Carbon and water dynamics of peat soils in the Australian Alps

Submitted by
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A thesis submitted in total fulfillment of the requirements for the degree of Doctor of Philosophy

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May 2006
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Terms in italics were not measured in this study.  

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Terms in italics were not measured in this study.
Summary

This research investigated carbon dynamics, water dynamics and peat formation at Wellington Plain peatland in the Victorian Alps. The properties of bog peat and dried peat were measured, and the ensuing results are outlined below.

The carbon chemistries of both bog peat and dried peat displayed changes with depth consistent with an increase in the extent of decomposition of the organic material. Representative changes in the alkyl:O-alkyl ratio down the profile were 0.14 to 0.96 for bog peat and 0.28 to 1.07 for dried peat. Laboratory incubations on the influence of chemistry, particle size, water content and sample preparation indicated that, in the absence of confounding factors, peat chemistry was the most important factor in determining the size of the mineralisable carbon pool. Water content was the most important factor in determining the rate of carbon mineralization. In the field, both bog peat and dried peat emitted an average of 2 g CO₂/m²/d from the surface. Carbon mineralisation was related to both soil temperature and soil water content, and this relationship was used to model peat mineralisation under a range of possible future climate scenarios. Below the surface, however, I measured lower rates of decomposition in the dried peat than in the bog peat.

The water-holding capacity of peat was measured in the laboratory, as was the rate of water movement through peat. Specific yield decreased down the profile in both bog peat (0.88 to 0.45 cm³/cm³) and dried peat (0.36 to 0.11 cm³/cm³). Hydraulic conductivity also decreased down the profile in both peats: 5.1x10⁻⁶ to 3.0x10⁻⁶ m/s in bog peat, and 1.0x10⁻⁴ to 7.0x10⁻⁶ m/s in dried peat. Relationships between the hydrologic properties of peat and its physical and chemical properties were identified. In the field, fluctuations in the watertable were monitored in concert with rainfall. These laboratory and field measurements enabled me to develop models of the hydrology of bog peat and dried peat.

Radioisotope dating indicated that both bog peat and dried peat began forming around 3300 years ago. The bog peat appeared to have drained to form dried peat between 131 and 139 years ago. Since that time, erosion appeared to have contributed more to the loss of organic material from dried peat than carbon mineralisation had.
Statement of Authorship

Except where reference is made in the text of the thesis, this thesis contains no material published elsewhere or extracted in whole or in part from a thesis submitted for the award of any other degree of diploma.

No other person’s work has been used without due acknowledgment in the main text of the thesis.

This thesis has not been submitted for the award of any degree of diploma in any other tertiary institution.

Samantha Patricia Power Grover
25th May 2006
Acknowledgements

Sincere thanks to all of my supervisors: Jeff Baldock, Warwick Papst, Ken Rowe and Judy Tisdall. A disparate and somewhat unwieldy team, the unique contribution that each of you made to this research has been extremely valuable. On questions chemical, botanical, ecological, grammatical, statistical and geological, I always had somewhere to turn, and I thank you all for your patience, enthusiasm and encouragement.

I have been fortunate to work with staff from a number of institutions, each of whose input has added to the breadth of this research. Thanks to the following people: from La Trobe University, Wolfgang Yunker, Joe Edwards, Jaikirat Singh Gill and Lesley Taskis; from Parks Victoria Heyfield, Peter Lawrence and Wayne McCullum; from CSIRO Land and Water Adelaide, Steve Szarvas, Ron Smernik and Simon Chamberlain; from the Australian Nuclear Science and Technology Organisation, Geraldine Jacobsen, Henk van der Gaast, Atun Zawadski, Jennifer Harrison and Henk Heijnis.

Assistance has also been provided by many people outside their work roles. Blair McKenzie made helpful comments on a draft of chapter 5. Peter Kershaw and Robert van de Graaff kindly lent peat corers to me, without which the secrets of the bog would have remained in the ground. Tineke Adolphus provided a home away from home during my visits to CSIRO in Adelaide. Heather Keith and Jane Mullet guided my design and construction of the chambers with which I measured CO$_2$ emissions. The aerial photograph of Wellington Plain peatland was taken by Henrik Wahren, and James Shannon ‘photoshopped’ it for my purposes. Nathan Wong taught me how to use ARCVIEW.

Elve Lode and the other organisers of “Ecohydrological Processes in Northern Wetlands: an international conference and educational workshop, Estonia, 2003” warmly welcomed a southerner. Trampling over both pristine bogs and drained cutover peatlands in the company of some of the northern hemisphere’s most esteemed peat scientists set my research on the right track, inspired me and gave me first hand experience of the techniques and theories of peat ecohydrology. Lisa Belyea and Andy Baird both took a chance on an unknown Australian and generously allowed me to be involved with their field work on bogs in the United Kingdom.
While such a community of peat scientists does not exist in Australia, I have been fortunate to be a part of the CRC for Greenhouse Accounting. Janette Lindesay and Robyn Harris have particularly looked after me and their dedication to the wellbeing of CRC students has added greatly to my enjoyment and skill development.

My field work in the Alps has been made more enjoyable by the assistance of many of my friends and family. Repeat offenders include Rebecca Sharkey, Domenica Settle, Liz Hobday and Zoe Loh. Jodie Matire and Susanna Venn even helped me in the laboratory, as well as in the field.

My family, Anne Marie Power, Joe Bolza and Will Power, have always supported my education- thanks guys, I think it may be over now! More recently, Susanna Venn has supported me enormously during the completion of my PhD- thank-you. My housemates at 72 Thomson St have encouraged and entertained me over the past four years- particular thanks to Camille Heisler, who has seen me through the whole thing. The Brunswick Women’s Choir and Luna Yoga School helped me to withstand, both physically and mentally, the pressures of completing a PhD.

Funding for this research was provided by grants from the CRC for Greenhouse Accounting and Parks Victoria, an Australian Postgraduate Award and an Australian Institute of Nuclear Science and Engineering Postgraduate Research Award.

Finally, I think it is appropriate to thank the inanimate beings who have made this research possible. Thanks to Wellington Plain peatland and Darebin Creek. The former provided both the physical basis for this research, and endless inspiration and joy. The later kept me sane and in touch while in town.
Definitions and abbreviations

**Acrotelm**: the upper layer of a bog, rapid exchange of matter and energy with the environment, see Table 1.3 for details

**Alkyl carbon**: a carbon atom bound to only hydrogen atoms or other carbon atoms

**ANSTO**: Australian Nuclear Science and Technology Organisation

**Aromatic carbon**: a carbon atom with a double bond to another carbon atom

**Bog**: a peatland with the watertable permanently above the surrounding groundwatertable, usually *Sphagnum*-based and actively accumulating peat, has a characteristic hummock and hollow topography, also known locally as a mossbed

**Bog peat**: the peat in a bog

**Capitula**: the top of the *Sphagna*, a headlike cluster of branches at the apex of the stem

**Carbonyl carbon**: a carbon atom with a double bond to one oxygen atom and a single bond to another oxygen atom

**Catotelm**: the lower layer of a bog, slow exchange of matter and energy with the environment, see Table 1.3 for details

**Dried peat**: a drained remnant of bog peat, without a permanent watertable, also known locally as humified peat

**EOD**: extent of decomposition

**Fibric peat**: undecomposed or weakly decomposed organic material; plant material remains are distinct and identifiable; yields clear to weakly turbid water; no peat escapes through the fingers when squeezed in the hand

**Groundwater**: water which has passed through soil or rock material

**Hemic peat**: moderately to well-decomposed organic material; plant remains recognisable but may be rather indistinct and difficult to identify; yields strongly turbid to muddy water, amount of peat escaping through the fingers ranges from none to up to one third; residue is pasty

**Mesotrophic**: water high in nutrients, generally groundwater

**Minerotrophic**: water high in nutrients, generally groundwater

**NMR**: nuclear magnetic resonance

**O-alkyl carbon**: a carbon atom bound to an oxygen atom

**Ombrotrophic**: water low in nutrients, generally rainfall
Peat: the organic soil of a peatland, including all material below the close surface of the *Sphagnum capitulum*

Peatland: an ecosystem with a peat soil

Permanent storage: storage of water for years

Sapric peat: strongly to completely decomposed organic material; plant remains indistinct to unrecognisable; amounts ranging from about half to all escape between fingers; any residue is almost entirely resistant remains such as root fibres and wood

Temporary storage: storage of water for hours or days
Carbon and water dynamics of peat soils in the Australian Alps

Submitted by
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A thesis submitted in total fulfillment of the requirements for the degree of Doctor of Philosophy

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May 2006
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Summary

This research investigated carbon dynamics, water dynamics and peat formation at Wellington Plain peatland in the Victorian Alps. The properties of bog peat and dried peat were measured, and the ensuing results are outlined below.

The carbon chemistries of both bog peat and dried peat displayed changes with depth consistent with an increase in the extent of decomposition of the organic material. Representative changes in the alkyl:O-alkyl ratio down the profile were 0.14 to 0.96 for bog peat and 0.28 to 1.07 for dried peat. Laboratory incubations on the influence of chemistry, particle size, water content and sample preparation indicated that, in the absence of confounding factors, peat chemistry was the most important factor in determining the size of the mineralisable carbon pool. Water content was the most important factor in determining the rate of carbon mineralization. In the field, both bog peat and dried peat emitted an average of 2 g CO₂/m²/d from the surface. Carbon mineralisation was related to both soil temperature and soil water content, and this relationship was used to model peat mineralisation under a range of possible future climate scenarios. Below the surface, however, I measured lower rates of decomposition in the dried peat than in the bog peat.

The water-holding capacity of peat was measured in the laboratory, as was the rate of water movement through peat. Specific yield decreased down the profile in both bog peat (0.88 to 0.45 cm³/cm³) and dried peat (0.36 to 0.11 cm³/cm³). Hydraulic conductivity also decreased down the profile in both peats: 5.1x10⁻⁴ to 3.0x10⁻⁶ m/s in bog peat, and 1.0x10⁻⁴ to 7.0x10⁻⁶ m/s in dried peat. Relationships between the hydrologic properties of peat and its physical and chemical properties were identified. In the field, fluctuations in the watertable were monitored in concert with rainfall. These laboratory and field measurements enabled me to develop models of the hydrology of bog peat and dried peat.

Radioisotope dating indicated that both bog peat and dried peat began forming around 3300 years ago. The bog peat appeared to have drained to form dried peat between 131 and 139 years ago. Since that time, erosion appeared to have contributed more to the loss of organic material from dried peat than carbon mineralisation had.
Statement of Authorship

Except where reference is made in the text of the thesis, this thesis contains no material published elsewhere or extracted in whole or in part from a thesis submitted for the award of any other degree of diploma.

No other person’s work has been used without due acknowledgment in the main text of the thesis.

This thesis has not been submitted for the award of any degree of diploma in any other tertiary institution.

Samantha Patricia Power Grover
25th May 2006
Acknowledgements

Sincere thanks to all of my supervisors: Jeff Baldock, Warwick Papst, Ken Rowe and Judy Tisdall. A disparate and somewhat unwieldy team, the unique contribution that each of you made to this research has been extremely valuable. On questions chemical, botanical, ecological, grammatical, statistical and geological, I always had somewhere to turn, and I thank you all for your patience, enthusiasm and encouragement.

I have been fortunate to work with staff from a number of institutions, each of whose input has added to the breadth of this research. Thanks to the following people: from La Trobe University, Wolfgang Yunker, Joe Edwards, Jaikirat Singh Gill and Lesley Taskis; from Parks Victoria Heyfield, Peter Lawrence and Wayne McCullum; from CSIRO Land and Water Adelaide, Steve Szarvas, Ron Smernik and Simon Chamberlain; from the Australian Nuclear Science and Technology Organisation, Geraldine Jacobsen, Henk van der Gaast, Atun Zawadski, Jennifer Harrison and Henk Heijnis.

Assistance has also been provided by many people outside their work roles. Blair McKenzie made helpful comments on a draft of chapter 5. Peter Kershaw and Robert van de Graaff kindly lent peat corers to me, without which the secrets of the bog would have remained in the ground. Tineke Adolphus provided a home away from home during my visits to CSIRO in Adelaide. Heather Keith and Jane Mullet guided my design and construction of the chambers with which I measured CO$_2$ emissions. The aerial photograph of Wellington Plain peatland was taken by Henrik Wahren, and James Shannon ‘photoshopped’ it for my purposes. Nathan Wong taught me how to use ARCVIEW.

Elve Lode and the other organisers of “Ecohydrological Processes in Northern Wetlands: an international conference and educational workshop, Estonia, 2003” warmly welcomed a southerner. Tramping over both pristine bogs and drained cutover peatlands in the company of some of the northern hemisphere’s most esteemed peat scientists set my research on the right track, inspired me and gave me first hand experience of the techniques and theories of peat ecohydrology. Lisa Belyea and Andy Baird both took a chance on an unknown Australian and generously allowed me to be involved with their field work on bogs in the United Kingdom.
While such a community of peat scientists does not exist in Australia, I have been fortunate to be a part of the CRC for Greenhouse Accounting. Janette Lindesay and Robyn Harris have particularly looked after me and their dedication to the wellbeing of CRC students has added greatly to my enjoyment and skill development.

My field work in the Alps has been made more enjoyable by the assistance of many of my friends and family. Repeat offenders include Rebecca Sharkey, Domenica Settle, Liz Hobday and Zoe Loh. Jodie Matire and Susanna Venn even helped me in the laboratory, as well as in the field.

My family, Anne Marie Power, Joe Bolza and Will Power, have always supported my education- thanks guys, I think it may be over now! More recently, Susanna Venn has supported me enormously during the completion of my PhD- thank-you. My housemates at 72 Thomson St have encouraged and entertained me over the past four years- particular thanks to Camille Heisler, who has seen me through the whole thing. The Brunswick Women’s Choir and Luna Yoga School helped me to withstand, both physically and mentally, the pressures of completing a PhD.

Funding for this research was provided by grants from the CRC for Greenhouse Accounting and Parks Victoria, an Australian Postgraduate Award and an Australian Institute of Nuclear Science and Engineering Postgraduate Research Award.

