losses were neither measured nor controlled, but they were estimated from Burns' model. Therefore, the unaccounted error term which represents denitrification contains an error which also includes errors in measurement and estimation of the other components of the $^{15}$N mass balance; thus it is a poor way of quantitatively estimating denitrification.

On the first sampling date (14/6/85), 41 per cent of the initial $^{15}$N application was not recovered, of which 29 per cent was attributed to leaching and the rest (12 per cent) to denitrification. Crop uptake was only 3 per cent during this period. Therefore the predicted leaching loss was the major factor which influenced the fate of the N, the reasons for this were given earlier.
Later in the season, at the second sampling date 3/7/85, 20 per cent was recovered in the crop, 31 per cent was retained in the soil, and 45 per cent was estimated to be lost by leaching. The amount not accounted for was smaller than in the first period. These are cumulative losses so that plant uptake increased from 3 per cent to 20 per cent, while loss by leaching was 16 per cent. Denitrification loss during this period probably was minimal due to increased plant uptake of N and water.

During maturation, at the third sampling date (15/8/85), recovery in the crop was 52 per cent, predicted loss by leaching was 53 per cent, only 4 per cent was retained in the soil and 9 per cent was unaccounted for.

These results suggest that crop uptake of NO$_3^-$-N and nitrate leaching losses were the major factors influencing the fate of the $^{15}$N applied. Losses of nitrate from the root zone were large for the entire season, because of the high mobility of NO$_3^-$-N, its susceptibility to denitrification, and its lower assimilation into the soil organic N pool (Jansson, 1963; Riga et al, 1980).

5.3.2.4 Mass balance sheet for soil-derived nitrogen

In this experiment residual NO$_3^-$-N present in the root zone prior to fertilization and planting was estimated using Equation (5.2) and considered to correspond to the difference between the soil nitrate content at the first sampling date (14/6/85) and the net amounts of nitrate mineralized and the residual nitrate fraction lost by leaching during the early part of the experiment (3/4 to 14/6/85). It was assumed that all of the NO$_3^-$-N was available to the spring crop, and was distributed uniformly within the crop rooting depth. The amount of residual NO$_3^-$-N at the start of the experiment which
remains available to the crop was estimated to be 80 kg ha\(^{-1}\). Results are given in Table 5.4.

Leaching loss of nitrate was appreciable and had a major influence on the fate of NO\(_3^-\)-N, during the early part of the experiment, the reasons were as for the \(^{15}\)N results mentioned earlier in this chapter. The predicted mineralization was lower than average due to the cold spring (see Chapter III) and its rate was also a major factor that influenced the fate of soil-derived N. The rate was 0.5 kg ha\(^{-1}\) day\(^{-1}\) in the effective root zone (50 cm depth) during the period (3/4 to 14/6/85). At the second sampling date, in July, the net mineralization rate had increased to 2.3 kg ha\(^{-1}\) day\(^{-1}\) due to increased temperature, and better aeration of the soil profile due to increased plant uptake of water. Plant uptake was a major factor and net mineralization was still having a pronounced influence on the fate of soil N. Later in the season towards maturity, 3/7 to 15/8/85, the rate of net mineralization decreased to 0.4 kg ha\(^{-1}\) day\(^{-1}\). This was probably due to increased moisture content and resulting anaerobic conditions following the heavy rainfall during this period. Crop removal of soil-derived N was also a major factor.

5.3.2.5 Effect of fertilizer addition on mineralization and the uptake of soil-derived nitrogen

A comparison between the fertilized plots (Table 5.5) and the unfertilized control plots (Table 5.4) shows that similar amounts of net mineralization occurred in both treatments during the most part of the growing season. During the early course of the experiment, the estimated net mineralization was higher in the fertilized plots.

This may have been an artefact due to mineralization-immobilization turnover (MIT) (Jansson and Persson, 1982).
Since mineralization and immobilization occur simultaneously, the addition of labelled inorganic fertilizer N to the soil will result in some immobilization of labelled N and some mineralization of non-labelled native soil N. Thus more non-labelled mineral N will occur in the fertilized soil than the smaller pool of mineral N in unfertilized controls. This does not necessarily mean that net mineralization of N has actually occurred, merely that labelled N is immobilized and at the same time unlabelled native N is mineralized. An alternative explanation is the so-called "priming effect" (Broadbent, 1965), i.e. the stimulation of net mineralization by the addition of fertilizer N. There is no obvious way of distinguishing between these possibilities.
6.1 Introduction

The macroporosity and microporosity (the organization of the pore volume) of a soil may produce highly irregular patterns of water movement as indicated by studies on the distribution of dyes and other tracers. (Bouma and Wosten, 1979; Bouma, 1981). However, in undisturbed naturally structured soil, especially those with macropores, only partial displacement of resident water and solutes by incoming water and solute occurs (White, 1985). Recognition of such behaviour, variously described as "channelling", "short-circuiting", "by passing", "preferential flow", or "partial displacement" (Scotter, 1978; Bouma, 1981; Beven and Germann, 1982; Smetten et al., 1983) is not new (Schumacher, 1864; Lawes et al., 1882) as pointed out by Thomas et al. (1978). But only recently has attention been focused on this phenomenon because of the possible consequences for rapid leaching of fertilizers, soluble and particulate waste materials, and other potential pollutants into surface waters and ground water (Thomas and Phillips, 1979; Bouma et al., 1983).

For soils that are not strongly aggregated, transient water and solute movement may be successfully described by a diffusion type equation (Nielsen et al., 1962; Jackson, 1963) which assumes the existence of local equilibrium in the soil, while for transient flow in highly aggregated soil, there may exist a disequilibrium between the water held within the aggregates (microporosity) and that in the pore space between the aggregates (macroporosity). Philip (1968) presented a model which assumed that water
transfer on Darcy's scale occurs only in macropores, and the micropores may be treated as a distributed sink in exchanging water with macropores. The degree of exchange between the two phases depend on the initial water content in the micropores and the velocity with which the water and solute moves through the soil.

6.2 The Principles of Solute Movement in Relation to the Process of NO$_3^-$ Leaching

Extensive literature exists on the theory and equations describing solute movement in porous media such as soils (Gardner, 1965; Biggar and Nielsen, 1967; 1968; Frissel and Poelstra, 1967; Fried and Combarnous, 1971; Boast, 1973; Nye, 1974; Wild, 1981 and Nielsen et al., 1982) and text books by Kirkham and Powers (1972), Marshall and Holmes (1979) and Hillel (1980).

6.2.1 Convection, diffusion and dispersion

Assuming that steady-state water conditions occurs in a homogeneous non-aggregated soil and no interaction between NO$_3^-$ ion and the soil, then the movement of NO$_3^-$ through the soil can be described by the above mentioned processes. In considering leaching of NO$_3^-$ we are, however, mainly concerned with the convective flux or mass flow, which refers to solute transport due to mass flow of water alone. The water and solute move in response to a hydraulic gradient and the rate of movement is dependent on the hydraulic gradient and hydraulic conductivity of the soil. If a nitrate solution is applied evenly to the top of a cylinder of soil aggregates to give a thin band of concentration C in the soil solution and the column is then leached with water, the downward flux of nitrate through the soil is given by
Equation (6.1) assumes that all the nitrate is in the soil solution at uniform concentration. The rate of movement through the soil pores is $U$, and if water is added at a rate $Q$ then $U = Q/\theta_v$. If the cylinder of soil is free-draining and is kept saturated, $\theta_v \geq 0.5$ then the nitrate band will move downward at a rate of $2Q$. If the water content downward the cylinder of soil is constant, the rate of change of nitrate concentration in the soil during leaching is

$$\frac{\partial C}{\partial t} = -U \frac{\partial C}{\partial x} \quad (6.2)$$

The effect on the solute ($NO_3^-$) distribution in the soil profile (cylinder) is illustrated in Figure 6.1a.

The diffusion process occurs when there is an uneven distribution of solute in soil solution, there is a diffusive flux of solute from areas of high concentration to areas of low concentration. In soil, solute diffusion can only occur in the fraction of soil volume occupied by water. In addition, the effective diffusion coefficient in a water saturated soil is less than that in bulk water because of the smaller volume of soil solution available for diffusion and the increased path length due to tortuosity of soil pore geometry. Moreover, in unsaturated soil, the effective diffusion coefficient is further reduced because of a decrease in volume fraction of water and an increase in tortuosity of the diffusion paths (Rowell et al., 1967). However, movement by diffusion is described below.
Figure 6.1 - Schematic diagram of various components of NO$_3^-$ leaching

- a. Convective transport alone
- b. Convection-diffusion-dispersion
- c. Anion adsorption
- d. Anion exclusion
- e. Macropore bypass and macropore leaching
The mechanical action of a solution flowing through soil causes mixing and tends to equalize the solute distribution by a process called "hydrodynamic dispersion". This process enhances the dispersive effect of diffusion and often completely masks it. Hydrodynamic dispersion occurs because: A) the flow velocity within a single pore is not uniform since it is fastest at the pore centre, B) the large variation in velocities (U) through pores of different diameter, C) the path length of pores fluctuates greatly due to tortuosity of pore geometry.

From equation (6.1) and applying the continuity equation to hydrodynamic dispersion (by analogy to diffusion) it can be shown (Kirkham and Powers, 1972) that the combined effects of the convective-diffusive-dispersive mechanism can be described by:

\[
\frac{\partial C}{\partial t} = E \frac{\partial^2 C}{\partial x^2} - U \frac{\partial C}{\partial x}
\]

(6.4)

where

\[
E = D_S + mU
\]

(6.5)

The value of E depends on the flow velocity and tends to increase with increasing value of U (Nielsen and Biggar, 1963; Passioura and Rose, 1971). As the value of E increases, breakthrough curves tend to become asymmetrical and this is sometimes dealt with by dividing the soil water into "mobile" and "immobile" regions (van Genuchten and Wierenga, 1976).

The effect of equation (6.4) on the nitrate distribution in the soil profile is illustrated in Figure 6.1b.
Equation (6.2), which essentially represents piston flow, was derived as above by De Smedt and Wierenga (1978) and from an alternative approach based on mass conservation by Rose et al. (1982a). Both authors proceed to show that during the infiltration and redistribution of an increment \((I, \text{ cm})\) of water, the distance \((a, \text{ cm})\) moved by the solute peak \((C(x)/C_{\text{app}})_{\text{max}}\) is given by

\[
a = I/\theta_{fC}
\]  

(6.6)

The effect of diffusion and dispersion on an assumed initially rectangular pulse at a depth \((\Delta F, \text{ cm})\) is then described using (Rose et al., 1982b) equation:

\[
C(x)/C_{\text{app}} = 0.5\left(\frac{\text{erfc} \left(\frac{x-a}{2(D_0 t+ma)^{0.5}}\right) - \text{erfc} \left(\frac{x-B}{2(D_0 t+mB)^{0.5}}\right)}{2(D_0 t+ma)^{0.5} - 2(D_0 t+mB)^{0.5}}\right)
\]  

(6.7)

The experimentally measured dispersion coefficient \((E)\) includes the results of diffusion i.e.

\[
E = D_s + mU
\]  

(6.8)

which does depend on concentration, but under many experimental conditions diffusion is comparatively slow and should be ignored (Wild, 1981).

6.2.2 Charge characteristics of soils

**a. Adsorption.** Nitrate adsorption has not been reported in the United Kingdom (Wild and Cameron, 1980a), but has been found where soils have a significant anion exchange capacity. Non-specific adsorption of \(\text{NO}_3^-\) does reduce its rate of leaching (Singh and Kanehiro, 1969; Kingo and Pratt, 1971a, b, c). Where it occurs, leaching equations can be modified (Davidson and Chang, 1972) by
the inclusion of the retardation factor \((1 + V_0 \frac{N}{V_0})\), the expression \(V_0 \frac{N}{\theta_v}\) effectively represents the apparent increase in pore volume as a result of adsorption. The effect on the leaching pattern is shown in Figure 6.1c.

b. Anion exclusion. Soil surfaces generally carry a net negative charge and as a result cations in soil solution distribute themselves near the surface so that electroneutrality is maintained forming a double layer (Arnold, 1978). Because of electrostatic repulsion anions such as \(\text{NO}_3^-\) are partly excluded from this volume. Thus the effective pore volume in leaching studies is less than the water content of the soil measured by drying at 105°C, which is usually described as one pore volume (Wild, 1981). Nitrate ions therefore travel correspondingly faster than predicted by conventional theory (Nielsen and Biggar, 1962). Examples of anion exclusion are given by Thomas and Swoboda, 1970 and Krupp et al., 1972. The effect on leaching pattern is shown in Figure 6.1d.

6.2.3 Macropore movement

A significant volume of water may flow through large cracks and channels in soil (macropores). Although macropores may comprise only a small fraction of the total soil volume (0.001 to 0.05), they can have a pronounced effect on the rate of the infiltration and redistribution of water under the right conditions (White, 1985). Macropores that are not open at the soil surface will not usually flow, those that are open and are continuous may transmit water rapidly to depths in soil (Ritchie et al., 1972; Shuford et al., 1977; Wild and Babiker, 1976b; Omoti and Wild, 1979; Smetten and Trudjill, 1983; Scotter
Macropores are formed in various ways: by shrinkage on drying (Brewer, 1964); chemical weathering (piping) (Reeves, 1980); freeze-thaw cycles, mole draining, and subsoiling (Beven and Germann, 1982); plant roots (Aubertin, 1971); and soil fauna (Green and Askew, 1965; Ehlers, 1975). Beven and Germann (1982) concluded that most soils contained some macropores, the nature and volume of which depend on a dynamic balance between constructive and destructive processes. The abundance of earthworm burrows is less in cultivated than in uncultivated soil (Ehlers, 1975; Abbott et al., 1979) because soil tillage generally destroys macropores (Thomas and Phillips, 1979). Large spaces between aggregates may be considered macropores (Ritchie et al., 1972).

In coarsely structured soil that receives rapid application of water, over half the water may move through the macropore system (Quiesenberry and Phillips, 1976). Movement of water in soil macropores has two important implications to the process of nitrate leaching: firstly, when nitrate is held within soil aggregates it will be protected from leaching when bypass flow occurs (Cunningham and Cooke, 1958; Wild, 1972; Thomas and Phillips, 1979). Secondly, if nitrate fertilizer has recently been added to the soil, or if soil-generated nitrate is held on the outside of the aggregates, then bypass flow causes it to leach faster than it would by uniform miscible displacement (Addiscott and Cox, 1976; Barraclough et al., 1983). The effect of macropores flow on nitrate leaching is given in Figure 6.1e.

6.2.4 Transformation and plant uptake of nitrogen

Biological transformation of NO$_3^-$ such as mineralization-
immobilization turnover (MIT) and denitrification occur in soils, and are extremely difficult to describe mathematically because often they are spasmodic rather than steady-state (Wild and Cameron, 1980a). Nevertheless, since they can act as major inputs and outputs of NO$_3^-$ to the system, an input-output term $S$ was included in equation (6.4) to account for the rate of NO$_3^-$ production or disappearance:

$$\frac{\partial C}{\partial t} = E \frac{\partial^2 C}{\partial x^2} - U \frac{\partial C}{\partial x} + S$$

(6.8)

6.2.5 Soil variability

Soil properties vary spatially, so that solute and water movement also vary (Addiscott and Wagenet, 1985). The above description of leaching has been deterministic in nature based on the underlying principles of solute movement related through parameters obtained experimentally (e.g. equation 6.4) which assumes that values for the required parameter (e.g. NO$_3^-$ concentration, average pore velocity) can be determined that are applicable over the domains of time and space in which the processes are occurring. There is generally wide spatial variability in soil NO$_3^-$ concentration within a field (Biggar, 1978; Nielsen et al., 1979; Burns, 1980; Cameron and Wild, 1984; MacDuff and White, 1984). Similarly, variability in arrangement of soil pores and their sizes makes it difficult to determine an average value for either pore water velocity or dispersivity. Recognition of the problem caused by variability of the soil properties has led to the use of stochastic approaches for prediction of solute movement in field soils or at least the inclusion of stochastic parameters in deterministic models (Nielsen et al., 1982).
EXPERIMENTAL RESULTS OF COLUMN LEACHING EXPERIMENTS

7.1 Summary

The objectives of this study were based on the early results from the $^{15}$N field experiment at Aberlady (Site B) in the summer of 1985. The field experiment results showed very low leaching efficiency of the $^{15}$N tracer recovered, when compared with model predictions (Burns model). It was therefore thought likely that the protection of the $^{15}$N tracer from loss by leaching was due to the presence of regions of immobile water (i.e. only a fraction of soil water contributes to flow) in this soil. Thus, it was decided to carry out laboratory experiments, early in autumn 1985 and 1986, putting forward the following objectives: A) to investigate the presence or absence of the immobile water; B) to study the influence of irrigation intensity and the antecedent soil water content on the extent of existence of immobile water; and C) to compare the experimental results with model predictions e.g. of Burns and Rose. These objectives were approached by the following experiments.

Large undisturbed cores (15 cm diam x 25 cm soil depth) were irrigated at rates of 0.05 to 4.52 cm h$^{-1}$ with 0.005 M CaCl$_2$ solution using NO$_3^-$-N as a tracer under saturated flow, or at rates of 0.06 - 1.12 cm h$^{-1}$ with 0.005 M CaSO$_4$ solution using Cl$^-$ and Br$^-$, as tracers under unsaturated conditions in which the average volumetric soil moisture content was less than the fractional pore space in all soil columns during the leaching process. Experimental results showed that, irrespective of application rate, antecedent soil moisture content and presence of solute in immobile phase (i.e. in micropores), all breakthrough
curves (BTCs) for NO$_3^-$-N, Cl$^-$ and Br$^-$ were markedly asymmetric, and skewed to values less than one pore volume of water filled porosity, unlike those reported for columns of packed aggregates, indicating that some of the pore water was being effective in solute transport during the leaching process. The ineffectiveness of the pore water in solute transport has been attributed to features of pore geometry, such as water in aggregates or in dead-end pores, where the velocity of pore water is zero, (i.e. immobile), and to anion exclusion. The latter is associated more with heavy soils, but does occur to some extent on light textured soils.