Finally, I think it is appropriate to thank the inanimate beings who have made this research possible. Thanks to Wellington Plain peatland and Darebin Creek. The former provided both the physical basis for this research, and endless inspiration and joy. The later kept me sane and in touch while in town.
Definitions and abbreviations

**Acrotelm**: the upper layer of a bog, rapid exchange of matter and energy with the environment, see Table 1.3 for details

**Alkyl carbon**: a carbon atom bound to only hydrogen atoms or other carbon atoms

**ANSTO**: Australian Nuclear Science and Technology Organisation

**Aromatic carbon**: a carbon atom with a double bond to another carbon atom

**Bog**: a peatland with the watertable permanently above the surrounding groundwatertable, usually *Sphagnum*-based and actively accumulating peat, has a characteristic hummock and hollow topography, also known locally as a mossbed

**Bog peat**: the peat in a bog

**Capitula**: the top of the *Sphagna*, a headlike cluster of branches at the apex of the stem

**Carbonyl carbon**: a carbon atom with a double bond to one oxygen atom and a single bond to another oxygen atom

**Catotelm**: the lower layer of a bog, slow exchange of matter and energy with the environment, see Table 1.3 for details

**Dried peat**: a drained remnant of bog peat, without a permanent watertable, also known locally as humified peat

**EOD**: extent of decomposition

**Fibric peat**: undecomposed or weakly decomposed organic material; plant material remains are distinct and identifiable; yields clear to weakly turbid water; no peat escapes through the fingers when squeezed in the hand

**Groundwater**: water which has passed through soil or rock material

**Hemic peat**: moderately to well-decomposed organic material; plant remains recognisable but may be rather indistinct and difficult to identify; yields strongly turbid to muddy water, amount of peat escaping through the fingers ranges from none to up to one third; residue is pasty

**Mesotrophic**: water high in nutrients, generally groundwater

**Minerotrophic**: water high in nutrients, generally groundwater

**NMR**: nuclear magnetic resonance

**O-alkyl carbon**: a carbon atom bound to an oxygen atom

**Ombrotrophic**: water low in nutrients, generally rainfall
Peat: the organic soil of a peatland, including all material below the close surface of
the *Sphagnum capitulum*

**Peatland:** an ecosystem with a peat soil

**Permanent storage:** storage of water for years

**Sapric peat:** strongly to completely decomposed organic material; plant remains
indistinct to unrecognisable; amounts ranging from about half to all escape between
fingers; any residue is almost entirely resistant remains such as root fibres and wood

**Temporary storage:** storage of water for hours or days
Chapter 1. General introduction

Summary
This chapter defines peat and outlines the current knowledge about its nature and function through consideration of the two major components of peat: carbon and water. This knowledge is exclusively drawn from research on northern hemisphere peats, and thus the subsequent Section addresses tropical and southern hemisphere peats. Limited research has suggested that some of the concepts developed from the study of northern hemisphere peatlands may not directly apply elsewhere, due to differences in vegetation and water chemistry. The peatlands of Australia are briefly outlined before a more detailed survey of Sphagnum bog peatlands of the Australian Alps. The vegetation dynamics of these peatlands are relatively well characterised, but the soil-water interactions of the peat soil are less thoroughly understood. The current research contributes to filling this knowledge gap and the specific aims are outlined in the final Section.
1.1 Peat

1.1.1 What is peat?

Peat is an organic soil formed by the build up of partially decomposed plant material (Clymo 1983). A combination of cold, wet and acidic conditions hinders the decomposition of plant material such that production of organic matter outweighs decay (Charman 2002). The botanical composition of peat is therefore one of its most important characteristics. The three broad categories of peat are moss peat, herbaceous peat and wood peat (Clymo 1983). It is the first category, moss peat, that is the subject of this thesis, and subsequent use of the word ‘peat’ refers to moss peat unless otherwise specified. *Sphagnum*, the dominant peat-forming moss, is thought to have chemical properties that assist it to resist decomposition and thus promote peat formation (van Breeman 1995). Peat is of interest in many different fields: energy, agriculture, horticulture, forestry, engineering, archeology, history, ecology, medicine, biodiversity conservation and, most recently, climate change.

1.1.2 The importance of peat

Peat stores carbon and history. The incomplete decomposition of plant matter in peat has resulted in the storage of an estimated 455 Pg of carbon, or more than one third of the world’s soil carbon pool, in northern peatlands alone (Gorham 1991; Post, Emanuel et al. 1982). Tropical and southern hemisphere peatlands, while less extensive than peatlands in the northern hemisphere, also store substantial carbon reserves (estimated at 70 Pg for the tropics, and unquantified for the southern hemisphere) (Gore 1983; Page, Wust et al. 2004). The plant material preserved in peat comprises an archive of environmental history (Charman 2002). From a popular fascination with ‘bog bodies’ (Glob 1977) to the more specialised fields of radiochemistry, isotope and pollen analyses (Frenzel 1983; Krull, Thompson et al. 2004), peat has contributed much to our understanding of past climates and civilizations. However, the preservation of organic matter in peat depends upon the peat remaining waterlogged. Drainage leads to aerobic conditions and accelerated rates of decomposition (Armstrong and Castle 1999). Stored carbon is released to the atmosphere and historical records may be lost when peat is drained.

Drainage is a prerequisite for many uses of peat (Armstrong and Castle 1999). Peat is mined for energy and as a growing medium for the horticultural industry.
Agriculture and forestry on peat soils require drainage. A balance between the growing demand for resources and the value of carbon and history stored in peat is being actively pursued by such projects as the ‘Statement on the Wise Use of Peatlands’ (IPS and IMCG 2002). This is a joint statement prepared by the International Peat Society (mainly representing industry) and the International Mire Conservation Group. The Kyoto protocol has also prompted increased interest in carbon fluxes from peat, as countries are required to account for their greenhouse gas emissions (Charman 2002).

1.2 Carbon cycling

Carbon is the major component of peat (Charman 2002). An average carbon content for a typical *Sphagnum* bog peat is 52% of dry matter (Charman 2002). This carbon is fixed by plants from the atmosphere as they photosynthesise. The dead plant material forms the basis of the peat. As the plant material decomposes, carbon is released back to the atmosphere in the form of carbon dioxide and methane. Smaller amounts of carbon enter and leave the peat in water, in the form of dissolved organic carbon and particulate carbon (Fig 1.1). The simplicity of Fig. 1.1 belies the complexity of the processes involved and the variability between years, between sites and within sites. The Swedish *Sphagnum* bog in Fig. 1.1 displayed a net carbon gain of 2 g C/m$^2$ in 1992 (Waddington and Roulet 2000). Measurement of the same variables the following year yielded a net carbon loss of 7.6 g C/m$^2$, under similar annual rainfall and temperature conditions.
Another way of considering the carbon cycle in peat is described in Equation 1.1.

Carbon inputs – carbon outputs = change in carbon stored  

Equation 1.1.

If the term on the right is positive, carbon is accumulating and plant production outweighs decomposition: a carbon sink. If the term on the right is negative, carbon is being released: a carbon source. The outcome of Equation 1.1 is determined by the rate of plant production and the rate of organic matter decomposition (Charman 2002).

Plant productivity is determined by the species present and the availability of sunlight, nutrients and water. Studies of carbon cycling in peat have measured plant production by both direct and indirect methods. Some direct measurements are described in Table 1.1. Indirect measurement of plant growth focuses on the amount of carbon assimilated by photosynthesis, measured by monitoring CO₂ concentrations in chambers on the peat surface (Komulainen, Tuittila et al. 1999; Tuittila, Vasander et al. 2004). Photosynthesis was reported to vary between 102 and 2320 mg CO₂/m²/h and between 0 and 800 mg CO₂/m²/h on two restored Finnish peatlands (Komulainen,
Tuittila et al. 1999; Tuittila, Vasander et al. 2004). Comparison of results between direct and indirect measurements of plant productivity is difficult because a) there are large errors associated with direct methods (Clymo 1983) and b) there is incomplete overlap between the components of biomass measured by the two methods. Direct measurement of productivity is labour intensive, while indirect measurement is capital intensive. Direct measurement results in a value for productivity which is averaged over a long time period (months or years), but as it is destructive, only one measurement can be taken. Indirect measurements of plant productivity only cover a few minutes or hours, and thus repeated measurements are required, which is possible as the process is non-destructive. An advantage of indirect measurement of plant productivity is that the same equipment can be used to measure carbon leaving the system as CO₂ and CH₄, the products of peat decomposition.

**Table 1.1 Methods of measurement of plant productivity in studies of peat**

<table>
<thead>
<tr>
<th>Method</th>
<th>Measurement of productivity (g/m²/yr)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Capitulum correction</td>
<td>Sphagnum</td>
</tr>
<tr>
<td>Harvest of fall litter</td>
<td>1106820</td>
</tr>
<tr>
<td>Harvest of all plant matter</td>
<td>1806790</td>
</tr>
<tr>
<td>Harvest of all plant matter</td>
<td>Root growth cores</td>
</tr>
<tr>
<td></td>
<td>Sphagnum</td>
</tr>
<tr>
<td></td>
<td>Other plants</td>
</tr>
<tr>
<td></td>
<td>Rootsg</td>
</tr>
<tr>
<td></td>
<td>all 3 components combined</td>
</tr>
</tbody>
</table>

*productivity is in g of biomass in the first two studies and g of carbon in Moore et al. (2002)

**Moore et al. (2002) harvested all biomass and used previously established relationships between biomass and annual growth rates to predict productivity

Decomposition includes leaching, comminution and carbon mineralisation (respiration) (Belyea 1996). These three processes enable carbon to leave the peat as dissolved organic carbon (DOC), particulate carbon and gaseous carbon (CO₂ and CH₄) respectively. Measurement of decomposition by determining the loss of mass of
peat buried in mesh bags incorporates all three of these processes (Belyea 1996) and has been widely used (Clymo 1965; Haraguchi, Hasegawa et al. 2003; Latter, Howson et al. 1998; Lieffers 1988; Limpens and Berendse 2003). However, DOC and CH$_4$ fluxes from undisturbed peatlands have been found to be one to two orders of magnitude smaller than CO$_2$ fluxes (Waddington and Roulet 2000). Thus, many studies of carbon cycling in peat focus on measuring CO$_2$ (Hogg, Lieffers et al. 1992; McNeil and Waddington 2003; Moore, Bubier et al. 2002; Scalon and Moore 2000; Stewart 1990; Turetsky 2004; Waddington, Rotenberg et al. 2001; Waddington, Warner et al. 2002). Results from the two methods (Table 1.2), mass loss and gas evolution, are not directly comparable, as there is incomplete overlap in the components of decomposition that they measure. Measurement of mass loss yields results that are the sum of environmental conditions over a long period (months to years). Measurement of gas evolution occurs over a shorter period (minutes to hours), over which environmental variables (temperature and water content) also vary (and may be measured). The former method is, arguably, a more accurate representation of present decomposition, while the later method is more useful for predicting decomposition under possible future environmental conditions.

Table 1.2 Methods of measurement of peat decomposition

<table>
<thead>
<tr>
<th>Study</th>
<th>Location</th>
<th>Method</th>
<th>Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Clymo 1965)</td>
<td>England</td>
<td>Mesh bags</td>
<td>Mass loss 2-20%</td>
</tr>
<tr>
<td>(Lieffers 1988)</td>
<td>Canada</td>
<td>Mesh bags</td>
<td>Mass loss 15-22%</td>
</tr>
<tr>
<td>(Limpens and Berendse 2003)</td>
<td>The Netherlands, Ireland</td>
<td>Mesh bags</td>
<td>Mass loss 5-30%</td>
</tr>
<tr>
<td>(Hogg, Lieffers et al. 1992)</td>
<td>Canada</td>
<td>CO$_2$: laboratory incubation of intact peat cores</td>
<td>0.44-11.4 g/m$^2$/d</td>
</tr>
<tr>
<td>(Buttler, Dinel et al. 1994)</td>
<td>Canada</td>
<td>CO$_2$: chambers on peat surface</td>
<td>0.98-5.24 g/m$^2$/d</td>
</tr>
<tr>
<td>(Waddington, Rotenberg et al. 2001)</td>
<td>Canada</td>
<td>CO$_2$: laboratory incubation of peat slurries</td>
<td>0.023-0.087 g/m$^2$/d</td>
</tr>
<tr>
<td>(Chimner and Cooper 2003a)</td>
<td>USA</td>
<td>CO$_2$: chambers on peat surface</td>
<td>2.4-14.4 g/m$^2$/d</td>
</tr>
</tbody>
</table>
Measurements of plant production and decomposition have informed numerous models of the structure and function of peat bogs. The accumulation of these models was initiated by the research of Clymo (Belyea and Clymo 2001; Clymo 1983; Clymo 1984; Clymo 1992; Clymo, et al. 1978), whose work has contributed significantly to the understanding of peatland function. Clymo’s models emphasise differential rates of decomposition in the acrotelm and the catotelm. Clymo’s ‘standard’ bog had a rate of decay of 0.6-0.12 yr\(^{-1}\) in the acrotelm and 0.0012-0.0006 yr\(^{-1}\) in the catotelm (Clymo 1984). An alternative school of thought emphasises soil physics and hydrology, in particular the low hydraulic conductivity (~ 5x10\(^{-4}\) cm/s) of the catotelm (Ingram 1982; Ingram 1983; Ivanov 1981). Clymo’s comment that Ingram’s model ‘fails badly for large diameter (several kilometers) bogs’ (pers. comm. in Yu, Campbell et al. 2001) hints at ongoing differences between these two schools of thought. More recent approaches have constructively combined hydrology and rates of decomposition (Hilbert, Roulet et al. 2000; Yu, Turetsky et al. 2001). The ensuing models may more closely approach reality, as they include more variables, dimensions and equations. However, complex models are often limited by data availability, and one would be wise to remember Clymo’s advice; a model is a useful aid, but no substitute for observation and experiment (Clymo 1992, p. 135).

The rate of peat decomposition is principally affected by temperature, water content, the microbes and animals present and the plant material (Charman 2002). Decomposition rates increase as temperature increases (Bergman, Lundberg et al. 1999; Scalon and Moore 2000). For example, CO\(_2\) emission increased from 140 to 1240 nmol/g dw/h, as Bergman et al. (1999) increased temperature from 7 to 17 °C. Decomposition rates increase and then decrease as water content decreases from saturation (Waddington, Rotenberg et al. 2001). For example, CO\(_2\) emissions of 12.5, 16, 19 and 16.5 µmol/g/d corresponded to peat saturations of 32, 57, 74 and 90 % (Waddington, Rotenberg et al. 2001). Different plant materials decompose at different rates (Latter, Howson et al. 1998). For example, after two years of field incubation, samples of the dominant non-Sphagnum vegetation in an English bog, Calluna vulgaris, Eriophorum vaginatum and Rubus chamaemorus, had lost 30, 37 and 54 % of their original masses, respectively (Latter, Howson et al. 1998). Plant material that is well decomposed to begin with decomposes more slowly than fresh plant material does (Buttler, Dinel et al. 1994; Clymo 1965; Turetsky, Wieder et al.
For example, *Sphagnum capitula* lost 25.8% of their weight over the same incubation period (103 days) as samples of ‘mature peat collected from 60 cm depth’ lost only 3% of their weight (Clymo 1965). However, the interactions between the aforementioned factors are complex (Charman 2002), and often site and even micro-site specific (Belyea 1996).

The increase in decomposition rates with increased temperature has led to concern that global warming may increase peat decomposition, possibly altering the balance between production and decomposition such that current peat-accumulating systems (carbon sinks) will become sources of carbon (Gorham 1991). Carbon released from peat in the form of CO$_2$ and CH$_4$ will further increase the enhanced greenhouse effect, which could lead to a positive feedback loop (Updegraff, Bridgham *et al.* 1998). Many areas of peat used for mining, agriculture and forestry currently function as carbon sources. The drainage required by these industries alters peatlands from carbon sinks to carbon sources, due to increased decomposition and changes in species (Charman 2002). For example, a cutover peatland in Canada emitted three times as much CO$_2$ as an undisturbed peatland did (Waddington, Warner *et al.* 2002).

Extensive research on how to return these drained peatlands to functioning as carbon sinks all points towards hydrology as the crucial factor (Komulainen, Tuittila *et al.* 1999; McNeil and Waddington 2003; Price and Whitehead 2004; Tuittila, Komulainen *et al.* 1999; Tuittila, Vasander *et al.* 2004; Van Seters and Price 2002; Waddington, Rotenberg *et al.* 2001; Waddington, Warner *et al.* 2002).

### 1.3 Hydrology

Water is critical to the existence of peat. It is the waterlogged conditions which slow decomposition and allow a deposit of organic material to build up (Charman 2002). The source of this water has traditionally been used to divide peatlands into bogs and fens, the former receiving water only from precipitation, while the latter receives both precipitation and groundwater (Gore 1983). While it is now recognised that some bogs receive input from groundwater (Lamers, Farhoush *et al.* 1999; Moore 1997), the two-layered model of the hydrology of a precipitation-fed bog (Fig 1.2) remains a useful model of how bogs function. Ingram (1978) proposed the terms ‘acrotelm’ and ‘catotelm’ when he introduced this model, developed in the USSR (Ivanov 1981), to an English-speaking audience. A bog is divided into two functionally different layers (Table 1.3). The acrotelm minimises variation in the depth of the watertable, due to
the decrease in the rate of water movement with depth (Ingram and Bragg 1984). For example, water moved at 0.36, 0.035 and 0.0086 cm/s at depths of 10, 20 and 30 cm in the acrotelm of a *Sphagnum* bog in Scotland (Ingram and Bragg 1984). This same property of the acrotelm also minimises surface erosion, because large volumes of water can move as throughflow through the rapidly-conducting upper acrotelm (Ingram and Bragg 1984). Thus, bogs in a catchment tend to delay peak streamflow in comparison with mineral soils; because in a bog more water moves as throughflow than as surface runoff, whereas mineral soils tend to produce more surface runoff than throughflow (Charman 2002). For example, peak runoff from a *Sphagnum* bog was 22 hours after peak runoff from mineral soils in a catchment in Scotland (Charman 2002).

Fig 1.2 A simple model of bog hydrology. The size of arrows indicates the size of water fluxes associated with each process.
The rate of water movement through peat is of interest both to those who wish to understand how bogs function and to those who wish to use bogs. The rate of water movement through a porous medium (or hydraulic conductivity) can be expressed by Darcy’s Law (Equation 1.2)

\[ Q = k \times (\Delta h/\Delta d) \]  

Equation 1.2

where  
\( Q \) = rate of flow  
\( k \) = hydraulic conductivity  
\( \Delta h/\Delta d \) = gradient of the water potential, change in height over change in distance

There has been some debate as to the applicability of Darcy’s Law to peat (Hemmond and Goldman 1985; Mathur and Levesque 1985; Rycroft, Williams et al. 1975a). Dai and Sparling (1973) reported a significant correlation between a) \( \Delta h/\Delta d \) and time, and b) \( k \) and \( \Delta h/\Delta d \). These results contradict the assumptions, which underlie Darcy’s Law, of steady state flow, and direct proportionality between \( Q \) and \( \Delta h/\Delta d \), respectively. A series of field experiments by Rycroft et al. (1975b) confirmed the correlations between \( \Delta h/\Delta d \) and time, and between \( k \) and \( \Delta h/\Delta d \). For example, Rycroft et al. (1975b) found that hydraulic conductivity increased from 0.5 to 1.7 cm/s x 10^4 as \( \Delta h/\Delta d \) increased from 20 to 80 cm. Rycroft et al. (1975b) concluded that Darcy’s Law applied to undecomposed peat, but not to well decomposed peat. The presence of gas bubbles in peat, produced by microbial respiration, was suggested as an explanation for the apparent deviation from Darcy’s Law (Mathur and Levesque 1985). This proposal has been tested on repacked peat cores and intact peat monoliths.

Table 1.3 Properties of the two functional layers in a bog, the acrotelm and the catotelm, from Ingram (1978)

<table>
<thead>
<tr>
<th>Property</th>
<th>Acrotelm</th>
<th>Catotelm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water table</td>
<td>Present</td>
<td>Absent</td>
</tr>
<tr>
<td>Rate of water movement</td>
<td>Rapid, decreasing with depth</td>
<td>Slow</td>
</tr>
<tr>
<td>Water content</td>
<td>Variable</td>
<td>Constant</td>
</tr>
<tr>
<td>Aeration</td>
<td>Usually aerobic</td>
<td>Anaerobic</td>
</tr>
<tr>
<td>Microbial activity</td>
<td>High</td>
<td>Low</td>
</tr>
<tr>
<td>Energy exchange with the</td>
<td>Rapid</td>
<td>Slow</td>
</tr>
</tbody>
</table>
Both studies found that gas concentrations increased and k decreased over time in unprepared peat, while sterilised peat displayed no build up of gas or change in k over time. For example, k decreased from 0.0054 to 0.0019 cm/s while volumetric gas content increased from 13 to 16 % over a 64 day incubation of an unprepared peat monolith (Beckwith and Baird 2001). Nonetheless, hydraulic conductivity remains a useful concept to understand and manage peatlands, though the scale of measurement needs to match the scale of the desired outcome (Bromley, Robinson et al. 2004).

Hydrology is central to the formation and functioning of peatlands and also to our ability to use them. Drainage is a prerequisite for mining, agriculture and forestry on peat soils (Charman 2002). Drains allow water to leave the peat more readily and lead to greater variation in the watertable. For example, Van Seters and Price (2002) found that variation of the watertable was 67% greater in a cutover bog than in an adjacent undisturbed bog in Canada. Shrinkage, compaction and an increase in bulk density of the peat follow drainage (Armstrong and Castle 1999). These physical changes result in hydrologic changes: decreased hydraulic conductivity (e.g. undisturbed bog 4.1 x 10⁻⁵ cm/s, cutover bog 1.3 x 10⁻⁵ cm/s (Van Seters and Price 2002)) infiltration and throughflow, and increased water retention and surface runoff (Charman 2002). These hydrologic changes, in turn, lead to changes in carbon cycling in the peat (Hogg, Lieffers et al. 1992; Updegraff, Bridgham et al. 2001; Waddington, Warner et al. 2002). For example, as mentioned in Section 1.2, a cutover peatland in Canada emitted three times as much CO₂ as an undisturbed peatland did (Waddington, Warner et al. 2002). Watertable variation and increased water retention inhibit the reestablishment of Sphagnum (McNeil and Waddington 2003; Van Seters and Price 2001). For example, natural Sphagnum recolonisation of a cutover peatland occurred predominantly in depressions, where the watertable remained within 5 cm of the surface (Price and Whitehead 2004). Reestablishing a surface cover of Sphagnum is the key to returning a drained peatland to a peat-accumulating system (McNeil and Waddington 2003). Some studies suggest that active restoration, including transplanting Sphagnum, can return drained peatlands to carbon sinks in a few years (Komulainen, Tuittila et al. 1999; Tuittila, Vasander et al. 2004). However, without intervention, natural regeneration of drained and mined peatlands may take decades, if it occurs at all (Price, Heathwaite et al. 2003).
1.4 Peat in the tropics and the southern hemisphere

The research drawn upon to describe the nature and function of peatlands in the preceding Sections (1.1-1.3) is all work from the northern hemisphere, above the tropic of Cancer. Peatlands in the tropics and the southern hemisphere have been comparatively little studied. Peat formation is less common than in the northern hemisphere, for several reasons. In the southern hemisphere there is less land at comparable latitudes (Gore 1983), and much of it is very dry. In the tropics, high temperatures cause organic matter to decompose rapidly, and wet conditions are often seasonal (Junk 1983). Thus peat formation in both the tropics and the southern hemisphere is hindered by a lack of suitable conditions. However, although peatlands are less extensive than in the northern hemisphere, they are locally important in the tropics and southern hemisphere, and are attracting increasing attention in global carbon budgets (Page, Wust et al. 2004).

Classification systems developed in the northern hemisphere are often not suitable to describe tropical and southern hemisphere peatlands, because of differences in vegetation and water chemistry (Thompson and Hamilton 1983; Wust, Bustin et al. 2003). In particular, the association of high nutrient status with groundwater and low nutrient status with rain, which is so firmly entrenched in peatland classification in the northern hemisphere (Gore 1983), may not hold across different geologic settings, as groundwater chemistry is heavily influenced by the regolith through which it passes. The ancient and well-leached soils of Africa result in groundwater with electrical conductivities less than 10 µS/cm, which would classify as rain under northern hemisphere classifications (Thompson and Hamilton 1983). Silvester (pers. comm. March 2006) recorded electrical conductivities less than 8 µS/cm in groundwater exiting peatlands in the Australian Alps. However, knowledge of the structure and function of peatlands in the tropics and southern hemisphere is as yet insufficient to develop locally applicable classification systems. Consequently, it would be prudent to apply theories developed from studies of peat in the northern hemisphere with caution to peatlands elsewhere.

The majority of studies outside the northern hemisphere focus on the climatic history preserved in the peat (Aucour and Hillaire-Marcel 1994; Biester, Kilian et al. 2002; Hong, Jiang et al. 2000; Hope 1976; Jacob and Hallmark 1996; Page, Wust et al. 2004; Yonebayashi and Minaki 1997), and not on the current structure and
function of the peatland. While these studies have made an important contribution to their field, a review of paleoecology is beyond the scope of this thesis and thus these studies are not considered further. In the remainder of this Section, I discuss a selection of research from the tropics and southern hemisphere which has addressed aspects of the structure and function of peatlands.

The Chilean ‘bofedal’ is a rapidly expanding peatland dominated by the cushion-forming rush *Oxychole* (Earle, Warner et al. 2003). This valley-bottom peatland has been moving upslope for the past 50 years, accumulating carbon at higher rates than those recorded anywhere else in the world. The long-term apparent rate of carbon accumulation ranged from 70 to 292 g C/m$^2$/yr, an order of magnitude higher than that recorded in *Sphagnum* peatlands in the northern hemisphere (Earle, Warner et al. 2003). Bofedales occur in the harsh climate of the Andean Altiplano, near the hydrological and biological limits for peat formation, and are thus likely to be sensitive to climate change. While bofedal peatlands cover only small areas, their rapid accumulation of carbon renders them 10 to 100 times more significant in global carbon cycling than the same sized area of *Sphagnum* peat (Earle, Warner et al. 2003). This study clearly demonstrated that peatlands in the southern hemisphere, particularly non-*Sphagnum* peatlands, are not always governed by the same axioms as peatlands in the northern hemisphere.

Antarctic peatlands are of particular interest because of their simple composition and extreme conditions. No higher plants grow in Antarctica, so peatlands are entirely composed of mosses and lichens. The permafrost peatlands are dominated by *Polytrichum alpestre* and *Chorisodontium aciphyllum*, and accumulate peat at rates similar to *Sphagnum* peatlands in the northern hemisphere (89-158 g/m$^2$/yr) (Fenton 1980). Peat accumulation, as explained in Section 1.2 above, is the sum of plant productivity and organic matter decay. Permafrost prevents any decay of peat and thus the similarity between accumulation rates in Antarctica and the northern hemisphere masks the differences in plant productivity. In the absence of permafrost, the extreme Antarctic climate hinders decomposition of *Ceratodon purpurea* peat such that carbohydrate carbon is less mineralised than that in peats from the northern hemisphere (Beyer, Blume et al. 1997).

The slow decomposition of South American and Antarctic peatlands contrasts with the rapid subsidence, largely attributed to decomposition, experienced by drained peatlands in Malaysia (Wösten, Ismail et al. 1997). Swamp forest peatlands were
extensively drained in the 1960s for agricultural use. They continue to shrink, and at higher rates than drained peatlands of the northern hemisphere do (Wösten, Ismail et al. 1997). With a watertable depth of 40 cm, peat in Malaysia and the Netherlands subsided at 3 and 0.5 cm/yr, respectively. When the watertable was lowered to 80 cm depth, subsidence rates increased to 6 and 1.6 cm/yr, respectively (Wösten, Ismail et al. 1997). This difference in decomposition rates is attributed to the higher temperatures of tropical peatlands than those in the Netherlands. More rapid subsidence decreases the useful lifespan of drained peatlands; acid sulfate soils below Malaysian peatlands are predicted to be exposed by 2072 (Wösten, Ismail et al. 1997). This study lends further weight to the argument that the theories developed from the study of peatlands in the northern hemisphere cannot be directly applied to manage peatlands elsewhere.

New Zealand is one of the few countries in the tropics or southern hemisphere to have an extensive literature on peatlands. Peat covers 0.7% of New Zealand (Mark, Johnson et al. 1995). In addition to studies of climate history (Armour and Kennedy 2005; Lowe, Newnham et al. 1999), peatlands in New Zealand have been classified (Johnson and Gerbeaux 2004) and research into their hydrology (Campbell, Laybourne et al. 2002; Campbell and Williamson 1997) and carbon cycling (Nieveen, Campbell et al. 2005; Schipper and McLeod 2002) is underway. Vegetation dynamics is also an active field of research (Clarkson 1997; Clarkson, Schipper et al. 2004; Clarkson, Schipper et al. 2005; Mark, Johnson et al. 1995).

Patterned mires in the low-alpine region of New Zealand’s South Island were the subject of the most comprehensive study of peatland structure and function in the southern hemisphere to date (Dickinson, Chague-Goff et al. 2002). This study investigated the relationships between vegetation and environmental variables, particularly water chemistry and hydrology. Seven distinct vegetation communities were identified, from data collected from four quadrats (0.5 x 0.5 m²), at each of 42 locations, within two patterned mires. There were significant correlations between the number of species present in the community and a) the availability of water (positive) and b) the nutrient status of the water (negative) (Dickinson, Chague-Goff et al. 2002). The pH and calcium concentrations of the mire waters, considered within a northern hemisphere classification, suggested that the smaller of the two mires (pH 4.79, Ca 0.26 mg/L) was mesotrophic, while the larger mire (pH 4.33, Ca 0.26 mg/L) was ‘mesotrophic to marginally ombrotrophic’ (Dickinson, Chague-Goff et al. 2002,
p. 382). Once again, this research demonstrates that peatlands in the southern hemisphere do not fit neatly within frameworks developed from the study of peatlands in the northern hemisphere. Given the limited breadth of research in the southern hemisphere, comparison with northern hemisphere systems is inevitable, and can be fruitful. However, further study of the structure and function of peatlands in the tropics and southern hemisphere is required, and ought to be informed, but not constrained, by theories developed in the study of peatlands of the northern hemisphere.

1.5 Peat in Australia

Peat forms in Australia where climate and topography combine to produce waterlogged conditions. Except in Tasmania, the Australian climate does not favour peat formation, and peatlands are not extensive (Cambell 1983). Wood peat, herbaceous peat and moss peat all occur, primarily in coastal and mountain areas. Coastal peats, which are mainly wood or herbaceous, have largely been drained for agricultural and urban use, although some are protected in National parks (Kakadu, Wilson’s Promontory and the World Heritage Areas of the Wet Tropics and the Tasmanian Wilderness) (Whinam and Hope 2005). Herbaceous and moss peats occur in mountain areas in the Eastern Highlands, far from the pressures of urban development or intensive agricultural use. Most of Australia’s moss peats are within National parks (Whinam, Hope et al. 2003), however, summer grazing of introduced livestock within the parks has damaged these peats (Cambell 1983). The small size of many peat deposits has prevented their appearance on soil maps and there is no accurate estimate of the extent of peat in Australia (McKenzie, Jacquier et al. 2004).

Peat as a soil is considered an Organosol under the Australian Soil Classification, and subdivided as fibric, hemic or sapric, and then subdivided further according to chemistry and the underlying substratum (Isbell 1996). Classification of different types of peatland in Australia is based upon vegetation (Whinam and Hope 2005). As discussed above, classification systems developed in the northern hemisphere cannot be directly applied to Australian peatlands. In particular, the terms ombrotrophic and minerotrophic do not retain their original meanings in Australia, where groundwater may be less nutrient-rich than rain (Whinam and Hope 2005). In an Australian context, ‘bog’ refers to shrub-moss-cushion plant vegetation with a complex structure raised above the local watertable, and ‘fen’ refers to graminoid
vegetation with the watertable generally at the surface (Whinam and Hope 2005). The main types of peatland found in Australia are listed in Table 1.4.