Because of the range of initial soil moisture contents, the soil columns adsorbed between 0 to 4.68 cm of irrigation water before drainage began. Once drainage began, flow through the soil columns was approximately steady and faster at higher application rates. The flow rate effect seems to be less important than the effect of the antecedent soil moisture content, but the trend shows that the lower the application rate the more effective was the solute leaching. The flow rate effect was more significant under unsaturated flow than under saturated conditions, and no appreciable effect of flow rate occurred under the latter conditions. The effect of initial soil moisture content on solute transport seems to have been due to the relatively higher mobility of intra-aggregate water due to relatively low water suction at higher initial soil moisture content compared to the higher suction at lower initial moisture content. The movement of the applied water into micropores was much reduced at higher initial moisture content, i.e. the applied water was moving in the large pores, resulting in early appearance of solute in the effluent (i.e. more efficient leaching). The results also show that the presence of solute in an immobile phase retards the
leaching, especially when the soil is initially dry and the application rate is highest and when bypass flow occurs.

Good agreement among replicates was observed and spatial variability in soil structure was not a problem, therefore water and solute moved uniformly, particularly under unsaturated flow, in this soil. The least variability was achieved when the soil was initially dry, though the flow rate was high under unsaturated flow. Generally, under saturated flow, the variability was higher at higher application rates; this may have been due to the differences in the efficacy of the macropores to conduct water.

7.2 Experimental Results

The experiment was conducted to evaluate the effects of a given initial soil moisture content combined with different application rates on the transport of the applied non-reactive solutes, namely, nitrate, bromide and chloride. The first tracer was used to study the above mentioned effects under saturated flow conditions, while the other two tracers were used to study the same effects under unsaturated flow. Tables 7.1, 7.2 and 7.3 summarize the different treatments of $\text{NO}_3^-$, $\text{Cl}^-$ and $\text{Br}^-$ respectively.

7.2.1 Saturated flow experiment

The leaching behaviour was investigated using columns of undisturbed soil from the Aberlady site early in the autumn of 1985. The columns were saturated from the base upwards using distilled water or 0.005 M $\text{CaCl}_2$ before an experimental run. A pulse of 100 cm$^3$ ($V_{\text{app}}$) of $\text{KNO}_3$ solution containing 2,600 g m$^{-3}$ $\text{NO}_3^-$ was applied; the
flow rate was not controlled, but a constant head of leaching water was maintained on the soil surface.

Table 7.1 Summary of different NO$_3^-$ saturated flow treatments (1985)

<table>
<thead>
<tr>
<th>Treatment</th>
<th>No. of cores</th>
<th>Q $\text{cm h}^{-1}$</th>
<th>$\theta_{iv}$ cm$^3$cm$^{-3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>L$\text{NO}_3$</td>
<td>2</td>
<td>0.05 (0.00) *</td>
<td>0.47 (0.03)</td>
</tr>
<tr>
<td>M$\text{NO}_3$</td>
<td>2</td>
<td>0.51 (0.06)</td>
<td>0.49 (0.005)</td>
</tr>
<tr>
<td>H$\text{NO}_3$</td>
<td>2</td>
<td>3.60 (0.90)</td>
<td>0.46 (0.04)</td>
</tr>
</tbody>
</table>

Remarks

A) Soil columns were initially saturated slowly by applying water from the bottom of each core.
B) Residual NO$_3^-$-N was leached before an experimental run.
C) Crust at either soil surface or base, to restrict the inflow or the outflow producing L$\text{NO}_3^-$ treatment.

7.2.2 Unsaturated flow experiment

The leaching behaviour was further investigated under unsaturated flow conditions (leaching processes in the field frequently occur under unsaturated flow and often at relatively low flow rates) using columns of undisturbed soil collected from the same site, early in the autumn of 1986. A pulse of 100 cm$^3$ of CaCl$_2$ solution containing 3400 to 3700 g m$^{-3}$ Cl$^-$ was applied at the soil surface and this was treated as indicated in Table 7.2.
Table 7.2 Summary of Cl⁻ different treatments under unsaturated flow (1986)

<table>
<thead>
<tr>
<th>Treatment</th>
<th>No. of Q</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>cores</td>
<td>cmh⁻¹</td>
</tr>
<tr>
<td>A</td>
<td>Lc₁</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Mc₁</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Hc₁</td>
<td>1</td>
</tr>
<tr>
<td>B</td>
<td>Mc₁</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Hc₁</td>
<td>2</td>
</tr>
<tr>
<td>C</td>
<td>Mc₁</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Hc₁</td>
<td>2</td>
</tr>
<tr>
<td>A⁺</td>
<td>Lc₁</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Mc₁</td>
<td>2</td>
</tr>
<tr>
<td></td>
<td>Hc₁</td>
<td>3</td>
</tr>
</tbody>
</table>

( )* Figures in brackets represent standard error (s.e)

Bromide addition was not originally planned in this experiment, but results from an early experimental run (treatment A) with chloride showed mass balances greater than unity due to presence of residual chloride in the soil columns (30 to 70 percent of the total Cl⁻ applied).
Table 7.3 Summary of Br\textsuperscript{−} different treatment under unsaturated flow (1986)

<table>
<thead>
<tr>
<th>Treatment</th>
<th>No of Cores</th>
<th>Q\textsubscript{in} cm\textsuperscript{3} h\textsuperscript{-1}</th>
<th>Q\textsubscript{div} cm\textsuperscript{3} cm\textsuperscript{-3}</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>D-HBr</td>
<td>2</td>
<td>1.06 (0.00)</td>
<td>0.16 (0.01)</td>
<td>(D) treatment: irrigation was applied immediately after tracer application. So columns allowed to dry first under evaporative conditions at root temperature.</td>
</tr>
<tr>
<td>A-HBr</td>
<td>2</td>
<td>0.85 (0.00)</td>
<td>0.24 (0.00)</td>
<td>(A) treatment: as with C\textsuperscript{−} tracer</td>
</tr>
<tr>
<td>A\textsuperscript{+}-HBr</td>
<td>4</td>
<td>0.94 (0.07)</td>
<td>0.36 (0.01)</td>
<td>(A\textsuperscript{+}) treatment: as with C\textsuperscript{−} tracer</td>
</tr>
</tbody>
</table>

( )* Figures in brackets represent standard error (s.e)

Therefore it was decided to use bromide as a tracer instead of chloride, because its effect on mass balance would be minimal due to the very low soil content of bromide. Therefore a pulse of 100 cm\textsuperscript{3} (V\textsubscript{app}) of CaBr\textsubscript{2}.2H\textsubscript{2}O solution containing 950 g m\textsuperscript{-3} was applied at the soil surface and was then treated as illustrated in Table 7.3. In this experiment a reservoir containing 0.005 M CaSO\textsubscript{4} irrigation solution was connected to a peristaltic pump so that application rate could be controlled by the size of the delivery tube. Three application rates were applied to chloride treatments and classified as low, moderate and high flow rates respectively (0.05, 0.27 and 1.12 cm h\textsuperscript{-1}), whereas only the highest rate was applied to cores used for bromide leaching.

7.2.3 Shape of breakthrough curves
7.2.3.1 Parameters for breakthrough curve characterisation

Three parameters have been calculated to describe the soil column BTCs. These are:
a) Mode ($V_{mod}$) i.e. the effluent volume expressed as a fraction of the water filled porosity at which solute relative concentration ($C_{ex}/C_{app}$)$_{max}$ occurs. It is calculated from the following relation

$$V_{mod} = \frac{V_p - 0.5 V_{app}}{V_o}$$ (7.1)

b) Median ($V_{med}$) i.e. the effluent volume expressed as a fraction of the water filled porosity at $S_{ex}/S_{app} = 0.5$, and calculated from:

$$V_{med} = \frac{V_{0.5} - 0.5 V_{app}}{V_o}$$ (7.2)

c) Mean ($V_{st}$) i.e. the effluent volume expressed as a fraction of the water filled porosity at the solute centre of mass location in BTCs, and calculated as follows:

$$V_{st} = \int_{0}^{\infty} \frac{V_{ex} C(V_{ex}) dV_{ex}}{C(V_{ex}) dV_{ex}}$$ (*)

The immobile water fraction ($V_{im}$) has been calculated using the value of $V_{st}$ (Dayson et al., 1987). Immobile water is defined as the effluent volume expressed as a fraction of water filled porosity which does not contribute to flow during the transport process of non-reactive solute, and it is estimated according to the following relationship:

$$V_{im} = \frac{V_o - V_{st}}{V_o}$$ (7.4)

$V_{mod}$, $V_{med}$, $V_{st}$, $V_{im}$ and $V_{ex}$ (excluded immobile volume due to anion exclusion) may be expressed as fractions of soil...
water content, i.e. cm$^3$ cm$^{-3}$ by multiplying each term by $\theta_{fv}$.

Assuming that $\theta_{fv} = \bar{\theta}_v$ (average volumetric soil water content - cm$^3$ cm$^{-3}$) during inert solute leaching under saturated flow, therefore the immobile fraction of the soil water can be calculated as follows:

$$\theta_{im} = \bar{\theta}_v - \theta_{st} \quad (7.5)$$

with the assumption that all the pore water is effective in the transport (i.e. all soil water contributes to flow), therefore $\theta_{st}$ and $\theta_v$ should be equal. Even when all the pore water is effective, $\theta_{med}$ and $\theta_{mod}$ will always be less than $\bar{\theta}_v$ (=$\theta_{st}$), because of the influence of the inlet boundary. Assuming solute undergoes no physical, chemical or biological changes during the period of observation (i.e. during leaching process), values of $\theta_{st}$ less than $\bar{\theta}_v$ may reflect the joint effects of anion exclusion, dead-end pores and "bypass" flow through macropores (Bouma, 1981). When $\theta_{ex}$ is very small ($\theta_{ex}$ can be determined experimentally in soil columns, (Vinten, et al., 1987), the difference between $\theta_v$ and $\theta_{st}$ is due to existence of immobile water due to other soil physical properties such as dead-end pores.

7.2.3.2 Dispersion length determination

In this experiment, dispersivity was determined from the saturated flow run in all soil columns (method of Kirkham and Powers, 1972). It was assumed that immobile water was not significant (i.e. all soil water was effective in transport, "$\theta"_{im} = 0"). The following steps were followed to calculate the dispersivity:
A) measurement of \((C_{ex}/C_{app})_{\text{max}}\) i.e. the peak position of the BTCs and the following equation then solved for the value of \(z\) in the equation:

\[
0.5 \frac{(C_{ex}/C_{app})_{\text{max}}}{(2\pi)^{0.5}} \int_{0}^{z} e^{-w^2/2} \, dw \quad (7.6)
\]

\(z\) can then be found from tables if \((C_{ex}/C_{app})_{\text{max}}\) is known.

B) calculation of mechanical dispersion coefficient from equation (7.7)

\[
E = Q L \left( \frac{(x_{o}/2L)^2}{2(1+x_{o}/2L)z^2} \right) \quad (7.7)
\]

C) from the following relation therefore, dispersivity (cm) can be calculated

\[
E = \frac{m}{Q} \quad (7.8)
\]

### 7.2.3.3 Saturated flow NO\(_3^-\)-N BTCs

In Figure 7.1 representative data of the relative NO\(_3^-\)-N concentration \((C_{ex}/C_{app})\) at three different application rates ranging from lowest to highest (0.005 to 4.50 cm h\(^{-1}\)) under saturated flow are plotted against the pore volume fraction \((V_{ex}/V_{o})\) which is the ratio of the cumulative effluent volume \(V_{ex}\) and the water filled pore volume \(V_{o}\). Water filled pore volume is defined as

\[
V_{o} = V_S \Theta_{fv} \quad (7.10)
\]
Figure 7.1 - Experimental measure breakthrough curves from a pulse of NO$_3^-$ -N leached through saturated soil columns at three application rates.

<table>
<thead>
<tr>
<th>Input pulse (PVR)</th>
<th>Flow velocity (cm sec$^{-1}$)</th>
<th>Treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.051</td>
<td>125.0$\times$10$^{-8}$</td>
<td>SH$_{NO3}$</td>
</tr>
<tr>
<td>0.042</td>
<td>13.0$\times$10$^{-8}$</td>
<td>SM$_{NO3}$</td>
</tr>
<tr>
<td>0.055</td>
<td>1.7$\times$10$^{-8}$</td>
<td>SI$_{NO3}$</td>
</tr>
</tbody>
</table>

$L=25cm$
Table 7.4 Summary of results from undisturbed saturated columns (1985)

<table>
<thead>
<tr>
<th>Core No.</th>
<th>Q (cm sec⁻¹) x10⁻⁵</th>
<th>U</th>
<th>K</th>
<th>Vmod</th>
<th>Vmed</th>
<th>Vst</th>
<th>x₀ m</th>
<th>θiv</th>
<th>(Cex/Capp)max</th>
<th>ML</th>
</tr>
</thead>
<tbody>
<tr>
<td>IVcb</td>
<td>1.4</td>
<td>4.0</td>
<td>1.0</td>
<td>0.61</td>
<td>0.61</td>
<td>0.68</td>
<td>1.9</td>
<td>1.6</td>
<td>0.50</td>
<td>0.08</td>
</tr>
<tr>
<td>IIcs**</td>
<td>1.7</td>
<td>4.5</td>
<td>1.2</td>
<td>0.57</td>
<td>0.61</td>
<td>0.83</td>
<td>2.1</td>
<td>2.7</td>
<td>0.44</td>
<td>0.08</td>
</tr>
<tr>
<td>III</td>
<td>13.0</td>
<td>31.0</td>
<td>9.2</td>
<td>0.48</td>
<td>0.61</td>
<td>0.79</td>
<td>1.6</td>
<td>1.9</td>
<td>0.54</td>
<td>0.06</td>
</tr>
<tr>
<td>II</td>
<td>16.0</td>
<td>56.0</td>
<td>11.4</td>
<td>0.38</td>
<td>0.41</td>
<td>0.65</td>
<td>3.1</td>
<td>2.2</td>
<td>0.44</td>
<td>0.12</td>
</tr>
<tr>
<td>IV</td>
<td>75.0</td>
<td>224.0</td>
<td>53.3</td>
<td>0.48</td>
<td>0.57</td>
<td>0.67</td>
<td>2.1</td>
<td>2.2</td>
<td>0.50</td>
<td>0.09</td>
</tr>
<tr>
<td>V</td>
<td>125.0</td>
<td>401.0</td>
<td>88.8</td>
<td>0.41</td>
<td>0.63</td>
<td>0.76</td>
<td>2.1</td>
<td>2.2</td>
<td>0.41</td>
<td>0.08</td>
</tr>
</tbody>
</table>

* Crust at the surface of soil column
** Crust at the bottom of soil column

where Vₜ is the total volume of the moist soil, and θfv is the final volumetric content at the end of the experimental run (average volumetric soil moisture content was 0.47 ± 0.02 during NO₃⁻ leaching process). The figure shows that irrespective of the application rate, all the BTCs were displaced well to the left of the point (Vex/Vo = 1 + 0.5 Vapp/Vo) pore volume which is the expected position for a well packed cylinder of soil (non-aggregated porous medium). The peak position (Cex/Capp)max occurred at 0.41, 0.48 and 0.56 pore volume for high, moderate and low flow rates, respectively. The figure also shows that the leading edges of the BTCs are quite sharp, but the tailing edge declines more gradually, suggesting that solute mixed with immobile water occurred by diffusion at a front moving through the soil and then was released gradually as leaching water flowed through...
the columns. Generally, the figure indicates that $C_{ex}/C_{app}$ rises more sharply and shows more tailing as application rate increases. In this experiment the displacement of the BTCs to the left of the above mentioned point suggests that only a fraction of the soil water participated in nitrate transport, while the rest was immobile. This type of displacement is often attributed to negative adsorption, dead end pores or some other structural feature of pore geometry (Biggar and Nielsen, 1962; Coats and Smith, 1964; Bresler, 1973; Thomas and Swoboda, 1970; van Genuchten and Wierenga, 1976). A summary of results from all the saturated flow columns experiment is given in Table 7.4

7.2.3.4 Unsaturated flow

a. $\text{Cl}^-$ BTCs

In Figure 7.2 (as results of Table 7.5), representative data of the relative concentration ($C_{ex}/C_{app}$) at three different application rates ranging from the lowest to highest (0.05 to 1.12 cm h$^{-1}$) during unsaturated flow are plotted against the pore volume fraction ($V_{ex}/V_{Q}$). The average volumetric soil moisture content was $0.38 \pm 0.01$ during the $\text{Cl}^-$ leaching process (second experimental run). Irrespective of application rate, the figure indicates that the peak position appeared earlier, and occurred at 0.78, 0.65 and 0.61 pore volume for high, moderate and low flow rate, respectively. The reasons for displacement of all BTCs to the left were given with the saturated flow experiment.

b. $\text{Br}^-$ BTCs

Figure 7.3 with additional data in Table 7.6, shows the influence of the soil moisture content on the shape of the bromide breakthrough curves during its transport under
Figure 7.2 - Experimental measured breakthrough curves from a pulse of Cl leached through unsaturated soil columns at three application rates

Relative concentration \((C_{ex}/C_{app})\times10^2\)

Input pulse (PVf)
- 0.047
- 0.051
- 0.046

Flow velocity (cm\(^3\)cm\(^{-3}\))
- 21.6\times10^{-5}
- 7.9\times10^{-5}
- 2.5\times10^{-5}

Treatment
- A\(^+\)H\(_{Cl}\)
- A\(^+\)M\(_{Cl}\)
- A\(^+\)L\(_{Cl}\)

Pore volume fraction \((V_{ex}/V_{o})\)

L=25cm
Table 7.5 Summary of Chloride Results from Undisturbed Unsaturated Columns (1986)

<table>
<thead>
<tr>
<th>Core Treat- No. ment</th>
<th>Q (cm sec⁻¹)</th>
<th>U</th>
<th>V_{mod}</th>
<th>V_{med}</th>
<th>V_{st}</th>
<th>θ_{iv}</th>
<th>θ_{fv}</th>
<th>(C_{ex}/C_{app})</th>
<th>C_{app}'max</th>
<th>MB corr</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 HCl 28.0 99.4</td>
<td>0.77 0.77</td>
<td>0.88</td>
<td>0.21</td>
<td>0.32</td>
<td>0.18</td>
<td>0.90 110</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 MCl 7.5 28.1</td>
<td>0.60 0.67</td>
<td>0.81</td>
<td>0.18</td>
<td>0.33</td>
<td>0.16</td>
<td>150</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 MCl 7.4 26.8</td>
<td>0.63 0.67</td>
<td>0.81</td>
<td>0.18</td>
<td>0.34</td>
<td>0.17</td>
<td>130</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 LCl 2.0 9.2</td>
<td>0.47 0.48</td>
<td>0.56</td>
<td>0.26</td>
<td>0.39</td>
<td>0.18</td>
<td>160</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 LCl 1.9 8.7</td>
<td>0.31 0.45</td>
<td>0.59</td>
<td>0.22</td>
<td>0.37</td>
<td>0.19</td>
<td>170</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>A +</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3 HCl 36.1 104.8</td>
<td>0.63 0.74</td>
<td>0.84</td>
<td>0.40</td>
<td>0.41</td>
<td>0.09</td>
<td>110</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>6 HCl 23.0 71.9</td>
<td>0.63 0.72</td>
<td>0.82</td>
<td>0.32</td>
<td>0.39</td>
<td>0.09</td>
<td>108</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>13 T 21.6 61.5</td>
<td>0.78 0.83</td>
<td>0.95</td>
<td>0.31</td>
<td>0.37</td>
<td>0.12</td>
<td>98</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 MCl 7.9 26.1</td>
<td>0.65 0.75</td>
<td>0.84</td>
<td>0.31</td>
<td>0.36</td>
<td>0.11</td>
<td>111</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 MCl 7.9 28.2</td>
<td>0.59 0.72</td>
<td>0.80</td>
<td>0.26</td>
<td>0.35</td>
<td>0.11</td>
<td>111</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4 LCl 2.5 8.0</td>
<td>0.61 0.64</td>
<td>0.80</td>
<td>0.37</td>
<td>0.39</td>
<td>0.11</td>
<td>85</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>5 LCl 1.6 5.9</td>
<td>0.42 0.56</td>
<td>0.71</td>
<td>0.37</td>
<td>0.38</td>
<td>0.10</td>
<td>102</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>B</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>9 HCl 29.4 86.0</td>
<td>0.69 0.87</td>
<td>0.99</td>
<td>0.17</td>
<td>0.36</td>
<td>0.14</td>
<td>149</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>12 HCl 26.5 75.7</td>
<td>0.68 0.87</td>
<td>0.99</td>
<td>0.17</td>
<td>0.35</td>
<td>0.13</td>
<td>153</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7 MCl 7.4 21.8</td>
<td>0.57 0.85</td>
<td>1.00</td>
<td>0.16</td>
<td>0.34</td>
<td>0.14</td>
<td>151</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>15 MCl 7.8 23.7</td>
<td>0.67 0.82</td>
<td>0.98</td>
<td>0.17</td>
<td>0.35</td>
<td>0.13</td>
<td>146</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>8 HCl 26.5 97.1</td>
<td>0.56 0.68</td>
<td>0.78</td>
<td>0.24</td>
<td>0.35</td>
<td>0.15</td>
<td>146</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>17 HCl 26.5 83.8</td>
<td>0.65 0.78</td>
<td>0.97</td>
<td>0.22</td>
<td>0.34</td>
<td>0.13</td>
<td>123</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>11 MCl 7.1 26.9</td>
<td>0.76 0.70</td>
<td>0.80</td>
<td>0.22</td>
<td>0.33</td>
<td>0.15</td>
<td>150</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>14 MCl 6.8 25.8</td>
<td>0.72 0.72</td>
<td>0.80</td>
<td>0.23</td>
<td>0.33</td>
<td>0.16</td>
<td>148</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

unsaturated flow. The relative Br⁻ concentration (C_{ex}/C_{app}) at three different antecedent soil moisture contents ranging from lowest to highest (0.16 to 0.34 cm³ cm⁻³) are plotted against the pore volume fraction (V_{ex}/V_{o}). The average irrigation application rate was (0.95 ± 0.04 cm h⁻¹) during the bromide transport
Figure 7.3 - Experimental measured breakthrough curves as a function of output volume from a pulse of Br leached through undisturbed soil columns at three initial soil moisture contents.
Figure 7.4 - Experimental measured breakthrough curves as a function of input volume from a pulse of Br⁻ leached through undisturbed soil columns at three initial soil moisture contents.

Initial moisture content (cm³/cm³)  Treatment

- 0.34  A⁺H₄Br⁻
- 0.24  A H₄Br⁻
- 0.16  D H₄Br⁻

L=25cm
Table 7.6 Summary of Br⁻ Results from Undisturbed-Unsaturated Columns (1986)

<table>
<thead>
<tr>
<th>Core Treat-</th>
<th>Q</th>
<th>U</th>
<th>V&lt;sub&gt;mod&lt;/sub&gt;</th>
<th>V&lt;sub&gt;med&lt;/sub&gt;</th>
<th>V&lt;sub&gt;st&lt;/sub&gt;</th>
<th>θ&lt;sub&gt;iv&lt;/sub&gt;</th>
<th>θ&lt;sub&gt;fv&lt;/sub&gt;</th>
<th>(C&lt;sub&gt;ex&lt;/sub&gt;/C&lt;sub&gt;app&lt;/sub&gt;)&lt;sub&gt;max&lt;/sub&gt;</th>
<th>%&lt;sub&gt;MB&lt;/sub&gt;</th>
<th>No. ment</th>
<th>(cm sec&lt;sup&gt;-1&lt;/sup&gt;)</th>
<th>-Pv Fraction-- cm&lt;sup&gt;-3&lt;/sup&gt;</th>
<th>cm&lt;sup&gt;-3&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>16 D-H&lt;sub&gt;Br&lt;/sub&gt;</td>
<td>29.4</td>
<td>86.0</td>
<td>0.64</td>
<td>0.78</td>
<td>0.92</td>
<td>0.17</td>
<td>0.38</td>
<td>0.11</td>
<td>115</td>
<td>16 D-H&lt;sub&gt;Br&lt;/sub&gt;</td>
<td>29.4</td>
<td>84.8</td>
<td>0.74</td>
</tr>
<tr>
<td>18 D-H&lt;sub&gt;Br&lt;/sub&gt;</td>
<td>29.4</td>
<td>86.0</td>
<td>0.72</td>
<td>0.81</td>
<td>0.92</td>
<td>0.24</td>
<td>0.33</td>
<td>0.12</td>
<td>133</td>
<td>18 D-H&lt;sub&gt;Br&lt;/sub&gt;</td>
<td>29.4</td>
<td>93.3</td>
<td>0.72</td>
</tr>
<tr>
<td>10 A-H&lt;sub&gt;Br&lt;/sub&gt;</td>
<td>22.1</td>
<td>72.8</td>
<td>0.72</td>
<td>0.81</td>
<td>0.91</td>
<td>0.24</td>
<td>0.35</td>
<td>0.12</td>
<td>116</td>
<td>10 A-H&lt;sub&gt;Br&lt;/sub&gt;</td>
<td>22.1</td>
<td>11.2</td>
<td>0.67</td>
</tr>
<tr>
<td>19 A-H&lt;sub&gt;Br&lt;/sub&gt;</td>
<td>23.5</td>
<td>74.6</td>
<td>0.72</td>
<td>0.81</td>
<td>0.91</td>
<td>0.24</td>
<td>0.35</td>
<td>0.12</td>
<td>116</td>
<td>19 A-H&lt;sub&gt;Br&lt;/sub&gt;</td>
<td>23.5</td>
<td>74.7</td>
<td>0.62</td>
</tr>
</tbody>
</table>

process. Irrespective of the initial soil moisture content, the figure shows that all BTCs were displaced to the left, as with chloride. The peak position occurred at 0.21, 0.39 and 0.71 pore volume for dry, moist and wet soil, respectively. The early peak position for the drier treatment could have two possible explanations. Firstly, less water occurred ahead of the advancing bromide solution at lower soil water content. Secondly, some water was isolated in part of the soil column, i.e. it was not displaced by the bromide solution as bromide passed through the column at this water content, and generally, at any water content below saturation. The fraction of the isolated water depends on the antecedent soil water content and the flow velocity the relative concentration of bromide. When (C<sub>ex</sub>/C<sub>app</sub>) is plotted against the input volume (i.e. irrigation), the peak positions occurred at similar pore volume irrespective of
the initial soil moisture content (Figure 7.4). This is because soil at the bottom of the column would drain only when the water suction was equal to zero.

In this experiment the application rate was high as mentioned above, therefore the fraction that was bypassed by the bulk of the soil must have been appreciable and resulted in less mixing and diffusion.

7.2.4 Effect of application rate
In Figures 7.5, 7.6 and 7.7 (data from Tables 7.7, 7.8 and 7.9 respectively) representative data for $S_{rem}/S_{app}$ at three different application rates ranging from the lowest to the highest (0.05 to 4.52 cm h$^{-1}$ and 0.06 to 1.30 cm h$^{-1}$) during saturated and unsaturated flow respectively, are plotted against the irrigation water depth (I-cm) required to leach the tracer applied. Figures 7.6 and 7.7 show that under unsaturated flow, the lower the application rate the lower was the irrigation depth needed to leach the same amount of the solute applied at similar initial soil moisture content. The average depth of irrigation required to leach 50 percent of tracer (Cl$^-$) applied was 7.4, 6.7 and 6.1 cm with the high, intermediate and low application rate respectively (Table 7.8). This is because a better diffusive mixing between mobile and immobile water occurred as flow rate declined and more of the soil pore water was involved in flow at lower flow velocities. Hence 50 percent solute displacement occurred at or near one pore volume at low flow rates. This has an important implication for nitrogen fertilizer application when added in the form of $\text{NO}_3^-$-N. Leaching processes in the field frequently occur under unsaturated conditions and often at relatively low flow rates, when resident solute will be effectively leached. At relatively high flow rates, such as during heavy irrigation or heavy rainfall, water is moving mainly
Table 7.7 Irrigation intensity effect of nitrate leaching under saturated flow ($\theta_{iv} = 0.47$)

<table>
<thead>
<tr>
<th>Treat. $\dot{Q}$ cmh$^{-1}$</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
<th>90</th>
<th>95</th>
</tr>
</thead>
<tbody>
<tr>
<td>$HNO_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4.50</td>
<td>3.7</td>
<td>4.1</td>
<td>4.9</td>
<td>5.6</td>
<td>6.3</td>
<td>7.3</td>
<td>8.7</td>
<td>10.7</td>
<td>13.5</td>
<td>16.5</td>
</tr>
<tr>
<td>2.70</td>
<td>4.0</td>
<td>5.0</td>
<td>5.9</td>
<td>6.6</td>
<td>7.5</td>
<td>8.1</td>
<td>9.0</td>
<td>10.0</td>
<td>13.0</td>
<td>15.6</td>
</tr>
<tr>
<td>$MNO_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.46</td>
<td>4.7</td>
<td>5.4</td>
<td>6.6</td>
<td>7.5</td>
<td>8.4</td>
<td>9.4</td>
<td>10.9</td>
<td>13.1</td>
<td>16.0</td>
<td>18.3</td>
</tr>
<tr>
<td>0.58</td>
<td>2.6</td>
<td>3.2</td>
<td>3.6</td>
<td>4.1</td>
<td>4.8</td>
<td>5.7</td>
<td>7.2</td>
<td>9.2</td>
<td>12.5</td>
<td>16.3</td>
</tr>
<tr>
<td>$LNO_3$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.06</td>
<td>3.8</td>
<td>4.8</td>
<td>5.6</td>
<td>6.2</td>
<td>7.0</td>
<td>7.6</td>
<td>8.6</td>
<td>9.8</td>
<td>11.1</td>
<td>12.8</td>
</tr>
<tr>
<td>0.05</td>
<td>3.9</td>
<td>5.2</td>
<td>6.2</td>
<td>6.9</td>
<td>7.6</td>
<td>8.1</td>
<td>8.7</td>
<td>9.6</td>
<td>11.0</td>
<td>12.2</td>
</tr>
</tbody>
</table>

Table 7.8 Irrigation intensity effect of chloride leaching under unsaturated flow at higher initial moisture content ($\theta_{iv} = 0.38$ cm$^3$cm$^{-3}$)

<table>
<thead>
<tr>
<th>Treat. $\dot{Q}$ cmh$^{-1}$</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
<th>90</th>
<th>95</th>
</tr>
</thead>
<tbody>
<tr>
<td>$A^+$ $HCl$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.30</td>
<td>4.8</td>
<td>5.7</td>
<td>6.4</td>
<td>7.1</td>
<td>7.7</td>
<td>8.5</td>
<td>9.6</td>
<td>11.0</td>
<td>13.4</td>
<td>15.7</td>
</tr>
<tr>
<td>0.83</td>
<td>4.5</td>
<td>5.4</td>
<td>5.9</td>
<td>6.3</td>
<td>7.0</td>
<td>7.8</td>
<td>8.9</td>
<td>10.3</td>
<td>12.7</td>
<td>15.5</td>
</tr>
<tr>
<td>$MCl$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.28</td>
<td>4.5</td>
<td>5.4</td>
<td>5.9</td>
<td>6.2</td>
<td>6.9</td>
<td>7.7</td>
<td>8.7</td>
<td>10.2</td>
<td>13.6</td>
<td>17.0</td>
</tr>
<tr>
<td>0.28</td>
<td>3.8</td>
<td>4.5</td>
<td>5.1</td>
<td>5.7</td>
<td>6.4</td>
<td>7.2</td>
<td>8.2</td>
<td>9.6</td>
<td>12.0</td>
<td>16.0</td>
</tr>
<tr>
<td>$LCl$</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.09</td>
<td>3.7</td>
<td>4.6</td>
<td>5.5</td>
<td>6.1</td>
<td>6.6</td>
<td>7.1</td>
<td>7.8</td>
<td>9.1</td>
<td>11.3</td>
<td>13.1</td>
</tr>
<tr>
<td>0.06</td>
<td>2.3</td>
<td>3.4</td>
<td>4.2</td>
<td>4.9</td>
<td>5.6</td>
<td>6.4</td>
<td>7.7</td>
<td>9.8</td>
<td>12.9</td>
<td>16.3</td>
</tr>
</tbody>
</table>

The relationship was not impressed with increasing application rate, illustrating the unsaturated character of the experiments. An increase in initial moisture content (Figure 7.3) can be achieved with water, and in agricultural practice, flow is unsaturated, where most of the large pores are suctioned and therefore flow is mainly in micropores and zones of the aggregates. This relationship was not impressed with increasing application rate, illustrating the unsaturated character of the experiments.
Table 7.9 Irrigation intensity effect on chloride and bromide leaching under unsaturated flow at lower initial moisture content ($\theta_{iv} = 0.22 \text{ cm}^3\text{ cm}^{-3}$)

<table>
<thead>
<tr>
<th>Treat.</th>
<th>$Q$ cm$^{-1}$</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
<th>90</th>
<th>95</th>
</tr>
</thead>
<tbody>
<tr>
<td>HBr</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.80</td>
<td>4.2</td>
<td>5.0</td>
<td>5.6</td>
<td>6.2</td>
<td>6.8</td>
<td>7.4</td>
<td>8.2</td>
<td>9.3</td>
<td>11.2</td>
<td>13.3</td>
<td></td>
</tr>
<tr>
<td>0.85</td>
<td>4.8</td>
<td>5.6</td>
<td>6.1</td>
<td>6.7</td>
<td>7.2</td>
<td>7.7</td>
<td>8.4</td>
<td>9.4</td>
<td>10.5</td>
<td>12.5</td>
<td></td>
</tr>
<tr>
<td>MCl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.27</td>
<td>3.1</td>
<td>3.9</td>
<td>4.5</td>
<td>5.0</td>
<td>5.5</td>
<td>6.0</td>
<td>6.8</td>
<td>7.7</td>
<td>9.3</td>
<td>11.0</td>
<td></td>
</tr>
<tr>
<td>0.27</td>
<td>4.0</td>
<td>4.5</td>
<td>5.1</td>
<td>5.5</td>
<td>6.0</td>
<td>6.4</td>
<td>7.0</td>
<td>7.6</td>
<td>10.5</td>
<td>18.5</td>
<td></td>
</tr>
<tr>
<td>LCl</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.07</td>
<td>2.7</td>
<td>3.4</td>
<td>4.0</td>
<td>4.4</td>
<td>4.8</td>
<td>5.2</td>
<td>5.7</td>
<td>6.3</td>
<td>7.0</td>
<td>7.6</td>
<td></td>
</tr>
<tr>
<td>0.07</td>
<td>2.1</td>
<td>2.6</td>
<td>3.2</td>
<td>3.8</td>
<td>4.4</td>
<td>5.3</td>
<td>6.5</td>
<td>7.9</td>
<td>9.2</td>
<td>10.5</td>
<td></td>
</tr>
</tbody>
</table>

through the larger pores and channel and hence unable to leach NO$_3^{-}$-N that is contained in the relatively immobile regions of the aggregates. This relationship was not apparent when the soil column was initially saturated (Figure 7.5) where large variability between soil cores occurred. The variability generally increased with increasing application rate, indicating variability in structural porosity, i.e. large variation in functional macroporosity resulted from variation in pore geometry between soil columns. The low variability at low application rate may be attributed again to better diffusive mixing between mobile and immobile water. It can be concluded that preferential flow was predominantly due to structural porosity. Variability is associated more with saturated flow when all soil pores are filled with water, and it is minimal when flow is unsaturated, where most of the large pores are emptied, and therefore flow is mainly in micropores.
Figure 7.5 - Effect of irrigation intensity on the pattern and extent of NO$_3^-$ leaching through undisturbed soil columns under saturated flow conditions.
Figure 7.6 - Effect of irrigation intensity on the pattern and extent of Cl⁻ leaching through undisturbed soil columns under unsaturated flow conditions at high initial soil moisture content.
Figure 7.7 - Effect of irrigation intensity on the pattern and extent of solute leaching through undisturbed soil columns under unsaturated flow conditions at low soil moisture content
7.2.5 Effect of initial moisture content