Table 1.4 Peatlands of Australia, from Whinam and Hope (2005) and Cambell (1983)

<table>
<thead>
<tr>
<th>Peatland Type</th>
<th>Also Known As</th>
<th>Occurrence</th>
<th>Typical Vegetation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Buttongrass moorland</td>
<td>Blanket bogs, mires</td>
<td>TAS</td>
<td>Gynnoschoenus sphaerocephalus</td>
</tr>
<tr>
<td>Cushion bog</td>
<td>TAS</td>
<td>Abrontanella, Dracophyllum, Donatia, Peterygopappus</td>
<td></td>
</tr>
<tr>
<td>Fens</td>
<td>Montane and subalpine NSW, ACT, VIC</td>
<td>Carex gaudichaudiana</td>
<td></td>
</tr>
<tr>
<td>Riverine swamp</td>
<td>Marshes, billabongs</td>
<td>All states</td>
<td>Varied, may include trees, edges, grasses</td>
</tr>
<tr>
<td>Salt marsh</td>
<td>Interdunal swales, swamp</td>
<td>Coastal all states</td>
<td>Varied, may include trees, edges, grasses</td>
</tr>
<tr>
<td>Sphagnum bog</td>
<td>Raised bogs, valley bogs, mossbeds</td>
<td>Montane and subalpine NSW, ACT, VIC</td>
<td>Sphagnum cristatum, Empodisma minus, Epacris paludosa</td>
</tr>
<tr>
<td>Spring mound</td>
<td>SA, WA, NT</td>
<td>Phragmites australis, Cyperus gymnocaulos, Juncus kraussi, Typha domingensis</td>
<td></td>
</tr>
<tr>
<td>Tropical upland swamp</td>
<td>Atherton Tablelands, QLD</td>
<td>Varied, may include trees, edges, grasses</td>
<td></td>
</tr>
<tr>
<td>Wet heath</td>
<td>Montane and subalpine NSW, ACT, VIC</td>
<td>Shrub</td>
<td></td>
</tr>
</tbody>
</table>

The majority of research involving peat in Australia has focused on climate history (Bell, Finlayson et al. 1989; Costin 1972; Dodson 1987; Green, Singh et al. 1988; Kershaw, Reid et al. 1997; Kershaw and Strickland 1989; Krull, Thompson et al. 2004; Martin 1999; McKenzie 1997). This work has contributed to our understanding of global and regional climate history and has provided some baseline data on peatland initiation. However, paleoecology is not concerned with the current structure and function of peatlands, and a comprehensive review of this work is beyond the scope of this thesis. The subsequent two Sections hone in on *Sphagnum*
bog peatlands of the Australian Alps and outline the research to date on vegetation, soil and water dynamics.

1.5.1 Vegetation

The vegetation dynamics within alpine and subalpine Sphagnum bogs have received considerable research attention. Research has focused on the relationships between the components of Sphagnum bogs: hummocks, hollows (Sphagnum lawns), pools, channels, shrubs, herbfields and stony pavements. Vegetation change after the removal of introduced livestock has been a component of most studies, due to the 150 year history of grazing in the Australian Alps. The concept of a ‘regeneration complex’ was introduced to Australian ecology by Costin (1954), from European research on bog structure. This theory, originally proposed by von Post and Sernander in 1910, suggests that the surface pattern of alternating hummocks and hollows also occurs through time (Charman 2002). Hummocks become hollows, as the more rapid accumulation of peat in hollows allows hollows to grow up and form new hummocks. This idea of cyclic regeneration has proven to be the exception rather than the rule, and more recent research has shown that hummocks tend to remain in the one location for thousands of years (Charman 2002). Thus, while long discredited in Europe, this theory remains prevalent in Australian bog research (Ashton and Hargraves 1983; Ashton and Williams 1989; Wahren, Williams et al. 1999; Williams and Costin 1994), which has been influenced by the original work of Costin (1954). However, one Australian study questioned the theory of cyclic regeneration (Clarke and Martin 1999). In a 32 year study of vegetation change within 13 Sphagnum bogs, Clarke and Martin (1999) found no evidence of cyclic regeneration, in surface vegetation or in peat profiles. Cyclic regeneration aside, the current vegetation patterns have been thoroughly documented in a number of peatlands in the Australian Alps.

Within-bog dynamics involve three main vegetation components and two hydrologic components: Sphagnum and tall shrubs, low shrubs, herbfields, pools and channels. Tall shrubs grow on deep peat. Low shrubs tend to be associated with channels and shallow or dried peat. Herbfields occur on gravelly or rocky substrata and are often associated with pavements (Wahren, Williams et al. 1999; Wahren, Williams et al. 2001). Pools linked to channels may be anywhere in the bog, but isolated pools occur only within the Sphagnum/tall shrub component (McDougall 1989). Previous land use and disturbance history affects the current structure of many
bog in the Australian Alps (Ashton and Williams 1989). The underlying geology is also an important factor, which influences hydrology and thus affects within-bog structure.

Removal of grazing by introduced livestock has resulted in channels being blocked by *Sphagnum* and an increase in the cover of *Sphagnum* and tall shrubs in bogs in Kosciuszko and on the Bogong High Plains (Ashton and Williams 1989; Clarke and Martin 1999; Wahren, Williams et al. 1999; Wahren, Williams et al. 2001; Wimbush and Costin 1979). In previously grazed sites on the Bogong High Plains, *Sphagnum* increased in cover by 7 and 17 % over 15 years, while *Sphagnum* at paired sites that continued to be grazed only increased in cover by 1 and 2 %, respectively (Wahren, Williams et al. 2001). The herbfield and low shrub components correspondingly decreased in extent following the removal of grazing (Wahren, Williams et al. 1999). Isolated pools were more common, and pools linked to channels were less common, in a bog fenced in 1945, than in an adjacent grazed bog (McDougall 1989). For example, the fenced bog had 189 and 41 m² of isolated and linked pools, respectively, while the grazed bog had 86 and 110 m² of isolated and linked pools, respectively (McDougall 1989). Continued grazing hindered the establishment of fragments of *Sphagnum* and two herbfield species in comparison with fragments protected from grazing (Wahren, Williams et al. 2001). However, the energy of the moving water had a greater effect than protection from grazing, as transplants in both grazed and ungrazed plots grew more where water moved slowly than where water moved rapidly (Wahren, Williams et al. 2001). For example, after 16 months, 12, 74, 16, and 77 % of fragments had survived, in environments characterised by: a) grazed + fast water, b) grazed + slow water, c) ungrazed + fast water, and d) ungrazed + slow water, respectively (Wahren, Williams et al. 2001).

Pressure on bogs from grazing has been compounded by frequent and extensive fires in the Alps. Weed invasion into bogs burnt in the 2003 fires has been extensive, and bogs, in comparison with other plant communities, experienced the greatest loss of structurally important species (Walsh and McDougall 2004). The slow recovery of bog vegetation (McDougall 1989; Wahren, Williams et al. 1999; Wimbush and Costin 1979) has lead to recommendations for active restoration of bogs damaged by grazing and fire (Walsh and McDougall 2004). Restoration involving weirs and planting/transplanting is underway in peatlands in Victoria, New South Wales and the Australian Capital Territory (Hope, Whinam et al. 2005; Wahren and
While initial results are promising, it is too early to determine the long term results of the restoration work, which aims to restore hydrological function to these long-degraded peatlands.

1.5.2 Soil and water

The peat soils of *Sphagnum* bogs in the Alps were first, and most extensively, described by Costin (1954). Costin differentiated ‘raised bog peat’, ‘valley bog peat’ and a drained variant ‘humified peat’\(^1\). Subsequent detailed chemical characterisation also suggested that dried peat is a drained remnant of bog peat (Grover, McKenzie *et al.* 2005). Typical profile descriptions of raised bog peat and dried peat are reproduced in Table 1.5. The presence of dried peats was attributed to climatic warming in some cases, and to recent drainage caused by trampling by livestock in other cases. Dried peat was extensive in both New South Wales and Victoria by the 1950s (Costin 1954; Costin 1957). The presence of bog peat was attributed to conditions of permanent wetness (Costin 1954). The importance of water for the formation of this soil was highlighted by the inclusion of *Sphagnum* bog peat as a type-soil for Organosols (soils governed by wetness) in ‘Australian Soils and Landscapes’ (McKenzie, Jacquier *et al.* 2004), data from (Grover 2001).

\(^1\) As noted in Definitions and Abbreviations, this thesis uses the adjective ‘dried’ rather than ‘humified’, to avoid confusion with the lower layers of bog peat, which are chemically well humified.
Table 1.5 Profile descriptions of raised bog peat and dried peat from Costin (1954)

OM is organic matter determined by the Walkley-Black method, pH was measured with a glass electrode on a paste of soil.

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Description</th>
<th>OM (%)</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>0618</td>
<td>Yellowish green, undecomposed Sphagnum moss; porous, spongy, wet</td>
<td>68.2</td>
<td>4.5</td>
</tr>
<tr>
<td>18633</td>
<td>Yellowish brown, undecomposed moss peat; layered structure; porous, spongy, saturated</td>
<td>45.7</td>
<td>5.3</td>
</tr>
<tr>
<td>33648</td>
<td>Brownish black, partly decomposed moss peat; layered structure; fairly open, greasy feel, saturated</td>
<td>23.3</td>
<td>5.4</td>
</tr>
<tr>
<td>48664</td>
<td>Slightly darker and more decomposed moss peat; layered structure; fairly open, greasy feel, saturated</td>
<td>29.1</td>
<td>5.4</td>
</tr>
<tr>
<td>64679</td>
<td>Black, more decomposed moss peat; layered structure; barely visible, fairly open, greasy feel, saturated</td>
<td>32.1</td>
<td>5.4</td>
</tr>
<tr>
<td>79694</td>
<td>Black, largely decomposed moss peat; structureless; fairly open, greasy feel, saturated</td>
<td>21.4</td>
<td>5.4</td>
</tr>
<tr>
<td>94610</td>
<td>Black, largely decomposed, gravelly sedge peat; structureless; fairly open, greasy feel, saturated</td>
<td>14.7</td>
<td>5.5</td>
</tr>
<tr>
<td>1096122</td>
<td>Black, thoroughly decomposed, gravelly sedge peat; single grain structure, slightly closed, greasy feel, saturated</td>
<td>16.1</td>
<td>5.6</td>
</tr>
<tr>
<td>1226132</td>
<td>Greyish white, clayey gravel; single grain structure, closed, tenacious; little organic matter, saturated</td>
<td>2</td>
<td>6.0</td>
</tr>
<tr>
<td>240633</td>
<td>Black silty clay, merging with layer below; greasy feel; mineral skeleton almost lacking; original peat largely humified; fine crumb structure; fine porous, mellow; humus and roots abundant; moist</td>
<td>22.8</td>
<td>4.0</td>
</tr>
<tr>
<td>33656</td>
<td>Greyish black silty clay, loam, with slight bleaching at 45 to 56 cm; clearly defined from layer below; greasy feel; mineral skeleton almost lacking; original peat largely humified; fine crumb to single grain structure; almost closed, slightly tenacious; humus and roots abundant</td>
<td>11.9</td>
<td>5.1</td>
</tr>
<tr>
<td>56684</td>
<td>Yellow silt loam; stones and gravel abundant; single grain structure; almost closed, sticky and tenacious; few roots and no humus; wet, watertable at 84 cm;</td>
<td>1.7</td>
<td>5.3</td>
</tr>
</tbody>
</table>
Water was thus early identified as central to the formation of both bog peat and dried peat. The importance of the Alps as a water catchment has generated considerable interest in the water dynamics of peat soils. However, this interest has resulted in more hypotheses (some of which are considered below in Section 1.5.3) than experimental studies.

The primary work applied a water-balance approach to two *Sphagnum* bogs in Kosciuszko National Park (Wimbush 1970). Wimbush (1970) measured the flow and temperature of water coming into and out of the main bog, natural rainfall and artificially applied rainfall, and atmospheric pressure. Typical diurnal fluctuations in flow were 227 and 341 L/hr for inflow and outflow, respectively, about median flow volumes of 568 and 1023 L/hr for inflow and outflow, respectively. Seasonal variation in the temperature of the inflow was less (4.5-10 °C) than the seasonal variation of temperature of the outflow (2-12 °C) (Wimbush 1970). Evapotranspiration was, at various times, estimated, measured and eliminated by covering the bog. In comparison with the adjacent grassland, evapotranspiration from the bog was high (maximums: 200 gallons/hr bog, 30 gallons/hr grassland) (Wimbush 1970). This research found that inflow appeared as outflow within several hours, and thus bogs had little ability to smooth streamflow by storing water temporarily (maximum temporary storage capacity 127 mm). Bogs enhanced streamflow during winter, by remaining unfrozen and thus melting overlying snow and transporting groundwater to streams. Bogs decreased streamflow in summer due to high evapotranspiration, except after heavy rains, when bogs transported more rainfall through to streams than adjacent (dry) mineral soils (Wimbush 1970). While this seminal research contributed greatly to our knowledge of bog hydrology in Australia, the study bog was small and steep in comparison with other bogs in the Australian Alps. Thus Wimbush’s (1970) conclusions should be applied with caution to large, gently sloping bogs elsewhere in the Australia Alps.

Forty-eight years after Wimbush began measurements, the same bog was studied again (Hahn 2004). Drought, grazing and fire had resulted in decreased peat depth and altered flow patterns. The bog appeared to have dried considerably and water flow had become concentrated in channels. Restoration work that aimed to spread water out of channels and into the peat itself was undertaken to assist vegetation recovery (Hahn 2004). The processes involved in water movement through
the bog were discussed but not directly measured by either Wimbush (1970) or Hahn (2004).

Water movement through *Sphagnum* peats was measured by Growcock (1999) and Grover (2001). Each study employed two different methods, and, while the results are not comparable, the findings concurred with northern hemisphere studies in suggesting that water moves slowly in the catotelm and rapidly in the acrotelm.

Growcock (1999) used a disc permeameter to measure unsaturated hydraulic conductivity, sorptivity and infiltration at the top of the catotelm (10-30 cm below the peat surface) of bog peat, and tritium as a tracer to measure water movement through the whole peat profile. Hydraulic conductivity, sorptivity and infiltration were slower in the catotelm than in a shallow mineral soil (25, 14 and 25 respectively in catotelm peat; 241, 77 and 244 respectively in mineral soil, no units given), however, water movement through the whole peat profile was more rapid than that through a shallow mineral soil (2 m/hr peat, 0.1 m/hr mineral soil) (Growcock 1999).

The second study used the recovery method to measure saturated hydraulic conductivity in the catotelm. Mini-disc permeameters were used to measure unsaturated hydraulic conductivity in the laboratory on intact samples collected from the acrotelm and the catotelm of bog peat and the surface of dried peat. The watertable was monitored at seven points through a hummock and rainfall was also recorded (Grover 2001). Hydraulic conductivity decreased with depth, and field and laboratory results were within one order of magnitude of each other (acrotelm $2.9 \times 10^{-2}$ m/s field, $1.4 \times 10^{-3}$ m/s laboratory; catotelm $1.8 \times 10^{-7}$ m/s field, $6.5 \times 10^{-6}$ m/s laboratory). The hydraulic conductivity of the dried peat was comparable to that of the hemic catotelm peat. Limited data suggested that the response of the watertable to rainfall depended on prior conditions. When the watertable was high, it displayed little or no response to rainfall. When the watertable was low, rainfall caused the watertable to rise (Grover 2001). The distance between the maximum and minimum watertables was 123 mm (in close agreement with Wimbush’s value of 127 mm), which supports Wimbush’s analysis that bogs have little capacity to store water temporarily (Grover 2001; Wimbush 1970).

Soil-water interactions in *Sphagnum* bog peats and the associated dried peats in Australia have thus only begun to be quantified. An integrated model of the hydrology of these peats is yet to be established. While experimental evidence is limited, hypotheses about the hydrologic function of peatlands abound.
1.5.3 Hypotheses about bog function

Bogs are said to regulate or smooth stream flow by absorbing and later releasing large quantities of water (Ashton and Williams 1989; Good 1992; Williams and Costin 1994). This hypothesis is based upon the large water-holding capacity of peat and the surface roughness of bog vegetation. Neither of these two properties has been directly measured in Australian bogs. Rather, the limited local evidence suggests that bogs have little capacity to temporarily absorb additional water (Grover 2001; Wimbush 1970).

The importance of bogs in catchment hydrology is oft-stated (Ashton and Williams 1989; Cambell 1983; Costin 1952; Good 1992; Williams and Costin 1994) but incompletely understood. An improved understanding of how bogs function could enhance restoration work and land management, and would contribute to the body of knowledge on peatlands in the southern hemisphere.
1.6 Aims of my research

This research aimed to improve understanding of the function of *Sphagnum* peatlands in the Alps. This was achieved by comparison of the properties of bog peat and dried peat in a *Sphagnum* peatland in the Victorian Alps. This peatland was chosen because the vegetation, soils and topography were characteristic of peatlands in the Australian Alps. The three aspects that this study focused upon were carbon dynamics, water dynamics and peat formation. Specific objectives are listed beneath each of these three headings.

*Carbon dynamics*

- Characterise the chemistry of the organic matter in profiles of peat, and quantify the extent of decomposition.
- Measure rates of carbon mineralisation under controlled conditions in the laboratory, and assess the influence of chemistry, particle size, water content and sample preparation.
- Measure daily and yearly rates of carbon mineralisation in the field, and relate these to soil temperature, soil water content and chemistry.
- Model peat mineralisation under a range of possible future climates.

*Water dynamics*

- Measure the water-holding capacity of peat.
- Measure the rate of water movement through peat.
- Measure fluctuations in water storage in peat.
- Identify relationships between the chemistry and the hydrologic properties of peat.
- Develop a model of the hydrology of bog peat and dried peat.

*Peat formation*

- Determine when peat formation began.
- Determine when bog peat drained to form dried peat.
- Determine the contributions of erosion and carbon mineralisation to the formation of dried peat.
Chapter 2. Site description and monitoring of environmental properties

Summary
Chapter 2 sets the scene for understanding the context of this research. Wellington Plain peatland is described in detail. The two peat types that were the focus of subsequent experiments are introduced and the results from monitoring rainfall, air temperature, soil temperature, soil water content and water table depth are presented. Bog peat and dried peat thus examined were found to be distinctly different soils, and the implications for peatland function are explored in the discussion.

2.1 Introduction

The Australian Alps are the highest parts of the Eastern Highlands (Ollier and Wyborn 1989). The Alps run roughly north-south in New South Wales, and east-west in Victoria. This difference in orientation, combined with the north-south structural grain of the bedrock and the inland retreat of the Great Escarpment, have resulted in a roughly continuous mountain range in New South Wales, while in Victoria the Alps are more dissected (Costin 1989; Ollier and Wyborn 1989). The term ‘Alps’ encompasses mountains from the Brindabella Ranges in the Australian Capital Territory, south through the Snowy Mountains in New South Wales and down to Mt Baw Baw in Victoria. This area covers roughly 0.3 % of mainland Australia, and includes land from 200 m above sea level up to the peak of Mt Kosciuszko at 2228 m (Costin 1989). Not all of the Alps is alpine, and areas that experience persistent snow constitute only 0.07% of mainland Australia (Costin, Gray et al. 2000). In Tasmania, the topography and climate are more akin to those of New Zealand than to those of the rest of Australia (Cambell 1983). Tasmania contains substantial alpine areas, however, they are quite different from the mainland Alps (Costin, Gray et al. 2000) and thus not considered further here.
The Alps are a mix of sedimentary, metamorphic and volcanic rocks, which range in age from Cambrian to Carboniferous (Rosengren 2002). Wellington Plain, in the south-east Gippsland Alps (Fig. 2.1), is underlain by two rock types: sedimentary rock from the lower Carboniferous/upper Devonian, and acid volcanic rock from the upper Devonian (Rosengren 2002). High plains are a characteristic feature of the Australian Alps. Due to drainage of cold air down the adjacent slopes, these high plains support treeless subalpine vegetation similar to the alpine vegetation found above the tree line. The low relief and high rainfall of the high plains make them particularly well situated for the development of wetlands, and peatlands constitute 10 % of the Bogong high plains (McDougall 1982) and 5.8 % of the Kosciuszko alpine area (Costin, Gray et al. 2000). Peatlands occur along valley bottoms and beneath springs and seepages where groundwater reaches the surface. My study was located at Wellington Plain peatland to build upon knowledge of peatland function ensuing from the peatland restoration research begun there after the Caledonia Fire in 1998 (Wahren and Papst 1999).
Wellington Plain peatland (484950 5849700 on map 8223-S (Tamboritha-Moroka), AMG 55) covers an area of approximately 43500 m² at 1480 m and experiences snow-lie for one to three months of the year. The average monthly maximum and minimum temperatures in 2004 and 2005 were 12.3 °C and -2.3 °C and 12.7 °C and -1.3 °C respectively. These data show a greater range than the long term average monthly maximum and minimum temperatures of 9.0 °C and 3.1 °C, measured at Mt Baw Baw from 1997 to 2005 by the Bureau of Meteorology. This is likely because I did not house my temperature logger in a Stevenson screen one metre above the ground, but rather in an unvented PVC container at ground level. Annual rainfall measured at Wellington Plain in 2004 and 2005 was >821 mm (January to October) and > 856 mm (May to December) respectively. Logger failure prevented collection of data for the entire years, however, annual rainfall in this area of the Alps is estimated to be about 1270 mm (Rowe and Downes 1960).

The aims of this chapter are to describe the Wellington Plain peatland and lay the foundations for understanding the subsequent chapters. Profiles of the two most extensive peat types, bog peat and dried peat, are presented, and the peatland vegetation is listed. Properties of the whole peatland are mapped and data from continuous monitoring of rainfall, temperature in air and soil, soil water content and watertable depth are presented. Consideration of these data and comparison with the properties of other peatlands leads to the conclusion that bog peat and dried peat are two quite different soils.
2.2 Methods

Methods for the data presented in each chapter are located at the beginning of each chapter, and thus the following Section includes only the methods used to describe the Wellington Plain peatland.

2.2.1 Profile descriptions

Profiles of bog peat and dried peat were photographed and described from soil pits dug with a sharpened spade and a serrated knife. Nomenclature follows the Australian Soil Classification (Isbell 1996; McDonald, Isbell et al. 1990) and the von Post humification (V.P.H.) scale (reproduced in Armstrong and Castle 1999).

2.2.2 Vegetation

The characteristic vegetation of the bog peat and of the dried peat was recorded. Nomenclature followed Walsh and Entwistle (1999).

2.2.3 Mapping peatland properties: peat depth, peat type, pH

Peat depth and peat type were recorded at every metre along 32 transects, each of 25 m, between grid points over the whole peatland. A stainless steel probe (200 cm length, 0.6 cm diameter), graduated every 10 cm, was pushed into the peat, down to the gravelly-clay substratum. The pH of peat sampled from 0-10 cm depth at the end and midpoint of each transect was measured in the laboratory. Two grams of peat were shaken in distilled water (20 mL) for one hour, in duplicate, and the pH was measured with a ThermoOrion pH meter.

2.2.4 Monitoring environmental properties

Data are presented for the period 15/2/2004 to 25/1/2006. Daily variation in selected properties is presented for the period 17/2/2004 to 19/2/2004. These particular three days were chosen because all loggers were functioning and rainfall occurred.

2.2.4.1 Rainfall

Rainfall was measured with a tipping bucket raingauge attached to a HOBO rainfall logger. This type of gauge is likely to underestimate precipitation falling as snow.
2.2.4.2 Air temperature

Air temperature was measured hourly at 10 cm above ground level, with a HOBO temperature logger inside a waterproof PVC pipe casing. Results were averaged to daily values.

2.2.4.3 Soil temperature

Soil temperature was measured hourly with 4 channel HOBO loggers attached to soil temperature probes. In the bog peat, duplicate loggers had probes buried at the surface and 10, 20 and 30 cm depth. In the dried peat, duplicate loggers had duplicate probes buried at 5 and 10 cm depth. All results were averaged to daily values, and only data from 10 cm are presented.

2.2.4.4 Soil water content

Soil water content was measured with time domain reflectometry (TDR) in the bog peat and capacitance in the dried peat. In the bog peat, five probes were logged hourly with a Trase TDR via a multiplexor. This instrument failed repeatedly and hence data collection was sporadic. Results were averaged to daily values, and data from 10 and 20 cm are presented. In the dried peat, five probes were logged hourly with an Echo logger, in duplicate. Results were averaged to daily values, and data from 5 and 10 cm are presented. Data are presented as gravimetric water content, rather than as volumetric water content, because the volume of the peat may have changed over time, and this was not recorded.

2.2.4.5 Watertable depth

Watertable depth was measured with Trutrack watertable loggers at six locations in the peatland. Two loggers were in wells in the dried peat, two loggers were in wells in bog flat peat and two loggers were in wells in hummocks of bog peat. Wells were slotted along their entire length and had an internal diameter of 4 cm. Loggers recorded the depth of the watertable hourly or half hourly.
2.3 Results

2.3.1 Profile descriptions

The profile photos and descriptions in Fig. 2.2, Table 2.1 and Table 2.2 show two quite different soils. The bog peat was dominated by fresh organic material which gradually became darker and less fibrous with depth, as the material became more decomposed (V.P.H. 3 to 9). The three peat types recognised by the Australian Soil Classification (Isbell 1996) were present: fibric, hemic and sapric peats occurred sequentially down the profile. The dried peat was a darker, more structured soil, with only hemic and sapric peat present. The dried peat, at 23 cm depth, was a shallower soil than the bog peat, at 140 cm depth. A watertable was encountered in the bog peat but not in the dried peat.

The surrounding landscape, a bog hummock and peat removed from soil pits are shown in Fig. 2.3 and Fig. 2.4
Table 2.1 Profile description of bog peat from a hummock

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-50</td>
<td>Fibric peat, V.P.H. 3, gradual change from live green <em>Sphagnum</em> to dead fawn coloured (2.5Y7/8) <em>Sphagnum</em>, plant matter totally intact. Clear water was squeezed out. Gradual boundary.</td>
</tr>
<tr>
<td>50-85</td>
<td>Hemic peat, V.P.H. 5, colour change from fawn (2.5Y7/8), through light brown to medium brown (10YR4/4). Much plant matter still recognisable, but beginning to decompose. Peat becomes less fibrous down the profile. Brown water was squeezed out. Gradual boundary. Watertable at 65 cm.</td>
</tr>
<tr>
<td>85-140</td>
<td>Sapric peat, V.P.H. 9, thick black viscous liquid (5YR3/2). Thoroughly decomposed, some woody roots. All material was squeezed out through the hand.</td>
</tr>
</tbody>
</table>

Table 2.2 Profile description of dried peat

<table>
<thead>
<tr>
<th>Depth (cm)</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>0-4</td>
<td>Hemic peat, very dark brown (10YR2/2), very weak non-sticky consistence, weak 2.5 mm polyhedral structure, fine roots abundant, medium roots many, sharp boundary.</td>
</tr>
<tr>
<td>4-13</td>
<td>Sapric peat, black (10YR2/1), wet, weak non-sticky consistence, weak 2.5 mm polyhedral (granular) structure, fine roots abundant, medium roots many, gradual boundary.</td>
</tr>
<tr>
<td>13-23</td>
<td>Peaty light clay, black (2.5Y2/1), wet, slightly sticky, slightly plastic, weak to moderate 2-5 mm sub-angular blocky structure, fine roots many, medium roots common, clear boundary.</td>
</tr>
<tr>
<td>23-28</td>
<td>Light clay, dark grayish brown (2.5Y4/2), yellowish brown (10YR5/8) mottles common, 3 mm pedal to weak 5-8 mm sub-angular blocky structure, fine roots few, over gravel.</td>
</tr>
</tbody>
</table>

Fig. 2.2 Profile photos of bog peat (top) and dried peat (bottom).
Fig. 2.3 Top: foreground bog pool, midground bog landscape with *Sphagnum* hummocks and shrubs, background subalpine woodland; bottom left: bog hummock; bottom right: bog monolith.
Fig. 2.4 Top: dried peat landscape after rain, note tussocks of *Poa* grasses; bottom: dried peat removed from sampling pit
2.3.2 Vegetation descriptions

There was much overlap between the characteristic species on the bog peat and the dried peat (Table 2.3). The exceptions were *Sphagnum cristatum*, which was characteristic of the bog peat but not the dried peat, and *Poa costiniana*, which was characteristic of the dried peat but not the bog peat. There was a greater cover of shrubs on the bog peat than on the dried peat.

<table>
<thead>
<tr>
<th>Peat type</th>
<th>Characteristic species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bog peat</td>
<td><em>Sphagnum cristatum, Empodisma minus, Baloskion australis, Epacris paludosa, Richea continentis, Baeckia gunniana, Astelia alpina, Carex gaudichaudiana</em></td>
</tr>
<tr>
<td>Dried peat</td>
<td><em>Empodisma minus, Baloskion australis, Poa costiniana, Epacris paludosa, Baeckia gunniana, Carex gaudichaudiana</em></td>
</tr>
</tbody>
</table>

2.3.3 Aerial photo and maps

The aerial photo in Fig. 2.5 was taken in February 2000 after substantial rainfall and thus surface water was abundant. However, the most intact areas of healthy bog peatland, surrounding grid points (x,y) 50,50 and 50,100, showed little surface water. Channels through the peatland were evident and, similar to surface water, channels were fewest in the most intact areas of healthy bog peatland surrounding grid points 50,50 and 50,100. In addition to water, the aerial photo (Fig. 2.5) shows the different colours of different vegetation. As a whole, the peatland had greener and darker vegetation than did the surrounding grassland. The exceptions were the white rocks (most evident along the central channel) and the light green/cream *Sphagnum* moss.

The peatland is irregularly shaped, as are the areas of bog peat and dried peat within the peatland. The overlay shows the locations of equipment referred to in this and subsequent chapters. Equipment in the dried peat was concentrated in two areas, 50,260 and 20,200. In the bog peat, equipment was primarily located around 65,160 and 70,50, with additional chambers near 100,100 and additional mesh bag stakes near 60,110.

The maps in Fig. 2.6 are 1/3 the size of the aerial photo. These three maps demonstrate a correlation between peat type, peat depth and peat pH. Bog peat was deeper (average depth 0.76 m) and had a lower pH, while dried peat was shallower (average depth 0.26 m) and had a higher (though still acid) pH.
Fig. 2.5 Aerial photo of peatland 1 on Wellington Plain with grid superimposed. Overlay shows the location of all equipment, excluding the rain gauge, air temperature logger and replicates of watertable loggers, which were located in peatland 2.
Fig. 2.6 Properties of peatland 1: top, peat type; middle, peat depth; and bottom, peat pH. Peat type and peat depth were measured in the field. Peat pH was measured in duplicate in the laboratory. Points are measured values (not shown for peat depth), colours are interpolated maps constructed with ARCVIEW.
2.3.4 Environmental properties: Air and soil temperature

Fig. 2.7 a) Daily average soil temperature measured at 10 cm depth in dried peat, b) daily average soil temperature measured at 10 cm depth in bog peat, c) daily average air temperature. All data were collected at Wellington Plain peatland from 15/2/2004 to 25/1/2006. Gaps indicate periods of logger failure.