In Figure 7.8 (data from Table 7.10) representative data for $S_{rem}/S_{app}$ with three different antecedent soil moisture content, ranging from the lowest to the highest ($0.16$ to $0.36$ cm$^3$ cm$^{-3}$) are plotted against the irrigation water depth ($I$-cm). The average irrigation application rate was $(0.95 \pm 0.04$ cm h$^{-1}$) during the leaching process. The figure shows that the lower the initial soil moisture content the greater was the irrigation depth needed to leach the same amount of solute applied ($Br^-$) with similar irrigation intensity. Flow will only be maintained in the macropores if the immediate soil micropores are saturated. Thus more irrigation water is needed for the low initial moisture content treatment to reach the stage of micropore saturation than for those with high initial soil moisture content. The movement of the applied water into micropores was much reduced at the higher initial soil moisture content, i.e. the applied irrigation water carrying the solute mainly moved in large pores during the early stage of the leaching process, resulting in early appearance of the solute in the effluent. The figure also indicates slight variability between replicates. These small variations indicate low soil structural variability between soil column of the same replicates.

7.2.6 Effect of time of equilibration before leaching

In Figure 7.9 (data from Table 7.11) representative data for $S_{rem}/S_{app}$ with four different tracer redistribution patterns namely, waiting and non-waiting period and either dry or wet conditions, are plotted against the irrigation depth applied ($I$-cm). The tracer Cl$^-$ was allowed to redistribute within the soil column either under evaporative or wet conditions, both at room temperature.
Figure 7.8 - Effect of initial soil moisture content at the pattern and extent of Br⁻ leaching through undisturbed soil columns under unsaturated flow conditions.
Table 7.10 Effect of soil initial moisture content on bromide leaching under unsaturated flow at high flow velocity (Q = 0.95 cm h\(^{-1}\))

<table>
<thead>
<tr>
<th>Treat.</th>
<th>( \theta_i ) cm(^{3}) cm(^{-3})</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
<th>90</th>
<th>95</th>
</tr>
</thead>
<tbody>
<tr>
<td>A(^+)-HBr</td>
<td>0.38</td>
<td>4.5</td>
<td>5.3</td>
<td>5.7</td>
<td>6.2</td>
<td>6.7</td>
<td>7.2</td>
<td>7.7</td>
<td>8.6</td>
<td>10.0</td>
<td>12.0</td>
</tr>
<tr>
<td></td>
<td>0.34</td>
<td>4.7</td>
<td>5.4</td>
<td>6.0</td>
<td>6.5</td>
<td>7.0</td>
<td>7.6</td>
<td>8.2</td>
<td>9.4</td>
<td>10.9</td>
<td>14.0</td>
</tr>
<tr>
<td>A-HBr</td>
<td>0.24</td>
<td>4.2</td>
<td>5.0</td>
<td>5.6</td>
<td>6.2</td>
<td>6.8</td>
<td>7.4</td>
<td>8.2</td>
<td>9.3</td>
<td>11.2</td>
<td>13.3</td>
</tr>
<tr>
<td></td>
<td>0.24</td>
<td>4.8</td>
<td>5.6</td>
<td>6.1</td>
<td>6.7</td>
<td>7.2</td>
<td>7.7</td>
<td>8.4</td>
<td>9.4</td>
<td>10.5</td>
<td>12.5</td>
</tr>
<tr>
<td>D-HBr</td>
<td>0.17</td>
<td>5.2</td>
<td>5.8</td>
<td>6.4</td>
<td>7.0</td>
<td>7.6</td>
<td>8.4</td>
<td>9.1</td>
<td>10.3</td>
<td>12.1</td>
<td>14.3</td>
</tr>
<tr>
<td></td>
<td>0.14</td>
<td>5.4</td>
<td>6.0</td>
<td>6.6</td>
<td>7.1</td>
<td>7.8</td>
<td>8.4</td>
<td>9.2</td>
<td>10.2</td>
<td>12.8</td>
<td>15.7</td>
</tr>
</tbody>
</table>

No redistribution was allowed for Br\(^-\); irrigation was immediately applied after the tracer disappearance from the soil surface of the dry or wet column. The figure shows that when redistribution occurred under evaporative conditions, the irrigation depth needed for solute leaching was greater than when redistribution occurred under wet conditions. In addition, allowing for solute redistribution under either dry or wet conditions was more effective in protecting solute from leaching than when no redistribution was allowed. The reason for this is that the applied water was moving mainly through large pores and channels, and possibly bypassed the solute which was contained largely in the immobile regions of the soil.
Figure 7.9 - Effect of time of equilibration on the pattern and extent of solute leaching through undisturbed soil columns under unsaturated flow conditions.
Table 7.11 The effect of time of equilibration of chloride and bromide leaching under unsaturated flow

<table>
<thead>
<tr>
<th>Treat. Q cmh⁻¹</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
<th>90</th>
<th>95</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-HCl 1.06</td>
<td>4.9</td>
<td>5.5</td>
<td>6.2</td>
<td>7.0</td>
<td>7.9</td>
<td>9.1</td>
<td>11.3</td>
<td>15.1</td>
<td>24.9</td>
<td>38.0</td>
</tr>
<tr>
<td>B-HCl 0.95</td>
<td>4.8</td>
<td>5.6</td>
<td>6.3</td>
<td>7.0</td>
<td>7.8</td>
<td>8.7</td>
<td>9.9</td>
<td>12.1</td>
<td>17.5</td>
<td>28.0</td>
</tr>
<tr>
<td>C-HCl 0.95</td>
<td>3.9</td>
<td>4.7</td>
<td>5.1</td>
<td>5.6</td>
<td>6.0</td>
<td>6.6</td>
<td>7.4</td>
<td>8.4</td>
<td>10.0</td>
<td>12.1</td>
</tr>
<tr>
<td>C-HCl 0.95</td>
<td>4.2</td>
<td>5.1</td>
<td>5.7</td>
<td>6.3</td>
<td>6.7</td>
<td>7.2</td>
<td>8.1</td>
<td>9.5</td>
<td>12.2</td>
<td>17.8</td>
</tr>
<tr>
<td>A-HBr 0.85</td>
<td>4.2</td>
<td>5.0</td>
<td>5.6</td>
<td>6.2</td>
<td>6.8</td>
<td>7.4</td>
<td>8.2</td>
<td>9.3</td>
<td>11.2</td>
<td>13.3</td>
</tr>
<tr>
<td>A-HBr 0.85</td>
<td>4.8</td>
<td>5.6</td>
<td>6.1</td>
<td>6.7</td>
<td>7.2</td>
<td>7.7</td>
<td>8.4</td>
<td>9.4</td>
<td>10.5</td>
<td>12.5</td>
</tr>
<tr>
<td>D-HBr 1.06</td>
<td>5.2</td>
<td>5.8</td>
<td>6.4</td>
<td>7.0</td>
<td>7.6</td>
<td>8.4</td>
<td>9.1</td>
<td>10.3</td>
<td>12.1</td>
<td>14.3</td>
</tr>
<tr>
<td>D-HBr 1.06</td>
<td>5.4</td>
<td>6.0</td>
<td>6.6</td>
<td>7.1</td>
<td>7.8</td>
<td>8.4</td>
<td>9.2</td>
<td>10.2</td>
<td>12.8</td>
<td>15.8</td>
</tr>
</tbody>
</table>

aggregates. On the other hand, when solute had recently been applied to the soil column, it was held on the outside of the aggregate, thus the passing flow caused it to leach faster. It can be concluded that the presence of solute in an immobile phase retards leaching when bypass flow occurs. This has an important implication for NO₃⁻-N fertilizer management in structured soils as mentioned earlier.

7.2.7 Effect of replication

a. Saturated flow: NO₃⁻-N

Figure 7.5 (Table 7.7) indicates that, under saturated conditions, the agreement between the replicates of the same treatment was better at lower application rate, whereas differences were higher at higher application rate. This means that the lower the flow rate the less
is the variability among the cores when saturated flow occurs. Part of the variability was due to the differences in flow rate of the same replicate. The flow rate for the same replicate differed by a factor of 0.67, 0.23 and 0.21 from the highest to the lowest (Table 7.7). The restriction of the flow rate in the treatment with the slow applicate rate was applied differently i.e. at the top and bottom of the soil column. Even though the variability was minimal, it could explain part of the variability, but it was not a major factor.

b. Unsaturated flow

1. Cl⁻

Figure 7.6 and 7.7 (also Tables 7.8 and 7.9) illustrate that under unsaturated flow the agreement among the replicates was quite good, indicating slight variability between the cores of similar flow rates. This suggests that the soil showed an overall uniform structure. The variability observed at the earlier stages of the leaching process (due to differences in the efficacy of macropores in conducting water) was overcome later on by diffusion, as leaching water flowed through the columns.

2. Br⁻

Figure 7.8, with additional data in Table 7.10, shows a similar relationship between replicates as with Cl⁻ mentioned above. The agreement among the Br⁻ replicates having similar initial moisture content was even better than those among Cl⁻ cores. The figure generally indicates that the drier the soil the smaller is the variability under unsaturated flow conditions. This is because more of the soil micropores are involved in transport, particularly at earlier stages of the leaching process.
In general, it seems that the number of replications planned in this experiment was sufficient for unsaturated flow runs. The higher variability observed with saturated columns, reflects, firstly, difference in soil conditions. Core collection from the field for the saturated flow was a year earlier. Secondly, under saturated flow, the incoming water was mainly flowing down macropores, and differences in functional macroporosity among the cores of the same replicate led to this variation in conducting water. Thirdly, variation in the rate of application (irrigation intensities) within the same replicate, was also a factor and exerted an influence in producing greater variability.
CHAPTER VIII

DISCUSSION

To be able to simulate and predict nitrate leaching losses, it is necessary to combine soil N transformations, plant uptake, and nitrate transport with water flow as described by Equations (5.2) and (5.5). If the other inputs and outputs were known, the first equation could be used to calculate leaching loss of $\text{NO}_3^-\text{N}$ by difference. This would be useful if the other inputs and outputs were easy to measure or predict, but extensive literature on the mineral N mass balance in soil show this is not usually, so as reported by Wild and Cameron (1980a).

The results of the $^{15}\text{N}$ experiment at Aberlady are summarized in the form of a comparison between the observed and predicted distribution of $^{15}\text{NO}_3^-\text{N}$ tracer in the crop root zone following the application of $\text{Ca}^{15}(\text{NO}_3)_2$ fertilizer to the micro-plots under a potato crop and summer rainfall (Figure 8.1).

Predictions were made using the analytical equation of Rose (Equation 6.7, Rose et al., 1982b), and the simple leaching equation of Burns (Equation 5.5, Burns, 1976), assuming that the $^{15}\text{NO}_3^-\text{N}$ fertilizer applied mixed uniformly with the soil in the ridges (10 cm). The field capacity of the soil was 0.20 (cm$^2$ cm$^{-2}$). The dispersivity, $m$, needed for Rose model was experimentally determined in an undisturbed soil column under saturated flow, and the molecular diffusion of nitrate was assumed to be 0.10 (cm$^2$ day$^{-1}$) at the field capacity. Both models assume zero crop uptake, no biological transformation, and no other losses of $\text{NO}_3^-\text{N}$ other than leaching. Figure 8.1 showed that both model predictions show poor agreement.
Figure 8.1 - Comparison of mean observed and predicted $^{15}\text{NO}_3-N$ distribution in soil following application of Ca$^{15}\text{NO}_3$ fertilizer to microplots in potatoes at Aberlady (1985).
with the mean of the measured \(^{15}\text{NO}_3^-\text{N} \) distributions on the first sampling date. Clearly, more tracer was recovered in the soil (ridges) than predicted on the first sampling date. The effect was less pronounced on the second date but still occurred. On the third sampling date, the observed \(^{15}\text{NO}_3^-\text{N} \) in the ridges was minimal, presumably because of large crop uptake by this time. Both models suggest that the fraction of \(^{15}\text{NO}_3^-\text{N} \) fertilizer lost was leached below the sampling depth, but the observed distribution of \(^{15}\text{NO}_3^-\text{N} \) suggests near-zero losses below the crop root zone, with much of it retained in the ridge up to the second sampling date despite the occurrence of large water movement \((D = 11.1 \text{ cm})\). However, recovery of \(^{15}\text{NO}_3^-\text{N} \) was poor (Table 8.1) so some appears to have been lost in some way. We have, then, two seemingly contradictory observations from these comparisons between models and the observed distribution of \(^{15}\text{NO}_3^-\text{N} \):

A) The very low leaching efficiency of the \(^{15}\text{NO}_3^-\text{N} \) fertilizer recovered compared with the model predictions.

B) The poor overall recovery of the tracer in crop and root zone. Most of this loss of \(^{15}\text{NO}_3^-\text{N} \) occurred prior to crop emergence.

Considering the first point, the possible reasons are: (i) immobility of a large fraction of the soil water during the process of leaching; (ii) over-estimation of the drainage term in the water balance; (iii) influence of uptake of \(^{15}\text{NO}_3^-\text{N} \) tracer by the soil biomass or by the crop.

The results from undisturbed soil columns from the same site under saturated flow suggest that in this study only a quarter (and 6 per cent due to observed anion exclusion,
Table 8.2) of the water filled porosity was not involved in \( \text{NO}_3^- \)-N transport, the rest being mobile. Water movement in the field often occurs under unsaturated flow, and low irrigation or rainfall intensity, in which case immobile water becomes less important. Therefore, it is likely that immobile water in this soil was not a major factor in the protection of \( ^{15}\text{NO}_3^- \)-N from loss by leaching. It is unlikely that drainage was seriously overestimated, because weekly monitoring of soil water (neutron probe) was carried out. At the first sampling date, crop uptake of \( ^{15}\text{NO}_3^- \)-N was small (only 3 per cent of the total applied), therefore the results point to temporary microbial uptake of tracer as suggested by Neeteson et al. (1985). These authors found an apparent uptake and subsequent release of N fertilizer over a period of thirty days in a range of arable soils, and they postulated that it was due to osmotic adjustment by soil micro-flora. However, Legg and Stanford (1967) suggested that \( \text{NO}_3^- \)-N is not readily taken up by micro-organisms, \( \text{NH}_4^+ \)-N being the preferred form of nitrogen.

Considering now the overall recovery of tracer, the losses may have been due to (a) denitrification, which occurs most readily under wet spring conditions after fertilizer N application (Batey and Killham (1985) observed a rate of loss up to 3 kg ha\(^{-1}\) day\(^{-1}\) on a sandy soil near Aberdeen during the same periods); (b) rapid leaching, if only a small portion of the soil water were mobile. In this case, when flow occurs solute present in the mobile water will be rapidly leached potentially below the sampling depth. The rest of the solute would move more slowly than the models predicted. The presence of the immobile water in this soil was discussed earlier and column experiments showed no major effect. Thus, it is likely that the main process responsible for poor recovery of \( ^{15}\text{NO}_3^- \)-N was denitrification. The wet spring, and the
single of a standard rate of N fertilizer in a mobile form, as well as the late crop emergence, were all likely to be contributing factors making the denitrification loss large. The uncertainty about the possible uptake and subsequent release of $^{15}$NO$_3^{-}$-N by soil micro-organisms makes it difficult to confirm which are the most influential processes affecting the distribution of the recovered $^{15}$NO$_3^{-}$-N and the overall recovery. It is clear that more work is necessary to determine whether the uptake by soil micro-organisms of NO$_3^{-}$-N can explain the poor mass balance of the tracer applied, and/or its distribution.

A subsidiary objective which arises is to compare the results observed in the column experiments with predictions of the models used in the field study. The findings are represented in Figure 8.2. Good agreement was obtained from a comparison between the model of Rose and the observed NO$_3^{-}$, Cl$^{-}$ or Br$^{-}$ BTCs from a column used for a second run with Cl$^{-}$. This is because: (a) the experimentally obtained dispersivity ($m$) was introduced to the model; (b) the mass balance for all tracers approached unity in most cases, indicating minimal nitrate nitrogen biological transformation and minimal losses other than loss by leaching.