Soil temperature followed the pattern of air temperature (Fig. 2.7), with a dampened amplitude of variation. While the daily average air temperature reached a minimum of -6.7 °C, the temperature in the peat at 10 cm never fell below 0 °C. Minimum temperatures in the peat occurred earlier than those in the air, likely due to the insulating effect of snow. This effect was more evident in 2004 than in 2005, and corresponded with a short snow season in 2005. The temperature in dried peat tended to be slightly higher than the temperature in bog peat.
2.3.5 Environmental properties: Rainfall and soil water content

Fig. 2.8 a) Daily average gravimetric soil water content measured at 5 cm and 10 cm depth in dried peat, b) daily average gravimetric soil water content measured at 10 cm and 20 cm depth in bog peat, c) daily rainfall. All data were collected at Wellington Plain peatland, from 15/2/2004 to 25/1/2006. Gaps indicate periods of logger failure.

Incomplete data sets inhibited my ability to determine the relationship between soil water content and rainfall (Fig. 2.8). It appeared that soil water content was more variable, and hence potentially more responsive to rainfall, in bog peat than in dried peat. Low soil water contents early in 2004 (Fig. 2.8) followed a very dry summer (monthly rainfall February and March 30 mm and 26 mm, which was only 32% and 28% respectively of the monthly average of 93 mm). In the bog peat, soil water content increased with depth, while in the dried peat, soil water content decreased with depth.
Over a time frame of several days, soil water content varied in bog peat but not in dried peat (Fig. 2.9). This variation in the water content of bog peat appeared to be influenced more by temperature than by rainfall (Fig 2.9).

Fig. 2.9 Variation in soil water content over three days, and the relationship with soil temperature and rainfall. In all graphs the x axis shows hours since midnight 17/2/2004. a) soil temperature at 10 cm depth in bog peat and dried peat, b) gravimetric soil water content in dried peat, c) gravimetric soil water content in bog peat, d) gravimetric soil water content in both bog peat and dried peat, and rainfall. Note the scales on the y axes are different in b) and c) than in d).
2.3.6 Environmental properties: Rainfall and watertable depth

The depth of the watertable was affected by rainfall in dried peat, bog hummock peat and bog flat peat (Fig. 2.10). Maximum and minimum watertable depths varied by about 400 mm in both the dried peat and the bog hummock peat. This represented the entire profile depth in the dried peat, but less than a quarter of the entire profile depth.
in the bog hummock peat. Thus the variation in watertable depth proportional to peat depth was greatest in the dried peat. The pattern of watertable variation was also different between the dried peat and the bog hummock peat. The watertable in the dried peat displayed frequent peaks and troughs, corresponding to small rainfall events, in contrast to the more stable watertable in the bog hummock peat, which tended to only respond to rainfall events greater than 20 mm. The watertable in the bog flat peat was even more stable. The watertable in bog flat peat experienced a maximum variation of less than 100 mm.

In none of the three peats did the recorded depth of the watertable reach the peat surface. For the bog hummock peat, this was an accurate representation, because the maximum recording level of the logger was above the peat surface. However, the maximum recording level of the logger was (accidentally) installed below the surface in both the bog flat peat (13 cm) and the dried peat (0.5 cm). Therefore, watertable depths above the recorded depths may have occurred in the bog flat peat and in the dried peat, when the watertables were highest (i.e. spring 2005 and the following summer). Surface flow may have occurred during these periods.

Daily variation in watertable depth is not evident in Fig. 2.10, and thus Fig. 2.11 presents watertable, rainfall and temperature data over a shorter period of time. Over a time frame of several days, watertable depth varied in the bog hummock peat and the dried peat, but not in the bog flat peat, even after rainfall (Fig. 2.11). The decrease in the depth of the watertable (about 1 mm) that occurred in the middle of the day in the bog hummock peat and the dried peat may have been due to water use by plants. This pattern was most obvious in the bog hummock peat.
Fig. 2.11 Variation in watertable depth over three days, and the relationship with rainfall. In all graphs the x axis shows hours since midnight 17/2/2004. a) detail of the daily variation in watertable depth in the dried peat, b) detail of the daily variation of watertable depth in (left axis) the bog flat peat and (right axis) the bog hummock peat, c) watertable depth over three days in bog flat peat, bog hummock peat and dried peat, and the response to rainfall. Note the scales on the y axes are different in a) and b) than in c).
Fig. 2.12 Response of the watertable to rainfall in a) bog hummock peat and bog flat peat, and b) dried peat. All rainfall events greater than 5 mm, from 15/2/2004 to 25/1/2006, were included. Note the different scales on the y axes.

The relationship between rainfall and watertable depth was further examined by collating the response of the watertable to each rainfall event greater than 5 mm. Rainfall might be expected to decrease the depth of the watertable in proportion to the size of the rainfall event. Such a simple linear relationship was not observed (Fig. 2.12). In the bog flat peat, there appeared to be two possible responses to rainfall: the watertable did not move (0-3 mm) or the watertable moved by about 30 mm (Fig. 2.12). The size of the rainfall event did not affect which response occurred. Of the 74 data points, only two fell outside of these two groups.

In the bog hummock peat, there also appeared to be two possible responses to rainfall (Fig. 2.12). The watertable either moved minimally (0-6 mm, within the range of daily variation observed in the absence of rainfall) or by about 46 mm. Again, the size of the rainfall event did not affect which response occurred. All 56 data points fitted within these two groups.

In the dried peat, the response of the watertable to rainfall was more evenly distributed across a range of values (Fig. 2.12). While the size of the rainfall event still did not appear to influence the response of the watertable, possible responses were spread from 0 mm to 250 mm.
2.4 Discussion

2.4.1 Profile descriptions

The difference in structure between the bog peat profile and the dried peat profile (Fig. 2.2, Table 2.1 and Table 2.2) may be expected to result in these two soils having different hydrologic properties. The loose, open structure of the dead Sphagnum material in the upper bog peat profile contrasted with the polyhedral to sub-angular blocky structure of the more compact organic material in the dried peat. Water moves through soil primarily via transmission pores of diameter 30 to 300 µm (White 1997). The more open-structured bog peat profile would have had more large pores and thus may have been expected to transmit water more freely. The hydrologic properties of the two peat types were measured directly in Chapter 5.

Colour also differed between the two peat profiles (Fig. 2.2, Table 2.1 and Table 2.2). The colour of organic material is a rough guide to how decomposed the material is. As organic matter decays, it becomes darker. Thus it might be expected that the bog peat became more decomposed with depth, and that the dried peat was well decomposed throughout the profile.

2.4.2 Vegetation

Sphagnum is the main peat-forming plant in bog ecosystems (Godwin 1981). The absence of Sphagnum cristatum from the dried peat (Table 2.3) thus indicates that these soils may no longer be accumulating peat. Sphagnum species require a close, reliable water source because they lack a vascular system to transport water (van Breeman 1995). The absence of Sphagnum on the dried peat thus suggests that the watertable varies more in the dried peat than in the bog peat. Poa costiniana occurred on the dried peat and not on the bog peat. This grass is not a characteristic bog species (Costin, Gray et al. 2000) and thus its presence on the dried peat indicates that conditions in dried peat are likely drier than conditions in bog peat. There was a greater cover of shrubs on the bog peat than on the dried peat. The co-occurrence of all other characteristic species on the bog peat and the dried peat suggests that conditions are suitable for these species in both peat types, and is consistent with the two peat types sharing a common origin.
2.4.3 Whole peatland properties

Fig. 2.6 shows that bog peat was underlain by deep (0.6-1.7 m) peat while dried peat was underlain by shallow (0-0.4 m) peat, with an intermediate depth category (0.4-0.6 m) occurring beneath both peat types. Upon drainage, peat soils undergo shrinkage and compression (Price and Scholtzhauer 1999). That bog peat is deep and dried peat is shallow is consistent with dried peat being derived from bog peat that has been drained.

Fig. 2.6 also shows an obvious difference in pH between peat types. The lowest pH values (3.4-3.8) occurred only on bog peat, the highest pH values (4.2-5.1) occurred only on dried peat, and intermediate pH values (3.8-4.2) occurred on both peat types. The greater acidity of bog peat was likely linked to the presence of *Sphagnum*, which actively acidifies its environment (van Breeman 1995). *Sphagnum* was characteristic of the bog peat but not of the dried peat (Table 2.3).

2.4.4 Environmental properties: Soil temperature and soil water content

2.4.4.1 Decomposition

An understanding of the behaviour of the basic properties of soil temperature and soil water content is critical to understanding peatland function. The build-up of peat soil depends upon the rate of decomposition of plant material being slower than the rate of plant production. Decomposition in peats is limited by low temperatures and high water contents (Charman 2002).

Soil temperature generally followed the seasonal pattern of air temperature (Fig. 2.7), as did peat temperatures in natural and cutover peatlands in Canada (Waddington, Warner *et al.* 2002). The Alps experience Australia’s lowest minimum and mean minimum temperatures (www.bom.gov.au), and is the only mainland area to receive regular snow (Costin, Gray *et al.* 2000). Thus it could be extrapolated that peat soils in the Alps are some of mainland Australia’s coldest soils, although minimum winter temperatures appear to be limited to about 0 °C when insulated by snow. Daily variation in soil temperature was greater in the bog peat than in the dried peat (Fig. 2.9) while average daily temperatures were higher in the dried peat than in the bog peat (Fig. 2.7). Waddington *et al.* (2002) also recorded greater variation in soil temperatures in a natural bog than in a cutover bog. Thus, in terms of temperature, bog
peat and dried peat at Wellington Plain appeared to be similar environments for decomposition.

Soil water content in the dried peat did not show seasonal or daily variation (Fig. 2.8 and Fig. 2.9). Decreased variation in soil water content in drained peatlands is due to the alteration of soil structure caused by the shrinkage and compression that accompany drainage (Price and Scholtzhauer 1999). Shrinkage and compression alter peat structure by decreasing both total pore volume and the size of pores. Lower total porosity and a higher proportion of small pores combine to maintain more constant soil water contents in drained peats.

In the bog peat there was some variation in soil water content. On a seasonal timescale, this variation was likely to have been related to rainfall, however, logger failure prevented the collection of sufficient data to confirm this hypothesis (Fig. 2.8). On a daily timescale, temperature had more effect on soil water content in bog peat than did a small (4.2 mm) rainfall event (Fig. 2.9). This may have been due to the increase in evapotranspiration as temperatures increase. Evapotranspiration from the surface of bogs is high, in comparison with other vegetation communities (Ingram 1983). In the Australian Alps, Wimbush (1970) measured higher evapotranspiration over a bog than over an adjacent grassland (maximums: bog 200 gallons/hour, grassland 30 gallons/hour). This high evapotranspiration is attributed to the structure of Sphagnum moss (Ingram 1983), and thus the dried peat, which lacks Sphagnum (Table 2.3), would be expected to evapotranspire less than would the bog peat. This may explain the greater daily variation in soil water content in the bog peat than in the dried peat.

The relationship between increased temperature and increased peat decomposition is well established (Bergman, Lundberg et al. 1999; Charman 2002; Gore 1983), however, the relationship between water content and decomposition is more complex. Laboratory studies have shown that decomposition of peat was limited by both high and low water contents (Hogg, Lieffers et al. 1992; McNeil and Waddington 2003; Waddington, Rotenberg et al. 2001). Decomposition was maximised at a volumetric water content of about 70% (Waddington, Rotenberg et al. 2001). The results in Fig. 2.8 are gravimetric water contents and thus a direct comparison is not possible.
2.4.4.2 Plants

Peat formation is a balance between decomposition and production (Charman 2002). Soil temperature and soil water content influence plant production, as well as the subsequent decomposition of plant material. At Wellington Plain peatland, soil temperature, as explained in Section 2.4.4.1, followed the pattern of air temperature. Plant growth in the Australian alpine and subalpine regions is limited by low temperatures (Ashton and Williams 1989). The characteristic vegetation of peatlands is adapted to wet conditions (Charman 2002). Both absolute water content and soil structure are important in determining the availability of water to plants (Price and Scholtzhauer 1999). Plants can more easily access water held in bigger pores. The compact structure of the dried peat (Fig. 2.2, Table 2.1 and Table 2.2) and the absence of Sphagnum on the dried peat (Table 2.3) suggest that, although the dried peat had a high water content, this water may have been held in pores too small for Sphagnum to access.

2.4.4.3 Hydrology

Soil temperature and soil water content influence the movement of water through soil and the storage of water in soil (White 1997). Soil temperature does so principally through its effect on evapotranspiration. Evapotranspiration involves the movement of water up through the soil to the surface, where the water is exchanged, in gaseous form, with the air. This process decreases the volume of water stored in soil. Evapotranspiration increases as air temperature and soil temperature increase (White 1997). Previous studies found that evapotranspiration was high over bog peat, in comparison with other types of ecosystem in the Australian Alps (Wimbush 1970). The similar soil temperatures recorded in bog peat and dried peat (Fig. 2.7) suggest that evapotranspiration may have been similar in bog peat and dried peat. While Van Seters and Price (2001) found that evapotranspiration was similar between a natural bog and a cutover bog, they suggested that vegetation was a critical control on evapotranspiration. Thus on the Wellington Plain peatland, the absence of Sphagnum on the dried peat (Table 2.3) and the different soil structure of bog peat and dried peat (Fig. 2.2, Table 2.1 and Table 2.2) may outweigh the effects of soil temperature and result in different rates of evapotranspiration on the bog peat and the dried peat.
Soil water content affects water movement and storage in soil more directly than does soil temperature. Water moves through soil pores at different speeds depending upon both the size of the pore and whether the pore is initially filled with water or filled with air. Water movement through initially dry soil is slower than water movement through initially wet soil (White 1997). As both bog peat and dried peat retained some water all year (Fig. 2.8), this would have facilitated water movement through the soil. However, 40% to 70% of water in peat is physically and chemically bound, with 10% to 15% very tightly bound (Volarovich and Churaev 1968) and thus not free to move. Bound water and its impact on peat hydrology are discussed further in Chapter 5.

Water storage in soil is determined by both soil water content and the depth of the watertable. The watertable will be considered in the following Section. The results for soil water content in Fig. 2.8 suggested that the volume of water stored in the soil changed during the measurement period in both bog peat and dried peat. However, there was considerably more change in soil water content in the bog peat than in the dried peat.

2.4.5 Environmental properties: Watertable

2.4.5.1 Hydrology

The watertable moved in different patterns in the dried peat, the bog flat peat and the bog hummock peat (Fig. 2.10). Overall, the watertable was most stable in the bog flat peat, and least stable in the dried peat. Research in natural and cutover peatlands in Canada also found that the watertable varied less in a natural peatland and more in a cutover peatland (Waddington, Warner et al. 2002). A natural bog in Sweden had lower watertables below hummocks than below flat areas (McNeil and Waddington 2003), as did the bog peat at Wellington Plain peatland (Fig. 2.10). However, the watertable in the Swedish bog varied more below flat areas in one year and more below hummocks the following year (McNeil and Waddington 2003), in contrast with the results in Fig. 2.10.

Below the maximum depth of the watertable, the water in the peat can be considered to be in ‘permanent storage’. Above the maximum depth of the watertable, up to the minimum depth of the watertable, is ‘temporary storage’ - a measure of the capacity of the peat to store incoming water. Temporary storage represents the capacity of the peat to smooth streamflow by absorbing rainfall and later releasing this.
water to streams. The temporary storage in the dried peat, the bog flat peat and the bog hummock peat was 39 cm, 10 cm and 36 cm respectively (Fig. 2.10). Bog peat is a mix of flat areas and hummocks, so the mix of temporary storage and permanent storage of the bog peat as a whole is dependant upon microtopography. The dried peat had no permanent storage because the maximum depth of the watertable was the base of the peat profile. Thus, the entire profile of dried peat was temporary storage.