The figure also shows that poor agreement was obtained when comparison was made between the Burns' model and the experimental results. The main reason for the poor relationships seems to be that Burns' equation does not presuppose the effect of dispersion which therefore increases the irrigation depth needed to leach similar fraction of tracer applied (e.g. the irrigation needed to leach 50 percent of the tracer applied "Cl$^{-}$" were 1.6 and 1.4 times higher than those observed and predicted by Rose model respectively). However, in terms of recovery,
Fraction remaining in soil \( \left( \frac{S_{\text{rem}}}{S_{\text{app}}} \right) \) = 0.36
Flow velocity (cm day\(^{-1}\)) = 24.3
Dispersion Coefficient (cm\(^2\) day\(^{-1}\)) = 51.0
Solute pulse (PVf) = 0.047
L = 25 cm

\( \theta_r \) (cm\(^3\) cm\(^{-3}\))

Figure 8.2 - Comparison of measured and predicted Cl\(^-\) pattern and extent of leaching through undisturbed soil column under unsaturated flow conditions
though not distribution under field conditions, Burns' model seems to do reasonably well (Table 8.1), especially when plant uptake and/or transformation, other N losses are minimal.

Table 8.1 Observed and estimated $^{15}$NO$_3$-N losses by leaching ($^{15}$N$_{(o)}$L) from $^{15}$N fertilized potatoes micro-plots during the 1985 growing season at Aberlady.

<table>
<thead>
<tr>
<th>Date</th>
<th>Observed$^a$</th>
<th>Burns</th>
<th>Model Prediction$^b$</th>
<th>Rose</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Kg ha$^{-1}$</td>
<td>%</td>
<td>Kg ha$^{-1}$</td>
<td>%</td>
</tr>
<tr>
<td>14/6</td>
<td>66.6</td>
<td>41</td>
<td>46.9</td>
<td>29</td>
</tr>
<tr>
<td>3/7</td>
<td>78.1</td>
<td>49</td>
<td>71.4</td>
<td>45</td>
</tr>
<tr>
<td>15/8</td>
<td>71.2</td>
<td>45</td>
<td>84.4</td>
<td>53</td>
</tr>
</tbody>
</table>

a. Calculated as "unaccounted for" $^{15}$N.

b. Assuming zero plant uptake.

Table 8.2 Range of values for mean water content, effective water content and calculated NO$_3$-anion exclusion water content from columns under saturated flow (1986)

<table>
<thead>
<tr>
<th>Treatment</th>
<th>$\Omega$ (cm sec$^{-1}$)</th>
<th>$\theta_v$</th>
<th>$\theta_{st}$</th>
<th>$\theta_{ex}$</th>
<th>$\theta_{im}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HNO$_3$</td>
<td>1000 (35.4)</td>
<td>0.46 (0.06) *</td>
<td>0.33 (0.02)</td>
<td>0.06 (0.01)</td>
<td>0.13 (0.03)</td>
</tr>
<tr>
<td>MNO$_3$</td>
<td>14.5 (1.5)</td>
<td>0.49 (0.07)</td>
<td>0.36 (0.01)</td>
<td>0.06 (0.01)</td>
<td>0.13 (0.02)</td>
</tr>
<tr>
<td>LNO$_3$</td>
<td>1.6 (0.1)</td>
<td>0.47 (0.04)</td>
<td>0.35 (0.00)</td>
<td>0.06 (0.00)</td>
<td>0.12 (0.04)</td>
</tr>
</tbody>
</table>

( ) *Figures in brackets are standard error (s.e)

sample size = 2
CHAPTER IX

SUMMARY AND CONCLUSIONS

This study was undertaken for three reasons. First, to construct nitrate mass balance which provides the basis for estimating $\text{NO}_3^-$ gains, losses and transformations for any agricultural system. This information was sought by the School of Agriculture, Edinburgh University, as part of a major concern with more efficient utilization of nitrogen by arable crops and with minimizing pollution problems.

The second was to describe the transport processes in more detail, in order to obtain information about dispersion length and the presence or absence of immobile water. The third reason was to compare the results observed in the field with model predictions to test the applicability of the models.

In terms of the first objective, the field-scale $^{15}\text{NO}_3^-$ mass balance under a potato crop in fertilized micro-plots was attempted in a cold and wet spring, and abnormal wet summer. Due to the late crop emergence, only 52 per cent of the $^{15}\text{NO}_3^-$ fertilizer was recovered in the crop, 4 percent retained in the soil, and the rest was attributed to loss by leaching. Most of the overall losses observed were lost early in the season prior to crop emergence. Losses of nitrate by leaching were greatly reduced as the crop uptake of $\text{NO}_3^-$ increased and crop uptake therefore was a major factor in protecting nitrate from loss by leaching.

These excessive nitrate losses by leaching from such a light textured soil are not surprising, in view of the
fact that excess water was present in the soil profile throughout the course of the experiment. The nitrate concentration in the soil solution was also high at the start of the experiment. The excess water was due to (i) an abnormal wet summer; (ii) the low water holding capacity of the soil; (iii) late crop emergence. The single application of a standard rate of fertilizer in a mobile form was responsible for the higher nitrate concentration in the crop root zone. These are the main two prerequisites for leaching to occur and losses can be large.

The unaccounted for $^{15}$NO$_3^-$-N was higher than that predicted by Burns' equation and Rose's model, up to the first sampling date, and was later greatly decreased. Considering the third objective, comparison between the calculated unaccounted for N and the model predictions were made. Poor agreement was obtained between unaccounted for N and both model predictions, indicating that more tracer was retained in the soil ridges than predicted. This was attributed to low leaching efficiency due to the presence of immobile water, microbial uptake and subsequent release. In terms of the second objective the theory of immobile water was not supported by the results of column experiments; immobile water was only a quarter of the total soil water, and cannot explain fully the large protection of nitrate. It is likely, therefore, that the temporary uptake of $^{15}$NO$_3^-$-N was a contributory factor. However, the poor mass balance observed earlier up to crop emergence suggests that three possible processes were responsible for the rapid loss, namely, permanent uptake by soil-biomass, denitrification, or a large fraction of soil water being immobile. Again, as indicated above, immobile water was not a major contributing factor. The uncertainty about the soil biomass uptake makes it difficult to confirm that
denitrification was responsible. It is clear, therefore, that there is a need for further investigation to see whether uptake of nitrate by soil micro-organisms can explain the poor mass balance and/or its distribution.

Both models were tested against the observed results of the column experiments, and the Rose model was much more successful than the model of Burns, due to the fact that experimentally-obtained dispersivity was included in the former, while the latter presupposes that there is no effect due to dispersion length on the extent of leaching.

In terms of overall recovery of the tracer and not its distribution, the model of Burns was more successful than Rose's analytical equation, under field conditions.


BURNS, I.G. (1976) Equations to predict the leaching of nitrate uniformly incorporated to a known depth or uniformly distributed throughout a soil profile. J. Agric. Sci., 86, 305 - 313.

BURRELL, R.E.; SCHUMAN, G.E.; SAXTON, K.E. and HEINEMANN,
H.G. (1976) Nitrogen in subsurface discharge from
Cameron, K.C. and WILD, A. (1982b) Prediction of solute
leaching under field conditions: An appraisal of
Cameron, K.C. and HAYNES, R.J. (1986) Retention and
movement of nitrogen in soils. In "Mineral
Nitrogen in the Plant-Soil System" (R.J. Haynes,
Press.
from nitrate leaching following the plowing of
temporary grassland. J. Environ. Qual., 13, 274 -
278.
and fertility. p. 173 - 271. In M. Schnitzer and
S.V. Kahn (eds.) Soil organic matter; developments
York.
CHANK, R.C. (1975) Toxicity of N-nitroso compounds.
CHICHESTER, F.W. (1977) Effects of increased fertilizer
rates on nitrogen content of runoff and percolate
from monolithysimeters. J. Environ. Qual., 6, 211
- 217.
peotic licence In "Terrestrial nitrogen cycles"
COATS, K.H. and SMITH, R.D. (1964) Dead end pore volume
and dispersion in porous media. Society of
Petroleum Engineering Journal, 4, 73 - 84.
COOKE, G.W. and WILLIAMS, R.J.B. (1970) Losses of
nitrogen, and phosphorous from agricultural land.
Water treatment and Examination, 19, 253 - 276.
CRISP, D.T. (1966) Input and output of minerals for an
area of Pennine moorland. The importance of
precipitation, drainage, peat erosion and animals.
CROSBY, N.T. and SAWYER, R. (1976) N-nitrosamines: A
review of chemical and biological properties and
22, 1 - 71.
II. Changes in levels of inorganic nitrogen in a
clay loam soil caused by fertilizer application, by
leaching and uptake by grass. J. Sci. Food Agri., 9,
317 - 324.
DAGAN, G. and BRESLER, E. (1979) Solute dispersion in
unsaturated heterogenous soil at field scale. I.


△ Mixing in glass beads


RIGA, A., FISCHER, V. and VAN PRAAG, H.J. (1980) Fate of fertilizer nitrogen applied to winter wheat as Na\textsubscript{15}NO\textsubscript{3} and (15\textsuperscript{NH}_\textsubscript{4})\textsubscript{2}SO\textsubscript{4} studied in microplots through a four-course rotation: 1. Influence of fertilizer splitting on soil and fertilizer nitrogen. Soil Sci., 130, 88 - 89.


VIETS, F.G.; HAMBERT, R.P. and NELSON, C.E. (1967)
Fertilizers in relation to irrigation. In
"Irrigation in Agricultural lands" (R.M. Hagan, H.R.

VIETZ, F.G. Jr. and HAGEMAN, R.H. (1971) Accumulation
of nitrate in soil, water, and plants. Agric.

VINOGRAOV, A.P. (1959) The geochemistry of rare and
dispersed chemical elements in soils, second ed.
Consultants Bruea, Inc. New York.

VINTEN, A.J.V.; YAZID, S.; NAYSMITH, D.B. and PARKES, M.
(1987) Solute leaching in light-texture soils:
prediction of solute leaching in light textured
soils using a chromatographic plate method.

In "Terrestrial Nitrogen Cycles: Processes,
Ecosystem strategies and management impacts" (F.E.
Clark and T. Rosswall, eds.) pp. 631 - 642.

In "Chemical Mobility and Reactivity in Soil
Systems" (D.W. Nelson et al., eds.) Special
publication of the Americna Society of Agronomy,
Madison, Wisconsin.

WESTERMAN, R.O.L. and KURTZ, L.T. (1973) Priming effect
of $^{15}$N labelled fertilizers on soil nitrogen in
field experiments. Soil Sci. Soc. Am. Proc., 37,
775 - 727.

and salts plus nitrogen-15-labelled ammonium
chloride in mineralization of soil nitrogen,
Am. Proc., 38, 602 - 605.

WHITE, R.E.; THOMAS, G.W. and SMITH, M.S. (1984)
Modelling water flow through undisturbed soil cores
using a transfer function model derived from $^{3}$HOH

WHITE, R.E. (1985) The influence of macropores on the
transport of dissolved and suspended matter through
soil. In "Advance in Soil Science" (B.A. Stewart,
under bare fallow at a
site in northern Nigeria. J. Soil Sci., 23, 315 -
324.

WIKLANDER, L. and VAHTRAS, K. (1975) Leaching of plant
nutrients in soils. II Loss of nitrogen as
influenced by the form of fertilizer. Acta Agric.

WILD, A. (1972) Nitrate leaching under bare fallow at a
site in northern Nigeria. J. Soil Sci., 23, 315 -
324.


APPENDICES

APPENDIX A: List of major symbols and definitions

\[ C_{\text{app}} \]  
Solute pulse concentration applied at soil surface - \( \text{ug cm}^{-3} \)

\[ C_{\text{ex}} \]  
Effluent solute concentration - \( \text{ug cm}^{-3} \)

\[ S_{\text{ex}} \]  
Amount of solute in effluent - \( \text{ug} = C_{\text{ex}} V_{\text{ex}} \)

\[ S_{\text{rem}} \]  
Solute amount remaining in soil profile - \( \text{ug} \)

\[ B.D \]  
Dry bulk density of soil - \( \text{g cm}^{-3} \)

\[ P.d \]  
Soil particle density - \( 2.65 \text{ g cm}^{-3} \)

\[ A_s \]  
Soil column cross sectional area - \( \text{cm}^2 \)

\[ I \]  
Irrigation depth - \( \text{cm} \)

\[ S_{\text{app}} \]  
Amount of solute applied - \( \text{ug} = C_{\text{app}} V_{\text{app}} \)

\[ m \]  
Pore space ratio

\[ E \]  
Dispersivity - \( \text{cm} \)

\[ U \]  
Dispersion coefficient - \( \text{cm}^2 \text{Sec}^{-1} \)

\[ K_{\text{sat}} \]  
Pore water velocity - \( \text{cm Sec}^{-1} = Q/O_{\text{st}} \)

\[ K \]  
Saturated hydraulic conductivity - \( \text{cm sec}^{-1} \)

\[ \Delta F \]  
Tracer slug length - \( \text{cm} \)

\[ Q \]  
Flow velocity - \( \text{cm sec}^{-1} \)

\[ V_{\text{ex}} \]  
Sample size

\[ n \]  
Effluent volume - \( \text{cm}^3 \)

\[ V_o \]  
Water filled pore volume - \( \text{cm}^3 \)

\[ V_s \]  
Total volume of moist soil - \( \text{cm}^3 \)

\[ V_{\text{app}} \]  
Volume of solute pulse applied - \( \text{cm}^3 \)

\[ V_p \]  
Effluent volume at peak position of BTCs - \( \text{cm}^3 \)

\[ V_{\text{st}} \]  
Transport volume as a fraction of water-filled pore volume (pvf)

\[ V_{\text{mod}} \]  
Effluent volume as a fraction of water-filled pore volume at peak position of BTC (pvf)

\[ D_0 \]  
Molecular diffusion coefficient \( \text{cm}^2 \text{ sec}^{-1} \)

\[ V_{\text{med}} \]  
Effluent volume as a fraction of water-filled pore volume at \( (S_{\text{ex}}/S_{\text{app}} = 0.5) \)(pvf)

\[ V_{\text{in}} \]  
Input volume (pvf)
$V_{0.5}$  \text{Effluent volume at } (S_{ex}/S_{app} = 0.5) - \text{cm}^3

$V_m$  \text{Effluent volume at solute mass centre location} - \text{cm}^3

$V_{im}$  \text{Immobile volume as a fraction of water-filled pore volume (pvf)}

$\theta_w$  \text{Gravimetric water content} - \text{g g}^{-1}

$\theta_{iw}$  \text{Initial gravimetric water content} - \text{g g}^{-1}

$\theta_v$  \text{Volumetric water content} - \text{cm}^3 \text{ cm}^{-3}

$\theta_{iv}$  \text{Initial volumetric water content} - \text{cm}^3 \text{ cm}^{-3}

$\theta_{fw}$  \text{Final gravimetric water content} - \text{g g}^{-1}

$\theta_{fv}$  \text{Final volumetric water content} - \text{cm}^3 \text{ cm}^{-3}

$\theta_{im}$  \text{Immobile fraction of soil water content} - \text{cm}^3 \text{ cm}^{-3}

$\theta_{st}$  \text{Transport volume as a fraction of soil water content} - \text{cm}^3 \text{ cm}^{-3}

$\theta_{med}$  \text{Effluent volume as a fraction of soil water content at } (S_{ex}/S_{app} = 0.5) - \text{cm}

$\theta_{mod}$  \text{Effluent volume as a fraction of soil water content at } (C_{ex}/C_{app})_{max} - \text{cm}^3 \text{ cm}^{-3}

$\theta_v$  \text{Average volumetric water content} - \text{cm}^3 \text{ cm}^{-3}

$\Delta H$  \text{Hydraulic head difference across soil column} - \text{cm}

$H$  \text{Hydraulic potential} - \text{K Pa}

$t$  \text{Observation time} - \text{sec}

$F$  \text{Solute flux} - \text{ug sec}^{-1}

$D_s$  \text{Effective diffusion coefficient in soil} - \text{cm}^2 \text{ sec}^{-1}

$a$  \text{F}

$L$  \text{Core length and reference depth of measurement} - \text{cm}

$N$  \text{Solute distribution between soil and solution}

$S$  \text{Rate of solute production or disappearance} - \text{ug cm}^{-3} \text{ sec}^{-1}

$erfc$  \text{Complementary error function}

$a$  \text{Distance moved by the solute peak} \text{cm}

$x_0$  $\Delta F/g_{st}$
Solute leaching in light-textured soils: prediction of solute leaching in light-textured soils using a chromatographic plate method

A. J. A. Vinten, S. Yazid, D. B. Naysmith and M. E. Parkes

ABSTRACT: The leaching of non-adsorbed tracer ions was studied at two field sites and in undisturbed columns. Results of field work are compared with leaching predicted using a simple chromatographic plate model. This comparison shows that in most cases less leaching than...
### Editorial Board