While the magnitude of temporary storage in the dried peat and the bog hummock peat was similar, the timing of watertable movement in these two peats was different (Fig. 2.10). In the bog hummock peat, the watertable rose in one step, in less than one hour (the time between measurements) and also fell in one large (70 mm) step, in less than one hour. In the dried peat the watertable rose faster than it fell, as has also been observed in cutover peatlands in Canadian studies (Price and Scholtzhauer 1999; Van Seters and Price 2001; Waddington, Warner et al. 2002). In the dried peat, the watertable rose in several steps, over several hours, and fell in several small (10-20 mm) steps, over one or two days. The watertable began descending immediately after reaching its minimum depth in the dried peat. In the bog hummock peat, on the other hand, the watertable often remained at its minimum depth for several days.

A possible explanation for this more rapid movement of the watertable in the bog peat than in the dried peat can be found in the profile descriptions in Fig. 2.2, Table 2.1 and Table 2.2. Water moved rapidly through the loose open material of the upper layer of the bog peat. Water movement through the more compact, structured dried peat was slower. This will be quantified in the hydraulic conductivity and water retention results in Chapter 5.

To summarise, in the bog peat the watertable moved infrequently, but when it did move, it moved quickly. In the dried peat, the watertable moved more often and more slowly. However, in both peat types the size of the movement of the watertable was not in proportion with the amount of rainfall (Fig. 2.12). Once again, an explanation for this counter-intuitive phenomenon may lie in the structure of the two peat types. Water could only move slowly through the compact, structured dried peat, which had two direct effects on the ability of the watertable to rise in response to rainfall. The watertable fell slowly in the dried peat, so that it often had not reached the base of the profile before another rainfall event occurred, and thus not all of the profile was available to store water. Secondly, infiltration in the dried peat would
likely have been low, which may cause surface runoff and prevent some of the rainfall from entering the soil profile. In the bog peat the loose open structure of the upper layers probably allowed rapid movement of water through the acrotelm and required a large amount of rainfall to raise the watertable. Thus most rainfall events caused no response in the watertable as all the water moved rapidly through the upper layers of peat above the watertable. Prior conditions were also relevant in the bog peat: initial watertable depths closer to the maximum depth showed more response to rainfall than did initial watertable depths closer to the minimum depth.

2.4.5.2 Decomposition

Decomposition of organic matter is hindered by waterlogging but favoured by cycles of wetting and drying (Hogg, Lieffers et al. 1992). Thus the movement of the watertable in the peat profile affects peat decomposition (Updegraff, Bridgham et al. 2001). The stable watertable in the bog flat peat (Fig. 2.10) provided an environment least favourable to decomposition. The watertable fluctuated most in the dried peat (Fig. 2.10), providing the cycles of wetting and drying that favour decomposition. The bog hummock peat experienced some movement of the watertable (Fig. 2.10), and thus cycles of wetting and drying occurred but were less frequent than in the dried peat. The bog hummock peat was thus likely an environment of intermediate suitability for decomposition. However, factors other than peat wetness also affect decomposition (Charman 2002) and they are considered further in Chapter 3 and Chapter 4.

2.4.5.3 Plants

The behaviour of the watertable affects the type of plants that can grow on the peat. *Sphagnum* requires a constant watertable close to the peat surface (Van Seters and Price 2002). The absence of *Sphagnum* from the dried peat (Table 2.3) can thus be partly attributed to the variation in watertable depth. Van Seters and Price (2001) also attributed the low incidence of *Sphagnum* that they measured on cutover peat to high variability in the watertable. While *Sphagnum* requires wet conditions, grasses such as *Poa* species require drier conditions and are not characteristic bog species (Costin, Gray et al. 2000). *Poa* species occurred on the dried peat but not on the bog peat (Table 2.3) and this can be attributed to a deeper watertable, on average, in the dried peat than in the bog peat.
2.4.6 Limitations

While equipment failure resulted in gaps in the data set, the results in this study nonetheless compare favourably with northern hemisphere studies, which often span only a few months over the summer growing season (Price and Scholtzhauer 1999; Van Seters and Price 2001; Waddington and Roulet 2000; Waddington, Warner et al. 2002).

Water content results were presented as gravimetric water content. Volumetric water contents would have been more useful to compare with other studies; however, the change in peat volume over time was not recorded.

2.5 Conclusions

In Chapter 2, I aimed to describe the Wellington Plain peatland and lay the foundations for understanding the subsequent chapters.

Bog peat was a deep, acidic soil which gradually became darker and more compact with depth. The presence of Sphagnum and the absence of Poa distinguished the vegetation of the bog peat from the vegetation of the dried peat. Soil temperature in the bog peat followed the pattern of air temperature, and soil water content in the bog peat appeared to be more responsive to soil temperature than to rainfall. Soil water content increased with depth in the bog peat. The watertable in bog flat peat was fairly stable at 18 cm depth, while the watertable in bog hummock peat varied from 58 to 25 cm depth.

Dried peat was a shallow, compact soil, still acidic but less so than the bog peat. Soil temperature in the dried peat followed the pattern of air temperature. Soil water content in the dried peat decreased with depth, and was generally unresponsive to rainfall. The watertable in dried peat varied from 35 to 3 cm depth i.e. through the entire profile of peat.

The site description and environmental properties described two distinctly different peat soils. The effects of these differences will be explored in the following chapters.
Chapter 3. Carbon cycling I - Chemistry and laboratory incubations

Summary

The carbon dynamics of Australian peat soils have received little research attention, yet an understanding of how bog peats and dried peats function is an essential base for developing restoration programs, particularly for areas damaged by grazing and burning. I measured the carbon chemistry of profiles of bog peat and dried peat, with $^{13}$C CP/MAS nuclear magnetic resonance. O-alkyl carbon dominated the bog peat at the surface, and, as depth increased, so did the contribution from alkyl, carbonyl and aryl carbons. The chemistry of the dried peat was similar to that of the bog peat below 60 cm. The extent of decomposition decreased with depth in both bog peat and dried peat; however, the dried peat was considerably more decomposed at the surface than the bog peat. A series of incubations of bog peat and dried peat suggested that, in the absence of confounding factors, peat chemistry is most influential upon the size of the pool of potentially mineralisable carbon. Peat which was poorly decomposed contained the largest pool of mineralisable carbon. Conversely, well decomposed peat had a small mineralisable carbon pool. The rate of carbon mineralisation was most affected by water content. Mineralisation was minimised at saturation, which supports the use of weirs to rewet dried peats in restoration works.
3.1 Introduction

Peat soils are estimated to store one third of the world’s soil carbon (Gorham 1991; Post, Emanuel et al. 1982). The role of peat bogs as contributors to, or ameliorators of, global warming has consequently attracted much research attention (Belyea and Clymo 2001; Blodau and Moore 2003; Chimner and Cooper 2003b; Stewart 1990; Updegraff, Bridgham et al. 2001; Waddington, Rotenberg et al. 2001). While the build-up of organic matter in peat is a store of carbon, this material is also decomposing, releasing CO$_2$ and CH$_4$ to the atmosphere. In some places, bogs appear to be acting as carbon sinks (Vitt, Halsey et al. 2000; Wieder 2001), while in others, bogs are currently sources of carbon. One of the central factors affecting the rate of peat decomposition is temperature (Hogg, Lieffers et al. 1992; Updegraff, Bridgham et al. 2001). As temperature increases, the balance between carbon accumulation and release may be tipped in favour of release (Gorham 1991). Thus, peat bogs have the potential to be both casualties and drivers of climate change, as increased carbon emissions from peat will have a positive feedback on both temperature and rates of carbon emissions in the future. Evidence of this is already appearing as permafrost bogs melt in Siberia and northern Canada (Pearce 2005; Turetsky, Wieder et al. 2000). It is unlikely that the breakdown of these largely natural, undeveloped areas of peat can be halted, other than by halting net increases in temperature through general reductions in greenhouse emissions. However, in peat systems altered by local human activity, opportunities may exist to reduce management-induced rates of carbon emissions and accumulation.

Rehabilitation of bogs drained by human activity may turn carbon sources into carbon sinks, or at least slow decomposition rates. The potential for this has been most explored in the northern hemisphere. Cutover peatlands in Canada, abandoned after peat mining, provide a ideal environment for the study of methods of bog rehabilitation (Petrone, Waddington et al. 2001; Waddington, Rotenberg et al. 2001). Interlinked studies of hydrology, carbon cycling and plant growth all point to rewetting the peat as the critical factor (Price, Branfireun et al. 2005). This research has contributed significantly to our understanding of carbon cycling in peat bogs, and how to tip the balance in favour of carbon accumulation. In the United Kingdom, some bogs drained for afforestation have recently been rehabilitated, by blockage of drains and removal of trees (Thompson, Smith et al. 2004). In the southern
hemisphere, management-induced carbon emissions from peat are associated with drainage for agricultural use, rather than for peat mining. The use of peat for agricultural production typically includes installation of drainage channels and application of nutrients and lime which can enhance carbon emissions (Saidy 2002). The now-abandoned Mega Rice Project in Indonesia drained over a million hectares of subtropical peat bog (Page, Wust et al. 2004). This land was found to be unsuitable for cultivation, and fires in the dry, drained peat emitted between 0.81 and 2.57 Gt of carbon in 1997 alone (Page, Siegert et al. 2002). Work has begun to block the drainage channels to rewet these peats, funded partly by Canadian and EU climate change mitigation programs (Aldhous 2004). On a smaller scale, peat bogs in the Australian Alps, drained inadvertently by cattle grazing, have been recommended for rehabilitation following extensive bushfires in 1998 and 2003 (Wahren and Papst 1999; Walsh and McDougall 2004). Restoration has begun (Hope, Whinam et al. 2005) and, while conservation of biodiversity is the primary motivator, the works may also contribute to limiting carbon emissions. Reduced carbon emissions will be more likely to eventuate if restoration is planned with an understanding of carbon cycling in bogs in the Australian Alps.

Aside from temperature, one of the main factors affecting how readily peat will decompose is the substrate quality, or the initial extent of decomposition (EOD) of the peat (Buttler, Dinel et al. 1994; Scalon and Moore 2000; Turetsky, Wieder et al. 2000). The ratio of alkyl carbon to O-alkyl carbon, determined via solid-state $^{13}$C nuclear magnetic resonance (NMR), is a sensitive measure of the EOD of organic materials including peat (Baldock, Oades et al. 1997). Solid-state $^{13}$C NMR is now routinely used to describe the chemical composition of peat (Huang, Stankiewicz et al. 1998; Krosshavn, Southon et al. 1992; Krull, Thompson et al. 2004; Norden, Bohlin et al. 1992; Preston, Axelson et al. 1989). This method has the advantage, over traditional wet-chemistry methods used to define carbon chemistry, of minimally altering the sample and directly measuring the different types of carbon present.

The aims of this study were to describe the carbon chemistry of peat at Wellington Plain in the Australian Alps, and to investigate the influence of carbon chemistry, water content, and particle size on carbon mineralisation from these peats. Solid-state $^{13}$C NMR was used to define the carbon chemistry and EOD in continuous profiles of bog peat and dried peat. A series of incubation experiments were conducted
to independently define the impact of carbon chemistry, size of peat particles and water content on carbon mineralisation.

3.2 Methods

3.2.1 Sampling

Wellington Plain peatland is described in Chapter 2. I surveyed the peatland extensively to choose five representative locations each of bog peat and dried peat to collect cores for chemical analysis. Continuous profiles of peat, from the surface to the underlying mineral material, were collected for chemical analysis. Bog peat profiles were collected in two sections. PVC pipe (8.5 cm diameter) was carefully inserted into the surface peat, to minimise compaction, and a Russian D-section corer (3.5 cm diameter) was used to collect cores from the deeper, less fibrous peat below 20 cm. The dried peat profiles were sampled with a hemispherical peat corer (2.8 cm diameter). All samples were collected in the summer of 2003/2004, immediately returned to the laboratory and frozen until required for analysis. Frozen cores were sawn into slices, freeze-dried or oven-dried at 60 °C, and ground to less than 0.5 μm with a mortar and pestle.

Peat required for the incubation experiments was collected from pits adjacent to core locations. Bulk samples of peat were collected with a spade and a serrated knife, in October 2004. The bog peat was sampled at each of three depths (5-15 cm, 30-40 cm and 90-110 cm) representative of fibric, hemic and sapric peat respectively, the three peat textures recognised in the Australian Soil Classification (Isbell 1996; McDonald, Isbell et al. 1990). The dried peat was sampled at the surface (1-4 cm depth) and at the base (18-22 cm depth), just above the underlying layer of gravelly clay. All samples were stored at 4 °C, then oven-dried at 60 °C and ground in a Retsch ZZ mill.

3.2.2 Carbon and nitrogen analyses

Carbon and nitrogen contents were determined in duplicate for all samples from the five profiles of bog peat and five profiles of dried peat and also for the five peats for the incubation experiments, on a Europa Roboprep carbon and nitrogen analyser.
3.2.3 $^{13}$C Nuclear Magnetic Resonance spectroscopy

Solid-state $^{13}$C NMR spectroscopy using a standard cross polarization (CP) pulse sequence (Wilson 1987) was used to characterise the chemical composition of organic carbon in the bog peat and the dried peat. A Varian Unity200 spectrometer operating at a $^{13}$C frequency of 50.3 MHz was used for all analyses. A pulse width of 5.9 μs and a contact time of 1 ms were used in all CP analyses. For each analysis, a measured mass of peat (0.15-0.35 g) was packed into a 7 mm diameter cylindrical zirconia rotor with Kel-F end-caps and spun at 5000 ± 100 Hz in a Doty Scientific magic angle spinning probe. Each free induction decay was acquired using a sweep width of 40 kHz. Over an acquisition time of 15 ms, 1216 data points were collected. All spectra were zero filled to 8192 data points. Data were processed with both Lorentzian and Gaussian functions of widths 50 Hz and 0.005 s respectively. Chemical shifts were externally referenced to the methyl resonance of hexamethylbenzene at 17.36 ppm. The area under each spectrum was integrated over eight spectral regions as defined by Baldock and Smernik (2002). This method corrects for signal otherwise misallocated due to the presence of spinning side bands. Signal intensity within the eight regions was then combined to determine the contribution from alkyl (0-45 ppm), O-alkyl (45-110 ppm), aryl (110-165 ppm) and carbonyl (165-210 ppm) carbon. The ratio of signal intensity derived from the alkyl and O-alkyl carbon regions was calculated, as this has been shown to be a sensitive index of the EOD of organic matter, given a constant vegetational background (Baldock, Oades et al. 1997).

To determine the appropriate recycle delay for the CP experiments, rates of proton spin-lattice relaxation in the static frame ($1/T_1^H$) were measured using the methodology of Smernik et al. (2000). An inversion recovery pulse sequence utilising 8 recovery delays (0.0001, 0.001, 0.008, 0.01, 0.02, 0.05, 0.08 and 0.1 s), a 1 ms contact time and a 1 s recycle delay was used. For each recovery delay, 100 transients were collected. A 0.5 s recycle delay was chosen for the CP experiments, as this was more than ten times the longest $T_1^H$ value determined for each sample.

To define the proportion of sample carbon observed in the CP experiments, rates of proton spin-lattice relaxation in the rotating frame ($1/T_{1\rho}^H$) were measured and the NMR observable carbon ($C_{obs}$) was calculated according to Baldock and Smernik (2002). To measure $T_{1\rho}^H$, a variable spin lock pulse sequence with a contact time of 1 ms, a recycle delay of 0.5 s, and spin lock times of 0, 1, 2, 3, 4 and 5 ms
were used. Five hundred transients were collected for each spin lock time for each experiment. T1pH was calculated as the inverse slope of ln (total signal intensity) versus spin lock time. \( C_{\text{obs}} \) was then determined for the CP analyses according to the equation presented in Baldock and Smernik (2002). This enabled me to determine how quantitative the CP analyses were.