<table>
<thead>
<tr>
<th>Name</th>
<th>Affiliation</th>
<th>Position</th>
</tr>
</thead>
<tbody>
<tr>
<td>B. J. BLUCK</td>
<td>University of Glasgow</td>
<td>(Executive Editor)</td>
</tr>
<tr>
<td>P. E. BROWN</td>
<td>University of Aberdeen</td>
<td>(Chairman)</td>
</tr>
<tr>
<td>E. N. K. CLARKSON</td>
<td>University of Edinburgh</td>
<td>(Executive Editor)</td>
</tr>
<tr>
<td>S. CRAMPIN</td>
<td>British Geological Survey</td>
<td></td>
</tr>
<tr>
<td>C. D. WATERSTON</td>
<td>Royal Society of Edinburgh</td>
<td>General Secretary</td>
</tr>
<tr>
<td>B. HARTE</td>
<td>University of Edinburgh</td>
<td>(Executive Editor)</td>
</tr>
<tr>
<td>R. MCQUILLIN</td>
<td>Britoil plc.</td>
<td></td>
</tr>
<tr>
<td>I. PARSONS</td>
<td>University of Aberdeen</td>
<td></td>
</tr>
<tr>
<td>V. B. PROUDFOOT</td>
<td>University of St. Andrews</td>
<td></td>
</tr>
<tr>
<td>W. RITCHIE</td>
<td>University of Aberdeen</td>
<td></td>
</tr>
<tr>
<td>B. G. J. UPTON</td>
<td>University of Edinburgh</td>
<td></td>
</tr>
<tr>
<td>W. DUNCAN</td>
<td>Royal Society of Edinburgh</td>
<td>Executive Secretary</td>
</tr>
</tbody>
</table>

### Consulting Editors

<table>
<thead>
<tr>
<th>Name</th>
<th>Affiliation</th>
</tr>
</thead>
<tbody>
<tr>
<td>H. P. BANKS</td>
<td>Cornell University, Ithaca</td>
</tr>
<tr>
<td>R. G. C. BATHURST</td>
<td>University of Liverpool</td>
</tr>
<tr>
<td>J. M. COLEMAN</td>
<td>Louisiana State University, Baton Rouge</td>
</tr>
<tr>
<td>J. F. DEWEY</td>
<td>University of Oxford</td>
</tr>
<tr>
<td>R. W. HUTCHINSON</td>
<td>Colorado School of Mines</td>
</tr>
<tr>
<td>E. JÄGER</td>
<td>Universität Bern</td>
</tr>
<tr>
<td>J. KONTA</td>
<td>Charles University, Prague</td>
</tr>
<tr>
<td>K. J. MÜLLER</td>
<td>Rhein. Friedrich-Wilhelms-Universität</td>
</tr>
<tr>
<td>J. V. SMITH</td>
<td>University of Chicago</td>
</tr>
<tr>
<td>D. F. STRONG</td>
<td>Memorial University, St Johns</td>
</tr>
<tr>
<td>V. C. THAKUR</td>
<td>Wadia Institute of Himalayan Geology</td>
</tr>
<tr>
<td>S. UYEDA</td>
<td>University of Tokyo</td>
</tr>
<tr>
<td>O. VAN BREEMEN</td>
<td>Geological Survey of Canada, Ottawa</td>
</tr>
<tr>
<td>R. WOODALL</td>
<td>Western Mining Co., Adelaide</td>
</tr>
</tbody>
</table>

*Publications Secretary, Royal Society of Edinburgh: E. A. Ingpen*
Solute leaching in light-textured soils: prediction of solute leaching in light-textured soils using a chromatographic plate method

A. J. A. Vinten, S. Yazid, D. B. Naysmith and M. E. Parkes

ABSTRACT: The leaching of non-adsorbed tracer ions was studied at two field sites and in undisturbed columns. Results of field work are compared with leaching predicted using a simple chromatographic plate model. This comparison shows that in most cases less leaching than predicted occurs. This suggests that nitrate ions may be protected from leaching in field soils because of the presence of immobile water, and column experiments support this hypothesis. The extent of protection is larger than observed in other work for soils of similar texture.

KEY WORDS: Bromide, dispersion, immobile water, water balance, $^{15}$N.

The poor efficiency with which fertiliser nitrogen is used by crops results in financial losses for farmers and increased amounts of nitrate nitrogen in surface and ground waters. One of the most important reasons is the leaching of nitrate nitrogen from the root zone during periods when rainfall and irrigation exceed water use by the crop. These losses occur chiefly in winter when soils are generally at or above 'field capacity', but may also occur in summer especially when high levels of nitrogen fertiliser have been applied and excess rainfall or irrigation occurs. It is with the latter case that we deal in this paper.

One of the keys to more efficient utilisation of nitrogen and to minimising pollution problems is to be able to predict how much nitrate nitrogen has been lost from the root zone. This is not an easy task because of (1) the variety of sinks and sources of nitrate nitrogen in the root zone (crop uptake, mineralisation and nitrification, denitrification, immobilisation by soil microflora, etc.), (2) the uncertainty, due to soil spatial variability, about the quantities of water passing through the root zone as drainage water, (3) the uncertainty about the efficiency with which nitrate nitrogen is leached by water passing through the root zone.

In the experimental work reported here we have tried to avoid problem (1) by using an analog of $\text{NO}_3^-$, namely $\text{Br}^-$, to study the physical process of leaching of a surface-applied solute. $\text{Br}^-$ does not undergo many of the transformations which $\text{NO}_3^-$ undergoes in the soil. The leaching of $\text{Br}^-$ during the growing season of two crops, lettuce and potatoes, was studied on an intensive horticultural farm in Fife and results are compared with the predictions of a simple chromatographic plate model. This approach was used by Smith et al. (1984). But their analysis was hampered by uptake of $\text{Br}^-$ by the crop. An attempt was made in this work to avoid this problem by applying an excess of $\text{Cl}^-$ with the $\text{Br}^-$ tracer. $\text{Cl}^-$ acts as a competitive inhibitor of $\text{Br}^-$ uptake (Epstein 1972). Results of field experiments with $\text{NO}_3^-$ and from column experiments are also presented. Problem (2) was tackled by making regular soil moisture measurements and by using an approximate water balance method to estimate drainage.

The results obtained were tested against a simple chromatographic plate model of solute transport (Bresler 1967) as one of the objectives of the work is to be able to make advisory recommendations about nitrate leaching based on the minimum of field measured parameters. This model is shown to be sounder theoretically than that of Burns (1975) and requires only a modest amount of input data. By comparing results with predictions we can make some assessment of the efficiency with which nitrate nitrogen is leached by water passing through the root zone.

1. Theoretical considerations

1.1. Choice of leaching model

The extreme variability of field measured parameters such as hydraulic conductivity and soil water potential makes it difficult to describe water and solute transport accurately using one of the many mechanistic models available (see Addiscott & Wagenet 1985, for a review). An alternative approach is to use a functional model such as that of Burns (1975) or Bresler (1976) which makes a number of simplifying assumptions about water and solute movement. The soil is divided into a number of effective plates or layers. In the Burns model rainfall or irrigation entering the top layer of soil causes a temporary increase in moisture content in that layer. Water and solute mix completely within the layer and if water content exceeds field capacity the excess drains to the following layer. The model predicts the fraction of surface applied solute leaching below a specific depth to be:

$$LF = \left(\frac{D}{D + H\theta_{fc}}\right)^{\alpha}.$$  (1)

Here, $LF =$ fraction leached below depth $X$ (dimensionless); $x =$ reference depth (cm); $D =$ depth of drainage water (cm); $\theta_{fc} =$ field capacity of soil (cm$^3$/cm$^3$); $H =$ plate thickness (cm). The Bresler (1967) model is based on conservation of mass. For the first soil layer from the surface the mass conservation equation is:

$$RC_R - DC_D = (A_1 - A_0)6H.$$  (2)

Here, $R =$ rainfall or irrigation (cm); $C_R =$ solute concentration in rainfall (g/m$^3$); $C_D =$ solute concentration in water drainage below layer (g/m$^3$); $H =$ thickness of layer from soil surface (cm); $\theta =$ water content of soil in layer during
transport \( \text{cm}^3/\text{cm}^3 \); \( A_0 = \) solute concentration in the soil layer at moisture content \( \theta \), prior to rainfall or irrigation \( \text{g/cm}^3 \); \( A_1 = \) solute concentration in soil layer at moisture content \( \theta \), following rainfall or irrigation \( \text{g/cm}^3 \). The model assumes:

1. That movement of solute occurs only by convection with excess water draining from the soil until the moisture content reaches field capacity. In any given soil layer any amount of water entering the layer in excess of the soil moisture deficit from field capacity drains to the following layer.

2. All water and solute movement takes place at a constant moisture content.

3. The average solute concentration of water leaving any soil layer, \( C_D \), is equal to the mean of the solute concentrations in the layer before and after irrigation:

\[
C_D = \frac{A_0 - A_1}{2},
\]

(3)

as long as the amount of drainage water, \( D \), is less than twice the moisture content of the layer, \( 2\theta H \).

For \( D > 2\theta H \):

\[
C_D = A_1.
\]

(4)

Substituting equation (3) or equation (4) into equation (2), we obtain for the first soil layer:

For \( D < 2\theta H \):

\[
RC_R - \frac{(R - F)(A_0 + A_1)}{2} = (A_1 - A_0)\theta H.
\]

(5)

For \( D > 2\theta H \):

\[
RC_R - \frac{2\theta H(A_0 + A_1)}{2} - (R - F - 2\theta H)A_1 = (A_1 - A_0)\theta H,
\]

(6)

where \( R = \) soil moisture deficit from field capacity in the layer at start of rainfall or irrigation \( \text{cm} \). These equations can be modified to allow for drainage through successive soil layers of thickness \( H \) at different moisture contents and with different field capacities. The average concentration of solute, \( C_R \), in water draining to the next layer is given by solving for \( A_1 \) in equation (5) or (6) and inserting thereafter into equation (4). This is then used as the input concentration to the next layer. \( R - F \) is the volume of water input into the next layer.

Implicit in both these models is the assumption that some longitudinal mixing occurs during solute and water transport through chromatographic plates. However, the degree of mixing which occurs in each plate is different in the two models. Figure 1 shows the results of numerical calculation of average solute concentration in a plate during steady leaching of solute from a plate of finite length (Brenner 1962). The extremes are shown, namely perfect mixing \( (P_e = 0) \) and piston displacement \( (P_e = \infty) \) within the plate. Two intermediate values are also shown. The Peclet number, \( P_e \), is given by:

\[
P_e = \frac{H}{4E_{\text{DIS}}},
\]

(7)

where \( H = \) plate length \( \text{cm} \) and \( E_{\text{DIS}} = \) dispersion length \( \text{cm} \). The dispersion length is a parameter describing the extent to which longitudinal mixing occurs during water flow through the soil. The Peclet number as used here describes the importance of diffusive transport in each plate relative to convective transport (see Bolt 1979, p. 310).

In packed sand columns \( E_{\text{DIS}} \) is small \((<0.1 \text{ cm})\) but in light field soils it is at least ten times this and it will be higher still in strongly aggregated or structured soils. Use of this parameter assumes that residence times of parcels of water in the soil are normally distributed during steady state flow. This would seem a reasonable assumption so long as preferential flow pathways do not occur. However, this assumption does not hold in many field soils (e.g. van der Pol et al. 1977, where residence times were found to fit a log-normal distribution).

The dispersion length is influenced by molecular diffusion and by the presence of intra-aggregate or immobile water. Bolt (1979) gives an expression for the effective dispersion length including these effects, assuming uniform, spherical aggregates:

\[
E^* = \frac{\theta D^*}{J_v} + \frac{\theta A E_{\text{DIS}}}{60\theta^2 D^* J_v},
\]

(8)

where \( E^* = \) effective dispersion length \( \text{cm} \); \( D^* = \) diffusion coefficient of the solute in soil \( \text{cm}^2/s \); \( J_v = \) flow velocity \( \text{cm}/s \); \( \theta_A = \) immobile water \( \text{cm}^3/\text{cm}^3 \); \( E_{\text{DIS}} = \) dispersion length in the absence of diffusion and immobile water effects. When longitudinal diffusion and/or immobile water are important, the value of \( E_{\text{DIS}} \) in equation (7) should be replaced by the effective dispersion length, \( E^* \) from equation (8).

Also shown in Figure 1 are leaching curves for the plate using the Bresler and Burns models. The Bresler model predicts displacement with Peollet number intermediate between perfect mixing and piston displacement \( (P_e = 0.4 \) fits it quite well). The version of the Burns model used is that given by Burns (1976) for an initially uniform solute concentration in the layer. The model over-estimates leaching for the initial volume of leachate but at larger leachate volumes approximates to perfect mixing. From equation (7), perfect mixing occurs only if the plate height tends to zero or the dispersion length tends to infinity. If the latter is the case, it is clearly inapplicable to light soils, while if the former is the case it will only be reasonable for short duration rainfall events, as pointed out by Cameron and Wild (1982). The Bresler model \( (P_e = 0.4) \) corresponds better with real dispersion lengths and the plate height required in order to obtain a Peollet number of 0.4 for a range of flow velocities and dispersion lengths \( (E_{\text{DIS}}) \) is given in Figure 2. The solid lines represent the case when no immobile water occurs and the dotted line the case when...
50% of the soil water is immobile. By adjusting the plate height in the model different values of $E_{DIS}$ and $J_V$ can be accommodated, if necessary. To some extent immobility of soil water within aggregates can be accounted for, although it is impractical to have a plate length of more than about 30 cm. Also, Passioura (1971, equation 19), has shown that the use of the effective dispersion length to describe the effect of immobile water is restricted by the condition:

$$\frac{D^*H}{E_{DIS}^2 J_V} > 0.075 \theta_A.$$  \hspace{1cm} (9)

This restricts the values of $H$ for which this method is valid to relatively low flow velocities and relatively small values of $E_{DIS}$ when immobile water is present.

To summarise, an adaptation of the Bresler model is used in this work on the basis that: (1) it provides a more realistic description of dispersion phenomena during solute transport so long as the plate height is adjusted as necessary; (2) it can be used when immobile water is present as long as flow rates and dispersion lengths are not too high; (3) it allows for more flexibility of initial conditions. Both uneven distribution of solute down the profile, and the presence of solute in rainfall or irrigation water can be incorporated. The adaptations necessary to this model for the present work are: (1) the water content during flow is assumed to be field capacity; (2) the plate height for the first layer from the surface is 1 cm, in which tracer is initially mixed; (3) the amount of water passing through each layer is calculated from the soil water balance as described in the following section, not by using field capacity.

Figure 3A shows the effect of changing the plate height on predictions of this model for a fallow plot (Plot L2, see Section 2.1.2 below) used in these studies and also the prediction of the Burns model (Fig. 3B) for comparison. Very much greater differences occur between the two models than between the different plate heights showing that choice of plate height for prediction of solute leaching is of secondary importance to the correct choice of model.

### 1.2. Soil moisture balance determination

Under irrigated agriculture in the absence of rainfall a useful field estimate of drainage below a given depth after an irrigation is given by:

$$D(L) = I - \int_0^L \frac{\int_0^L \left( \theta_r(x) - \theta_i(x) \right) dx}{S(x, t)} dt,$$

where $D(L) =$ drainage below depth $L$ (cm); $I =$ irrigation amount (cm); $\theta_i =$ initial water content (cm$^3$/cm$^3$); $\theta_r =$ soil moisture extraction rate (cm/day) between time $t_i$ and the irrigation; $t_i =$ time of initial soil moisture measurement; $t_f =$ time of start of irrigation. This approach is not possible when random rainfall events occur because soil moisture contents prior to each rainfall event are not known. However, another equation can be used if regular soil moisture measurements are made (every 1–2 weeks) and if soil moisture extraction can be estimated independently:

$$D(L) = \int_{t_i}^{t_f} (R + I) dt - \int_0^L \frac{\int_0^L \left( \theta_r(x) - \theta_i(x) \right) dx}{S(x, t)} dt,$$

where $\theta_i, \theta_r$ are successive measurements of moisture content at times $t_i$ and $t_f$, respectively. This approach also

![Figure 2](image1.png)  \hspace{1cm} ![Figure 3](image2.png)

Figure 2 Appropriate plate heights for the Bresler model as a function of flow velocity, dispersion length $E_{DIS}$ and immobile fraction $\theta_I$.

Figure 3 Predicted Br$^-\text{Br}^-$ distribution in an experimental fallow plot to which 1600 mg/m$^2$ Br$^-\text{Br}^-$ was applied; A = Bresler model; B = Burns model; figures on the curves are the plate heights used.
has the advantage that there is no need to assume that drainage ceases when field capacity is reached. Thus in our work the right-side of equation (11) was used to replace \( R - F \) in equations (5) and (6).

2. Materials and methods

2.1. Field experiments

Field testing of this model was done at three sites on two farms in two years. Microplots to which tracer solution was applied were used in both cases.

2.1.1. Site A. In 1985 a potato field near Aberlady, East Lothian, Scotland (NG 348679) was used. Details of the soil are given in Table 1. Four microplots were set up in each field. The profile of the ridge was obtained and the average height of the ridge above the level of the furrow was calculated to be 10-4 cm. Samples of soil in the ridge were taken by mixing the whole cross-section of the ridge in the field and subsampling. Below the ridge samples were taken using a 6-7 diameter intact soil corer. In three microplots two samples were taken and in the fourth three samples were taken. Samples were taken on three dates (14 June, 3 July, 15 August). Extraction and distillation methods for \( ^{15} \text{N} \) labelled NO\(_3^-\) in soil are described by K. A. Smith et al. (1984). \( ^{15} \text{N} \) was determined in distillates from soil extracts and in plant material by an automated system combining a Carlo Erba ANA1400N analyser and a VG Isogas Q2 mass spectrophotometer. Results were calculated assuming the soil bulk density in the ridge was 1.1 g/cm\(^3\) and 1.4 g/cm\(^3\) below the ridge.

The evapotranspiration from the bare soil surface prior to crop emergence (19 June) and between crop emergence and the second sampling data was calculated by the method for light soils of Smith and Douglas (1975). Weekly rainfall and evapotranspiration estimates from Meteorological Office and site data are given in Table 2. Approximate field capacity values were chosen by observation of the weekly soil moisture data to be: 0–20 cm: 15%; 20–40 cm: 20%; 40–60 cm: 25%. The 40–60 cm section was probably within the capillary fringe of the water table at least on some dates, so this value may over-estimate true field capacity. However, this will be a better estimate of the water content to which the soil drains.

2.1.2. Site B. In 1986 two fields at a site near Ladybank, Fife, Scotland (NG 332708) were used. Details of the soils and crops in the two fields are given in Table 1. The microplots consisted of areas 0.5 m x 0.5 m to which 250 ml of tracer solution containing 400 mg Br\(^-\) as CaBr\(_2\) (16 kg/ha) was applied as evenly as possible using a spray gun. Plastic rings were driven about 5 cm into the soil in the centre of the plot to mark the sampling area and to prevent run off or run on of water. In the lettuce field microplots were set up so that one plant was at each corner of the plot (except for the fallow plot). In the potato field microplots were set up before emergence. One plant emerged in each plot. Both ridge and furrow microplots had to be widened and flattened slightly so that each entire microplot was level. Details of the plots set up in each field are given in Table 3. In plots L1–L3, RIDGE 1–2 and FURROW 1–2, the tracer solution used was a mixture of CaCl\(_2\) and CaBr\(_2\) containing 5 mol of Br\(^-\) and 50 mol of Cl\(^-\). This was done to try to prevent crop uptake of Br\(^-\) by supplying an excess of Cl\(^-\) which competitively inhibits Br uptake (Epstein 1972). In plots L4 and RIDGE 3 the CaCl\(_2\) was omitted from the tracer solutions. At the end of the experiment plant samples were taken from plots L1, L3, L4, RIDGE 1, RIDGE 3

### Table 1 Soil characteristics

<table>
<thead>
<tr>
<th>Site</th>
<th>Soil series (texture)</th>
<th>Crop</th>
<th>Depth (cm)</th>
<th>Coarse sand</th>
<th>Fine sand</th>
<th>Silt</th>
<th>Day</th>
<th>Organic matter</th>
<th>Approximate field capacity* (cm(^3)/cm(^2))</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Peffer (loamy sand)</td>
<td>Potatoes (planted early April)</td>
<td>0–40</td>
<td>21.0</td>
<td>62.8</td>
<td>9.1</td>
<td>7.2</td>
<td>NA</td>
<td>15–25</td>
</tr>
<tr>
<td>B</td>
<td>Hexpath (sandy loam)</td>
<td>Iceberg lettuce (planted 1–4 April)</td>
<td>5</td>
<td>32.7</td>
<td>44.3</td>
<td>16.0</td>
<td>6.9</td>
<td>3.9</td>
<td>NA</td>
</tr>
<tr>
<td>B</td>
<td>Hexpath (sandy loam)</td>
<td>Potatoes (planted 5–9 May)</td>
<td>5</td>
<td>32.7</td>
<td>44.3</td>
<td>16.0</td>
<td>6.9</td>
<td>3.9</td>
<td>NA</td>
</tr>
</tbody>
</table>

* From field measurement.

### Table 2 Weekly rainfall and evapotranspiration data, site A (in mm H\(_2\)O)

<table>
<thead>
<tr>
<th>Interval</th>
<th>Potential ET</th>
<th>Actual ET</th>
<th>Rainfall</th>
</tr>
</thead>
<tbody>
<tr>
<td>15 May–21 May</td>
<td>11</td>
<td>7.5</td>
<td>15.0</td>
</tr>
<tr>
<td>22 May–28 May</td>
<td>17</td>
<td>11.5</td>
<td>28.0</td>
</tr>
<tr>
<td>29 May–4 June</td>
<td>23</td>
<td>6.4</td>
<td>0.0</td>
</tr>
<tr>
<td>5 June–11 June</td>
<td>15</td>
<td>3.9</td>
<td>10.0</td>
</tr>
<tr>
<td>12 June–18 June</td>
<td>18</td>
<td>10.4</td>
<td>14.0</td>
</tr>
<tr>
<td>19 June–25 June</td>
<td>14</td>
<td>6.0</td>
<td>10.0</td>
</tr>
<tr>
<td>26 June–1 July</td>
<td>18</td>
<td>7.2</td>
<td>9.0</td>
</tr>
<tr>
<td>Total</td>
<td>116</td>
<td>52.9</td>
<td>86.0</td>
</tr>
</tbody>
</table>

### Table 3 Microplot treatments, site B

<table>
<thead>
<tr>
<th>Microplot</th>
<th>Crop</th>
<th>Position</th>
<th>Tracer solution</th>
<th>Sampling date (s)</th>
<th>Sampling depth</th>
</tr>
</thead>
<tbody>
<tr>
<td>L1</td>
<td>Lettuce</td>
<td>In bed</td>
<td>Br(^-) + Cl(^-)</td>
<td>2/6/86</td>
<td>50 cm</td>
</tr>
<tr>
<td>L2</td>
<td>Lettuce</td>
<td>Fallow area</td>
<td>Br(^-) + Cl(^-)</td>
<td>2/6/86</td>
<td>50 cm</td>
</tr>
<tr>
<td>L3</td>
<td>Lettuce</td>
<td>In bed</td>
<td>Br(^-) + Cl(^-)</td>
<td>2/6/86</td>
<td>50 cm</td>
</tr>
<tr>
<td>L4</td>
<td>Lettuce</td>
<td>In bed</td>
<td>Br only</td>
<td>2/6/86</td>
<td>50 cm</td>
</tr>
<tr>
<td>L1*</td>
<td>Lettuce</td>
<td>In bed</td>
<td>Br only</td>
<td>2/6/86</td>
<td>50 cm</td>
</tr>
<tr>
<td>L2*</td>
<td>Lettuce</td>
<td>In bed</td>
<td>Br only</td>
<td>2/6/86</td>
<td>50 cm</td>
</tr>
<tr>
<td>RIDGE 1</td>
<td>Potatoes</td>
<td>Ridge</td>
<td>Br + Cl</td>
<td>7/7/86</td>
<td>75 cm</td>
</tr>
<tr>
<td>FURROW 1</td>
<td>Potatoes</td>
<td>Furrow</td>
<td>Br + Cl</td>
<td>7/7/86</td>
<td>75 cm</td>
</tr>
<tr>
<td>FURROW 2</td>
<td>Potatoes</td>
<td>Furrow</td>
<td>Br + Cl</td>
<td>7/7/86</td>
<td>75 cm</td>
</tr>
<tr>
<td>RIDGE 3</td>
<td>Potatoes</td>
<td>Ridge</td>
<td>Br only</td>
<td>7/7/86</td>
<td>75 cm</td>
</tr>
</tbody>
</table>

* 80 mm water ponded on microplot and soil samples taken the next day.
Table 4  Rainfall and evapotranspiration data, site B (in mm H$_2$O)

<table>
<thead>
<tr>
<th>Interval</th>
<th>Potential $ET$</th>
<th>Actual $ET$</th>
<th>Fallow $ET$</th>
<th>Rainfall + irrigation</th>
</tr>
</thead>
<tbody>
<tr>
<td>12 May–26 May</td>
<td>45</td>
<td>23-8</td>
<td>14-3</td>
<td>39-0</td>
</tr>
<tr>
<td>27 May–2 June</td>
<td>18</td>
<td>10-0</td>
<td>6-0</td>
<td>14-0</td>
</tr>
<tr>
<td>3 June–9 June</td>
<td>18</td>
<td>5-2</td>
<td>3-1</td>
<td>13-0</td>
</tr>
<tr>
<td>10 June–23 June</td>
<td>31</td>
<td>22-6</td>
<td>13-6</td>
<td>50-0</td>
</tr>
<tr>
<td>Total</td>
<td>112</td>
<td>89-9</td>
<td>54-0</td>
<td>142-0</td>
</tr>
</tbody>
</table>

* We assumed that 2/3 of the area was ridge with a depth of 15 cm. 40% of the uptake (on a whole area basis) occurred from the ridge with the rest removed evenly from both ridge and furrow to a depth of 60 cm.

RIDGE 5 and from outside the area of the microplots. These were dried and analysed for Br$^-$ content (see below).

In addition to the studies under natural rainfall and irrigation two microplots (P1, P2) were also established to study leaching when water was applied by ponding. The microplots were established as above, allowed to stand for thirty to sixty minutes to allow equilibration of the solute with intra-aggregate pore water and then water was applied using a double ring infiltrometer to ensure that 80 mm of water infiltrated in the central section of the plot. Sampling was done, allowing one day for redistribution.

At the appropriate dates, soil samples were taken using a 6-7 cm diameter soil corer. The soil was sectioned into 5 cm increments for analysis and stored in a freezer. Sampling details are given in Table 3. After thawing, soil samples (20 g) were extracted with 20 ml of saturated CaSO$_4$ solution over night and centrifuged. The Br$^-$ concentration in the supernatant was determined with an ORION Br$^-$ specific ion electrode and an ORION model 90-single function reference electrode. Standard solutions were prepared using the same solution. No Cl$^-$ correction was made as the interference from Cl$^-$ in the samples was less than 5%.

Detection limit was approximately 0.1 g Br$^-$/m$^2$ soil. Plant samples (1 g) were extracted with 100 ml of saturated CaSO$_4$ solution in a liquidiser. Br$^-$ levels were determined in the same way as above.

A Wallingford neutron moisture probe was used to determine soil moisture content on a weekly or biweekly basis from access tubes sited 0.5-1 m from each microplot. Site rainfall and irrigation data were available from the farm and potential evaporation data were obtained from the Meteorological Office. Details are given in Table 4. Soil moisture extraction was estimated using the method of Smith and Douglas (1975) for fallow soils and using the output from an irrigation scheduling program of Parkes (unpublished) for the results from site B. Soil moisture contents were measured every 1–2 weeks at all field sites considered. The moisture contents on the first measurement date (12 May) were used as estimates of field capacity.

2.2. Column experiments

Intact soil cores, 15 cm in diameter containing a 25 cm depth of soil, were removed from the Aberlady site for further leaching study. The columns were saturated from the base upwards using distilled water or 0.005 M CaCl$_2$ before an experimental run. A pulse of 100 ml of KNO$_3$ containing 2,800 g/m$^2$ NO$_3$-N was applied to the soil surface and this was followed by distilled water or 0.005 M CaCl$_2$ at constant head. Leachate from the columns was collected using a fraction collector and the aliquots were analysed for NO$_3$-N using an auto analytical method (Henriksen & Selmer-Olsen 1970). In two cases a gypsum crust was applied to the surface of the column or to the base of the column in order to restrict flow rate. A summary of the treatment flow rates and experimental results are given in Table 5. The high hydraulic conductivity of the soil used meant that edge flow down the sides of the column was unlikely to be a major problem in these studies. However, the filter paper used to restrict loss of sediment from the columns tended to restrict flow giving variable flow rates in some experiments.

3. Results

3.1. Site A

The recovery of $^{15}$N from the soil and crop in the four microplots used in the potato field at site A is given in Table 6. The values for the soil were very variable so a geometric mean was taken of the nine samples. Values for crop uptake were more consistent, so an arithmetic mean was used. On 14 June, when crop emergence had only just occurred, very little was in the plant but the total recovery was only 91 kg (160 kg was applied). On following dates the recoveries were not statistically different from this figure. There are several possible reasons for this rapid loss of $^{15}$N–NO$_3$.

Leaching prior to the first sampling is not suggested from model predictions. Rainfall was high (53 mm) during the period from establishment of the microplots to the first sampling but there was also a lot of rainfall (33 mm) in the two weeks between the first and second sampling dates, and no further loss occurred. Uptake by the soil biomass is also possible, but work by Legg and Stanford (1967) suggests that NO$_3$ is not readily taken up by micro-organisms, NH$_4$ being the preferred form of nitrogen. The most likely source of loss is by denitrification which occurs most readily under wet conditions in spring after fertiliser application. Rates of loss up to 3 kg N/ha/day on sandy soils near Aberdeen were observed (Batey & Killham 1985) during the same period.

<table>
<thead>
<tr>
<th>Column No</th>
<th>Flow rate ($cm/s \times 10^{-3}$)</th>
<th>Position (pore volumes)</th>
<th>PEAK Relative concentration</th>
<th>Mass balance %</th>
</tr>
</thead>
<tbody>
<tr>
<td>II</td>
<td>16</td>
<td>0.36</td>
<td>0.123</td>
<td>95</td>
</tr>
<tr>
<td>II</td>
<td>1.7</td>
<td>0.57</td>
<td>0.076</td>
<td>89</td>
</tr>
<tr>
<td>III</td>
<td>13</td>
<td>0.58</td>
<td>0.061</td>
<td>97</td>
</tr>
<tr>
<td>IV</td>
<td>4.4</td>
<td>0.67</td>
<td>0.088</td>
<td>NA</td>
</tr>
<tr>
<td>IV</td>
<td>63</td>
<td>0.53</td>
<td>0.084</td>
<td>96</td>
</tr>
<tr>
<td>V</td>
<td>120</td>
<td>0.38</td>
<td>0.075</td>
<td>97</td>
</tr>
</tbody>
</table>

Crust at surface

Crust at base
The distribution of the $^{15}$N recovered from the soil (all plots) is shown in Figure 4. These are compared with the model predictions of solute distribution (mean of three plots on which soil water measurements were made), assuming surface application, no losses and zero crop uptake of tracer, as shown by the solid lines. As Ca$^{15}$NO$_3$ was used, we can assume that nearly all the tracer recovered in the soil is still in the NO$_3$ form. Despite the large scatter of experimental values from the nine replicate plots, clearly more tracer was retained in the ridges than predicted, on the first date. The effect was more pronounced on the second sampling date and still occurred, with some samples at least, on 15 August, when up to 75 kg/ha fertiliser-derived nitrogen still remained in the ridge. Predicted distributions assume that upward water loss was solely from evaporation, which is a reasonable assumption up till the second sampling date, but not beyond it. Thus no predicted distribution is possible on the third sampling date.

The predictions of the model are not radically altered by increasing the plate height from 5 to 10 cm to increase dispersion and the results suggest that much of the fertiliser-derived nitrate was protected from leaching by being present in soil pores in which the water is immobile (i.e. does not participate in water flow). A model of this soil which includes explicitly mobile and immobile zones of water is required.

### 3.2. Column studies

This leaching behaviour was further investigated using columns of soil from the field. Figure 5 shows the relative concentration of leachate from a 25 cm column to which a pulse of 0.049 pore volume containing 2800 g/m$^3$ NO$_3$ as KNO$_3$ was applied. The flow rate was not controlled, but a constant head of leaching water was maintained on the soil surface. The peak of the breakthrough curve occurred at 0.53 pore volume, well before the expected position for a non-aggregated porous medium (1.024 pore volumes). This again suggests that only a fraction of the soil water contributed to flow, while the rest was immobile. The leading edge of the breakthrough curve is quite sharp but the trailing edge declines more gradually. This is because solute mixed to some extent, by diffusion, with the immobile water, and then was released gradually as leaching water flowed through the column. The shape of this curve and of similar results for other columns (see Table 5) cannot be predicted by increasing the effective dispersion coefficient to account for immobile water (using equation 8) and using Brenner's (1962) solution for leaching from a finite column.

Part of the reason for the early breakthrough observed may be that a small amount of anion exclusion occurs. This is associated more with heavy soils (Thomas & Swoboda 1970) but does occur to some extent on light soils (see Smith & Davis 1974). This was demonstrated for the present case by sieving and re-packing soil from one column and measuring the breakthrough from the disturbed soil column.
transport will be lower. The field although in the field water contents during compliance of low leaching losses found in to be encountered in the field. These results, therefore, transport processes even in the range of flow velocities likely was, however, still an important effect of immobile water on conductivity/water content relationships of this soil. There details about the moisture characteristic and hydraulic pore water was involved in flow at lower flow velocities. It is difficult to separate these two effects without obtaining more details about the moisture characteristic and hydraulic conductivity/water content relationships of this soil. There was, however, still an important effect of immobile water on transport processes even in the range of flow velocities likely to be encountered in the field. These results, therefore, comply with the observation of low leaching losses found in the field although in the field water contents during transport will be lower.

**Figure 6** Breakthrough curves for disturbed soil column leaching experiment for two electrolyte concentrations.

3.3. Site B

The results of the experiments with the Br⁻ microplots are summarised in Table 7 and Figures 8-10. As with the ¹⁵NO₃ experiment, there were serious problems in obtaining a mass balance (Table 7). In the lettuce plots recovery was 47-59% on the first date and 2-36% on the second date. Addition of CaCl₂ helped reduce crop uptake on one plot (L3), but not on the other (L1). The losses were not entirely due to above ground crop uptake which only accounted for 28-59% on the second date. In the fallow plot (L2) only 30% recovery occurred on the second date and even in the plots sampled the day after tracer application only 36-84% recovery occurred. This may be partly due to poor distribution of the tracer, but this cannot be the main explanation as the overall mean recovery should then be about 100%. Incubation of the soil with Br⁻ for three weeks in a constant temperature (10°C) environment also revealed a significant loss of Br⁻. This suggests that uptake by the soil microflora or incorporation into the soil organic matter in some non-extractable form occurred. On the potato plots recoveries were somewhat better, though still very variable. The effect of CaCl₂ addition was not significant. Crop uptake was much smaller (1-15%), partly because the crop only emerged towards the end of the experimental period.

These mass balance problems make it more difficult to interpret the soil profiles, but some points are clear. In the potatoes (Fig. 8) there was less leaching of tracer than predicted in RIDGE 1 even taking into account the poor recovery. In the other two ridge plots the position of the peak corresponded quite well with the prediction but dispersion was greater. There was more retention in the surface layers in RIDGE 3 than predicted and preferential movement of some tracer to deeper layers than predicted occurred in RIDGE 2.

The two furrow plots gave very different profiles. In furrow 1 total recovery was very low yet much more tracer than predicted was recovered in the first 5 cm. Furrow 2 shows no clear peak indicating a large dispersion coefficient, though if the two replicates are taken separately this is found to be because one has a peak at 10-15 cm while the other is at 45-50 cm. On the whole, however, agreement between replicates was closer than at site A.

In the lettuce plots (Fig. 9) the poor mass balance again makes interpretation of results difficult. However, there was less leaching than the model predicts, particularly on the second date. It is difficult to say whether this was because of physical protection from leaching in immobile water within soil aggregates, or because of Br⁻ interaction with the soil biomass and organic matter.

Figure 10 shows the results from the experiment in the lettuce field with ponded water. The tracer remained mainly in the top 20 cm of soil despite the large depth of water applied. This is an extreme case as the average infiltration velocity was very high (0.03 cm/s). The figure also shows the predicted distribution, which corresponds surprisingly well with observed results. A piston flow model would have given very different results. This conveniently demonstrates that there are some problems with the use of the Bresler model because of the assumptions made. The model assumes that for each leaching event the concentration of solute in water entering any layer is a constant. Particularly in the case where a large single application of water occurs to a very thin, concentrated band of fertiliser, this will be an inaccurate assumption. Moreover, the first layer is thinner, which implies a smaller Peclet number than in the layers below. Therefore prediction of leaching will be closer to the perfect mixing assumption than in the layers below. This
Table 7 Percent recovery of Br⁻ from soil and plant, site B

<table>
<thead>
<tr>
<th>A. Lettuces</th>
<th>Date</th>
<th>Plant uptake (23 June)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2 June</td>
<td>23 June</td>
</tr>
<tr>
<td>L1</td>
<td>59</td>
<td>2</td>
</tr>
<tr>
<td>L3</td>
<td>48</td>
<td>36</td>
</tr>
<tr>
<td>L4</td>
<td>47</td>
<td>2</td>
</tr>
<tr>
<td>L2</td>
<td>49</td>
<td>30</td>
</tr>
<tr>
<td>P1</td>
<td>—</td>
<td>39</td>
</tr>
<tr>
<td>P2 I</td>
<td>—</td>
<td>36</td>
</tr>
<tr>
<td>II</td>
<td>—</td>
<td>84</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>B. Potatoes</th>
<th>Replicate</th>
<th>Plant uptake (7 July)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I</td>
<td>II</td>
</tr>
<tr>
<td>RIDGE 1</td>
<td>35</td>
<td>33</td>
</tr>
<tr>
<td>RIDGE 2</td>
<td>77</td>
<td>51</td>
</tr>
<tr>
<td>RIDGE 3</td>
<td>40</td>
<td>39</td>
</tr>
<tr>
<td>FURROW 1</td>
<td>18</td>
<td>22</td>
</tr>
<tr>
<td>FURROW 2</td>
<td>47</td>
<td>61</td>
</tr>
</tbody>
</table>

Plant uptake (7 July)

<p>| | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>(No CaCl₂)</td>
<td>15</td>
</tr>
<tr>
<td>Fallow</td>
<td>1</td>
</tr>
<tr>
<td>80 mm Ponding</td>
<td>7</td>
</tr>
</tbody>
</table>

The model is adapted to predicting leaching of salts in irrigation water when such discrete concentrated bands of solute will not occur. This problem also influences the effect of changing plate height. The larger the plate height, the more accurate the assumption of constant concentration entering each layer becomes. Hence in Figure 3 we see a shifting of the peak and centre of mass upwards as it changes from 15 to 1 cm.

4. Discussion

Figure 11 gives a summary of the field work in the form of a comparison between the predicted position of the centre of mass of tracer and observed results. Predictions are made using the Bresler model (equations 3–6), the Burns model (equation 1) and the piston displacement model of Wild and Babiker (1976) for comparison. The piston model simply assumes that the centre of mass of solute will be located at a distance $X = D/\theta_k$ from the soil surface. For all three models, the points fall well to the right of the 1:1 line. However, three of the values for the potato field at site B fit the 1:1 line well. Excluding these three points, the relationship between observed and predicted leaching using the Bresler model is:

$$Y = 1.93 + 0.235X \quad r = 0.67$$

where $Y$ = observed mean displacement of tracer (cm), $X$ = predicted mean displacement of tracer (cm).

The slope of this line is much less than a line calculated by Wild and Babiker (1976) for nitrate leaching in a range of...
field soils of varying textures during winter. Using the piston displacement model, they obtained a slope of 0.57 (the piston model in our case gives a slope of 0.268). Assuming perfect mixing (Fig. 11B), a slightly closer agreement between observed and predicted results occurs but the slope is still only 0.343 (see Table 8).

There are three points that need explanation from these results: (A) the very low leaching efficiency of the tracer recovered compared with water movement which occurred in the other plots; (B) the difference between three of the plots in the potato field at site B and the rest; and (C) the poor recovery of tracer which occurred, even in the fallow plots. Considering the first point, we can suggest causes in the same categories that were mentioned in the Introduction, namely: (i) influence of uptake of tracer by soil biomass or crop; (ii) overestimation of the drainage term in the water balance; (iii) immobility of a large fraction of the soil water during leaching. Tracer uptake by the soil biomass or by the crop will move the centre of mass of solute remaining in the soil downwards (Rose et al. 1982) if we assume that soil microbial and root activity decreases with depth. However, if tracer is taken up and later released by roots or biomass, this would have the effect of reducing leaching. Uptake and subsequent release of nitrate nitrogen fertiliser has been observed by Nectescu et al. (1985) over a period of thirty days in a range of arable soils. They postulate that the response is due to osmotic adjustment by soil microflora. The osmotic pressure of the tracer solutions used at site B was approximately 3 MPa when CaCl₂ was used. Until this was diluted by diffusive mixing within the soil or by rainfall, there would be a considerable osmotic stress on microflora. In two of the cases where no CaCl₂ was used (osmotic pressure = 0.3 MPa) either piston displacement occurred (RIDGE S) or very little tracer was detected when sampled (L4). The situation at site A is less clear as the ¹⁵N was applied dry to the soil. Nevertheless, until dissolution of fertiliser had occurred osmotic pressures around fertiliser grains would be quite high.

The possibility of overestimation of drainage has been investigated by a sensitivity analysis on predictions based on Bresler’s model (Table 8). The largest change from the default value of the slope (row 4) occurs when equation (10) is used to calculate the soil water balance instead of equation (11). The slope only increases to 0.360 which is still much lower than that of Wild and Babiker (1976). Moreover, under conditions of intermittent rainfall equation (11) will estimate drainage better. Increasing the water content at which flow is assumed to occur from field capacity to 1.5 times field capacity increases the slope to 0.321.

Further work on the soil hydraulic properties is needed to decide on a suitable value for this parameter, but it clearly does not fully explain the discrepancy. If we assume all the soil moisture extraction occurs in the top 15 cm of soil, the intercept moves from 1.9-3 to 3.00 but the slope decreases to 0.212 so wrong assumptions about the water extraction pattern cannot explain the results.

These results therefore suggest that, for most of the plots, between 60 and 75% of the water-filled porosity is not involved in solute transport. Downward adjustment of this range is necessary if osmotic uptake by soil biomass of tracer is important, or if the soil moisture content at which much of the transport occurs exceeds 1.5 times field capacity. This range is larger than the range of values obtained in our column experiments and the results obtained by other workers.

For three plots the model seems to predict results well. These three plots all occur in one small area of one of the fields and further investigation is required to determine if soil hydraulic properties in this area are such that little immobile water occurs. Other investigators have shown soil conditions where leaching can be predicted by piston displacement (Cameron & Wild 1982; Rose et al. 1982), and Bresler’s model has also been used successfully to simulate field data on soils irrigated with saline water by Vinten (unpublished data) and Bresler (1967).

The third point that needs discussion is the poor mass balance obtained in all field experiments. There are two possible ways to explain this: (a) microbial uptake of tracer or (in the case of ¹⁵NO₃⁻) denitrification. These possibilities have already been discussed and seem to be feasible explanations. (b) If only a small fraction of the soil water is mobile, when flow occurs solute present in this water will be rapidly leached. The rest of the solute moves more slowly than piston displacement or the Bresler model predicts, because it is in immobile water. This explanation would certainly seem correct in explaining the poor mass balance in the ponded sites (P1, P2). Moreover, soil moisture measurements made before and after 80 mm water application show only a 36 mm change in soil water storage to 45 cm depth fourteen minutes after completion of

![Figure 11](image-url) Comparison of predicted and observed mean tracer displacement using three models for all field data.

<table>
<thead>
<tr>
<th>Leaching model</th>
<th>Water balance model</th>
<th>Water content during flow</th>
<th>Rooting depth</th>
<th>Plate height</th>
<th>Regression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Burns (eq. 1)</td>
<td>Eq. 11</td>
<td>θₑ</td>
<td>45</td>
<td>60</td>
<td>1</td>
</tr>
<tr>
<td>Piston</td>
<td>Eq. 11</td>
<td>θₑ</td>
<td>45</td>
<td>60</td>
<td>NA</td>
</tr>
<tr>
<td>Bresler (eqs. 3-6)</td>
<td>Eq. 10</td>
<td>θₑ</td>
<td>45</td>
<td>60</td>
<td>5</td>
</tr>
<tr>
<td>Bresler (eqs. 3-6)</td>
<td>Eq. 11</td>
<td>1.5θₑ</td>
<td>45</td>
<td>60</td>
<td>5</td>
</tr>
<tr>
<td>Bresler (eqs. 3-6)</td>
<td>Eq. 11</td>
<td>θₑ</td>
<td>15</td>
<td>15</td>
<td>5</td>
</tr>
<tr>
<td>Bresler (eqs. 3-6)</td>
<td>Eq. 11</td>
<td>θₑ</td>
<td>45</td>
<td>60</td>
<td>15</td>
</tr>
</tbody>
</table>

NA - Not applicable.
infiltration. The water content at 30–45 cm depth was still below field capacity at this time and gradually increased as redistribution proceeded. This shows that a sizeable fraction (about 50%) of the infiltrating water moved very rapidly below the depth of sampling through large structural pores and worm channels.

This process is much less likely to be important under conditions of natural rainfall and irrigation, because the soil does not approach saturation. If we assume that the fraction of mobile water in the soil is about 0.25$\frac{cm}{cm}$ (as suggested by Fig. 11) and that this water has the same solute concentration as the immobile water, then during a major infiltration event of 20 mm the centre of mass of solute present in the mobile water would move about 30 cm if no diffusive mixing with the immobile water occurred. If this occurred, we would still expect to be able to detect this rapidly-moving solute at the bottom of the soil profile, especially on the first sampling data at site B. Thus it seems unlikely that rapid transport of a fraction of the solute below depth of sampling explains poor mass balance, except in the case of the ponded plots. However, more work is clearly necessary to determine whether soil biomass uptake can explain the poor recovery of tracer.

5. Summary and conclusions

The Bresler (1967) model has been adapted for predicting nitrate leaching in field situations. It helps to assess the importance of the presence of immobile water inside soil aggregates in preventing leaching of nitrates. To a limited extent it can be modified by increasing plate height to allow for the presence of immobile water. However, experimental results in most cases showed less leaching than the model predicts even if such modifications are made. The extent of this protection from leaching is much larger than observed by other workers for soils of similar texture. This may be due to temporary uptake of tracer by soil biomass for osmotic adjustment. Incomplete tracer recovery may be due to rapid leaching beyond depth of sampling or permanent uptake by the soil biomass. Further work is needed to find out which of these processes is responsible.

6. Acknowledgements

The technical assistance of I. J. Crichton is gratefully acknowledged.

7. References


36, 411-424.


Burns, I. G. 1976. Equations to predict the leaching of nitrate uniformly incorporated to a known depth or uniformly distributed throughout a soil profile. J AGRIC SCI, CAMBRIDGE 86, 305-313.


London: Her Majesty’s Stationery Office.


MS received 16 October 1986. Accepted for publication 13 July 1987.
Instructions to authors

Transactions of the Royal Society of Edinburgh: Earth Sciences appears quarterly, publishing studies on all aspects of the earth sciences and related planetary sciences. Substantial contributions to both information and understanding that emphasise principles and are relevant to a worldwide readership are welcome. Normally there is an upper limit of 25000 words, but most contributions are expected to be shorter. Discussions of papers previously published in the Transactions and reviews of topics of current interest are also invited. There are no page charges but subventions towards cost are welcome. If the use of foldouts or colour illustrations is envisaged, the Editorial Office should be consulted prior to submission.

1. Submission

Membership of the Society is not a pre-requisite for submission. Three copies of manuscripts should be sent to the Publications Secretary, The Royal Society of Edinburgh, 22 George Street, Edinburgh EH2 2PO, Scotland. Three copies of illustrations at publication size should also be submitted; for these sets, photocopies of line drawings are adequate, but not of photographs. Illustrations suitable for reproduction (see 3.1) may be requested subsequently. All submissions will be sent to two reviewers. Papers by more than one author must be submitted with a statement signed by each author, to the effect that the paper in its entirety is approved by the joint authors and naming the author who will be responsible for correspondence.

2. Preparation of papers

2.1. Manuscripts

Manuscripts should be typed on A4 (295×210 mm) or quarto paper with double spacing throughout and wide margins. A title that is concise and informative, a heading of not more than 50 typewriter strokes for use at the top of text pages and name(s) of author(s) are to be given on the first page. An abstract of not more than 200 words, intelligible without reference to the text or references, should be given on the second page, with a list of key words not in the title making up no more than 150 typewriter strokes. The text should begin on the third page. Where possible, annotated illustrations and tables should be used in place of text. Give full postal addresses at the end of the references. Table and a list of figure captions should be on separate pages.

Editorial details. Words to be printed in italics, e.g. names of taxa, should be underlined. Use capital letters for formal terms only, in both text and headings. The metric system should be used throughout. Abbreviations should omit the full-stop, e.g. 2 mm, 3 km and 6 kb. Compass points are to be abbreviated to N, NW, NW-SE etc. Map references should be in square brackets, e.g. [NM 4437 0293]. Do not use footnotes except in tables. Examples of references in the text are: Jennings and Smith (1967) record... Bracketed references should be as follows: (James 1931), (Jennings & Smith 1967, p.132), (Jenkins 1947, 1950; Brock 1975). Indicate in the margins approximate positions for insertion of illustrations and tables. For particular treatment of palaeontological specialities consult PALAEONTOLOGY 15, 676-81.

2.2. Headings

Primary headings, including Acknowledgements and References, are to be numbered 1, 2, 3 etc. (as in these Instructions) and secondary headings 1.1, 1.2, 1.3 etc.; these are to begin at the left-hand margin and should not be underlined. Show tertiary headings by wavy underlining. These should be indented and followed by a full-stop, four spaces and then the text of the sub-section. The introductory section requires no heading. Cross-references in the text should be to a section or sub-section, e.g. (see 2.3), not to a page.

3. Illustrations and tables

3.1. Illustrations

Illustrations, labelled figures (Fig. 1, 2, 3 etc.) are printed within the body of the text at column (85 mm) or page (177 mm) width, or page length (253 mm), but allowance must be made for figure captions. Where appropriate, group material into one figure and label a, b, c etc. In the case of groups of photographs, labels and annotation should be on the appropriate photograph, not in the space between photographs. No lettering should be less than 1 mm high at reproduction size (the use of capital letters throughout improves clarity after reduction). Transfer lettering is preferred. Large figures can be subdivided for reproduction on facing pages. Photographs should be high quality glossy prints with good contrast at final size and with a scale, or magnification in the caption. They should be mounted on white card, even if a black background is required in the published version (this requirement should be specified in an accompanying letter). In the case of fossil illustrations illumination should be top left. Originals of line drawings are usually required, either at publication size, or ×150%, but high quality prints on matt paper at publication size may be acceptable.

3.2. Tables

Tables (1, 2, 3 etc.) will generally be set up in type and reproduced at column or page width, although certain tables are better presented using transfer lettering; these should be submitted in the same way as line illustrations. Each table should have a heading and be on a separate sheet. For layout of analytical data see tables published in previous issues. Authors will be asked to send published analyses of igneous rocks to the UK-IGBA file.

4. References

Set out as indicated below. Abbreviate journal and series titles according to Part 2 (1975) of BS 4148 (The abbreviation of titles of periodicals. Word-abbreviation list. London: British Standards Institution). This system uses capitals throughout and no full-stops. Authors who are unable to obtain this list should give journal titles in full (in capitals). Indicate volume numbers of journals and series by wavy underlining and book titles by single underlining.


5. Proofs and offprints

One set of proofs will be sent to the author (or senior author of a joint paper). Fifty free offprints are provided and additional copies can be ordered when proofs are returned.
The policy of the Transactions of the Royal Society of Edinburgh: Earth Sciences is to publish substantial contributions to both information and geological understanding that are relevant to an international readership. This journal appears quarterly as successor to the Transactions of the Royal Society of Edinburgh which has published substantial contributions to the natural sciences for nearly two centuries. It covers all aspects of earth and related planetary sciences and rather than locally orientated topics contains contributions that emphasize principles and represent a world-wide authorship. Its international and wide-ranging character is indicated by the editorial personnel and the range of topics covered.

**Subscription rates.** The cost per volume (4 parts), post paid, is £35.00 for subscribers in the United Kingdom and US$90.00 for overseas subscribers. The corresponding rates for single quarterly parts are £10.00 and US$25.00. Subscriptions and requests for further information should be sent to THE ROYAL SOCIETY OF EDINBURGH, 22 GEORGE STREET, EDINBURGH EH2 2PQ, SCOTLAND.