The \( C_{\text{obs}} \) values obtained for the CP analysis of some samples were low (less than 50%). As a result, a direct polarization (DP) analysis was completed for one sample in an effort to ascertain whether or not the CP analysis resulted in selective loss of carbon signal. The DP analysis used a 5.9 µs (90°) \(^{13}\text{C}\) pulse with a 90 s recycle delay (Wilson 1987). Other instrument and data analysis parameters were as described for the CP analysis with the exception that the DP spectra were corrected for the background signal from the Kel-F end caps. This was completed by subtracting the free induction decay acquired for an empty rotor from that of the sample prior to Fourier transformation (Smernik and Oades 2001). Instrument malfunction prevented the completion of DP analyses for further samples.

CP \(^{13}\text{C}\) NMR analyses were also completed for three known chemicals: cellulose, lignin and gliadin (protein from wheat). The same approach was used as described above for the peat samples. This was completed to identify the potential origin of the resonances observed in the peat samples.

Replicate CP \(^{13}\text{C}\) NMR analyses of the peat samples were not completed. Previous work using the same instrument has demonstrated that variations in signal intensity between chemical shift regions that are greater than 2% of total signal intensity can be considered significant (Baldock and Smernik 2002). For the DP analysis, variations greater than 5% can be considered significant.
3.2.4 Carbon mineralisation

Carbon dioxide emissions from bog peat and dried peat were measured, under controlled conditions in the laboratory, to ascertain the influence of chemistry, particle size and water content. Under natural conditions, these factors tend to be intermingled. The objective of these incubations was not to determine absolute decomposition rates indicative of those that occur in the field, but rather to investigate the mechanisms involved in peat decomposition. To complete this task, it was considered essential to minimise any confounding influences that variables such as bulk density, availability of oxygen and water, and particle size may have on carbon mineralisation. This can best be achieved by mixing a small amount of sample, ground to a uniform size, into a large amount of an inert support matrix (e.g. sand), so that the physical conditions of the incubation are controlled by the inert matrix rather than by the properties of the sample itself. Thus, I incubated oven-dried (60 °C), ground peat samples mixed through a sand matrix.

The sand used in this study was sieved to less than 2 mm and oven-dried at 105 °C. The water retention properties of the sand were determined on four replicate cores (234 cm³) on a 10 kPa pressure plate attached to hanging columns of water of 0 (saturation), 10, 20 and 100 cm length. The corresponding volumetric water contents were 0.40, 0.37, 0.31 and 0.04 cm³/cm³, respectively. The water content corresponding to 10 cm suction (0.37 cm³/cm³) was used in all experiments except Experiment 3, in which water content was varied (see Table 3.1).

A total of four incubation experiments were completed in this study. Experiment 1 measured the mineralisation of carbon from peats with five different chemical compositions. These included three bog peats (fibric, hemic and sapric) and two dried peats (surface and base). The carbon chemistry of each sample was determined using ¹³C CP/MAS NMR, as described in Section 3.2.3. See Table 3.1 for experiment details.

In Experiment 2, the five peat types used in Experiment 1 were ground to three different sizes to investigate the effect of particle size on the mineralisation of carbon. Whole peat samples were ground, rather than sieving out extant different sized particle fractions, to minimise variations in chemical composition between the differently sized particles. It has been shown that extant smaller particles tend to have
chemistries consistent with a higher EOD (Norden, Bohlin et al. 1992; Preston, Axelson et al. 1989). See Table 3.1 for details.

In Experiment 3, mineralisation of carbon from the two peats most likely to experience varied water content in the field, fibric bog peat and surface dried peat, was measured at four different water contents. See Table 3.1 for details.

In Experiment 4, carbon mineralisation from five field-moist samples maintained in their original state (i.e. not ground, not dried, and not mixed with sand) was compared with that obtained from dried, ground and mixed samples of the same five peats. This was completed in an attempt to gain an insight into how the various applied treatments may have altered rates of mineralisation compared to that from peat maintained in a state more indicative of its natural environment. The field-moist samples had various bulk densities, particle sizes and water contents, in addition to different chemistries. See Table 3.1 for details.

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Peat types*</th>
<th>Oven dried at (°C)</th>
<th>Ground to &lt; (µm)§</th>
<th>Volumetric water content (cm³/cm³)</th>
<th>Sand</th>
<th>Samples (#)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Chemistry</td>
<td>1,2,3,4,5</td>
<td>60</td>
<td>0.5</td>
<td>0.37</td>
<td>+</td>
<td>20</td>
</tr>
<tr>
<td>2. Particle size</td>
<td>1,2,3,4,5</td>
<td>60</td>
<td>0.2, 0.5, 1.5</td>
<td>0.37</td>
<td>+</td>
<td>60</td>
</tr>
<tr>
<td>3. Water content</td>
<td>1,4</td>
<td>60</td>
<td>0.5</td>
<td>0.40, 0.37, 0.31, 0.04</td>
<td>+</td>
<td>32</td>
</tr>
<tr>
<td>4. Preparation</td>
<td>1,2,3,4,5</td>
<td>½ at 60</td>
<td>½ to 0.5</td>
<td>½ 0.37</td>
<td>½†</td>
<td>40</td>
</tr>
</tbody>
</table>
| | | ½ field-moist | ½ intact | ½† 0.91, 0.95, 0.94, 0.84, 0.83 | ½ - | * 1 = fibric bog peat, 2 = hemic bog peat, 3 = sapric bog peat, 4 = surface dried peat, 5 = base dried peat § peats were ground to less than or equal to the indicated particle sizes † water contents of fresh peat in Experiment 4 are gravimetric (g/g) and refer to peat types 1, 2, 3, 4 and 5 respectively.

For each of the four incubation experiments, four replicates of each treatment were prepared. The mass of peat required to provide 200 mg of carbon (calculated from the carbon content) was mixed with 40 g of sand in a 50 mL vial and wet to the desired water content. The exception was Experiment 4, in which half of the jars contained a mass of fresh peat yielding 200 mg of carbon in a 50 mL vial (not dried, ground or mixed through a sand matrix). In all experiments, each sample was placed in a 1 L mason jar with a vial containing 10 mL of water and a strip of CO₂ indicator gels.
The CO₂ indicator gels change from pink to yellow in response to increasing concentrations of CO₂ in the headspace of the jars. The indicator gel was made from cresol red (12.5 µg/mL), potassium chloride (150 mM), and sodium bicarbonate (2.5 mM) in agar. The gel was set in detachable eight-well microplate strips, and each plate was read at 590 nm on a microplate spectrophotometer (Molecular Devices Spectramax 250) before and after incubation, to determine the magnitude of colour change (Cambell, Chapman et al. 2003).

The indicator gels were calibrated by injecting a known volume of CO₂ into ten mason jars with septa-fitted lids. A new batch of calibration gels was read each time gels were changed during the incubations. Initial and final absorbance readings were logged, and the log of the difference was plotted against the volume of CO₂ injected. The calibration equations (p<0.001, r²>0.86) were fitted to the associated batch of gel readings from peat samples, to determine the volume of CO₂ released by each sample.

Each experiment ran for 38 days. Gels were changed every one to ten days, when the volume of CO₂ evolved came within the range of the calibration gels. Incubation jars with only sand and water were used to account for background CO₂. The incubations were laid out in a randomised complete block design (one treatment replicate per block) in a dark, constant-temperature room (20 °C).
3.2.5 Data analysis

To quantify the kinetics of carbon mineralisation in the peat incubations, I fitted two models to the cumulative curves of CO\textsubscript{2}-C released over time. The one pool model (Equation 3.1) assumes that all the carbon in the peat decays at the same rate. The two pool model (Equation 3.2) assumes that there are two pools of carbon, one that decays quickly and one that decays slowly.

One pool model \[ C_t = C_0(1-e^{-kt}) \] \hspace{1cm} \text{Equation 3.1}

Two pool model \[ C_t = C_q(1-e^{-qt}) + (TC-C_0)(1-e^{-st}) \] \hspace{1cm} \text{Equation 3.2}

Where \( t = \text{time} \)
\( C_t = \text{cumulative carbon released after time } t \)
\( C_0 = \text{potentially mineralisable pool of carbon} \)
\( k = \text{rate of carbon mineralisation} \)
\( C_q = \text{quickly mineralisable pool of carbon} \)
\( q = \text{rate of mineralisation of quick pool} \)
\( TC = \text{total carbon present in the peat} \)
\( (TC-C_0) = \text{slowly mineralisable pool of carbon} \)
\( s = \text{rate of mineralisation of slow pool} \)

The models were fitted to the measured carbon mineralisation data with the SOLVER function in EXCEL, which was set to minimise the residual sum of squares. To determine which model best fit the data, the F test was performed (Equation 3.3).

\[
F = \frac{(RSS1-RSS2)/[(n1-p1)-(n2-p2)]}{(RSS2)/(n2-p2)}
\] \hspace{1cm} \text{Equation 3.3}

Where \( RSS1 = \text{residual sum of squares of the one pool model} \)
\( RSS2 = \text{residual sum of squares of the two pool model} \)
\( n = \text{number of sampling times} \)
\( p = \text{number of model variables} \)
If the p value for the F test was significant ($\alpha = 0.05$), then the two pool model yielded a significantly better fit to the experimental data than the one pool model. This occurred in most incubations of fibric bog peat and surface dried peat. Incubations of the remaining three peat types (hemic bog peat, sapric bog peat and base dried peat) had an insufficient number of measurements of CO$_2$ to test the goodness of fit of the two pool model and thus the F test could not be performed. Consequently I chose the one pool model to describe all incubations, in order to be able to compare the different peat types. The rate constant and the pool size were not correlated.

I used the rate constants and pool sizes to analyse the data for differences between treatments using ANOVA as follows: a one-way analysis was used for Experiment 1, a 5x3 factorial design was used for Experiment 2, a 2x4 factorial design was used for Experiment 3, and a 5x2 factorial design was used for Experiment 4. Where significant treatment effects were identified by ANOVA, Tukey’s HSD post hoc test was used to identify differences between treatments at $\alpha=0.05$. Normality and equality of variances were investigated with plots of residuals versus predicted values and Levienes’ test. All data were normally distributed. Where the data displayed unequal variances, transformations (log or square root) were applied. All analyses were performed with STATISTICA 7.
3.3 Results

3.3.1 Carbon and nitrogen analyses

Carbon content in the bog peat remained around 400 g/kg down the profile until one metre depth, below which some profiles showed an increase and others a decrease in carbon content (Fig. 3.1a). Nitrogen content in the bog peat profiles showed a steep increase from 6 g/kg at the surface down to 60 cm depth, where values stabilised around 20 g/kg. Below one metre, the nitrogen content tended to decrease slightly.
Thus the carbon/nitrogen ratio in the bog peat profiles decreased from about 75 at the surface down to around 25 from 60 cm down to the base of the profile (Fig. 3.1c).

In the dried peat there was greater variation between profiles than in the bog peat (Fig. 3.1). However, overall, both the content of carbon and nitrogen decreased with depth, resulting in little change in the carbon/nitrogen ratio, which remained about 20 throughout the profile (Fig. 3.1d, e and f).

3.3.2 $^{13}$C Nuclear Magnetic Resonance spectroscopy

$^{13}$C CP/MAS NMR spectroscopy yields detailed information about the chemical conformation of organic materials; however, there are valid concerns about quantitation (Mao, Hu et al. 2000; Preston 1996). To address this issue, I performed spin-counting experiments to calculate the percentage of NMR observable carbon ($C_{\text{obs}}$) (Baldock and Smernik 2002) (Fig. 3.2). $C_{\text{obs}}$ values ranged from 54 % to 88 % for samples of bog peat and from 22 % to 79 % for samples of dried peat. Thus the spectra ought to be considered qualitatively, rather than quantitatively. Low observability could be caused by paramagnetics, low carbon content, molecular motion or a lack of protons in the vicinity of carbon (e.g. as found in the unsaturated structures of charcoal) (J. Baldock pers. comm. 2006).

Direct polarization (DP) analysis was run on one sample to determine whether this signal attenuation was specific to certain carbon types. Instrument malfunction prevented DP analyses of further samples. The sample had a carbon content of 451 g/kg. Direct polarization yielded improved observability (91 % compared with 73 %) over cross polarization, and showed that signal attenuation was spread fairly evenly across all carbon types (Fig. 3.3). Signal intensity was 4.2 % less for O-alkyl carbon and 3.5 % more for aryl carbon in DP, compared with CP. Variations less than 5 % are not significant in DP, and thus, despite low observability, the CP analyses provided a quantitative measure of the carbon types present in the peat samples.
Fig. 3.2 Percentage of organic carbon observed ($C_{obs}$) in CP/MAS $^{13}$C NMR analyses of a) bog peat profiles 1-5 and b) dried peat profiles 1-5. Note T1pH was measured for all samples in profiles 2-5 (bog peat and dried peat), but only for some samples from profiles 1 (bog peat and dried peat).

Fig. 3.3 Spectrum from solid-state $^{13}$C NMR analyses top) cross polarization and bottom) direct polarization of a sample of bog peat from profile 5.
Fig. 3.4 Solid state $^{13}$C CP/MAS NMR spectra from peat and the major biopolymers found in natural organic materials: cellulose, gliadin (protein), lignin, and stearic acid (lipid).

The spectra in Fig. 3.4 demonstrated that the peat displayed resonances consistent with a mixture of the major biopolymers found in natural organic materials (cellulose, lignin, protein and lipid). Fig. 3.4 also indicated that some chemical shift regions contain resonances from multiple types of compounds. The peat spectrum displayed the resonances typically seen in peat (Wilson 1987): alkyl (32 ppm), N-alkyl/methoxyl (56 ppm), O-alkyl/di-O-alkyl (74, 104 ppm), protonated aryl carbon
(116 ppm), non-protonated aryl carbon (129 ppm), O-aryl (152 ppm) and carbonyl carbon (173 ppm). The general shape of the peat spectrum was similar to spectrum for Sphagnum peat presented elsewhere (Krosshavn, Southon et al. 1992; Norden, Bohlin et al. 1992; Norden, Fyfe et al. 1986; Preston, Axelson et al. 1989; Preston, Shipitalo et al. 1987; Purwanto, Watanabe et al. 2005).

Fig. 3.5 showed a selection of spectra from a profile of bog peat and a profile of dried peat. All the peat samples displayed resonances at essentially the same chemical shift values described for the peat presented in Fig. 3.4 and were consistent with mixtures of the major biopolymers found in natural organic materials. However, the height and width of the various resonances changed with depth and from bog peat to dried peat.

The upper samples in the bog peat profile were dominated by O-alkyl carbon, at 74 and 104 ppm, indicative of the presence of cellulose or other carbohydrates. As depth in the bog increased, alkyl carbon (32 ppm) increased in contribution to the total, and was likely derived from microbes and/or plants (Wilson 1987). The relative intensity of the aryl (110-165 ppm) and carbonyl (165-210 ppm) regions also increased with depth.

In the dried peat, a similar trend with depth occurred over a much shorter physical distance. However, the dried peat had considerably less carbohydrate carbon at the surface than the bog peat did. The spectra from the surface to the base of the dried peat profile were comparable with the lower half of the bog peat profile, from 60 cm to the base at 127 cm.
Fig. 3.5 Solid state $^{13}$C CP/MAS NMR spectra from bog peat (profile 4) and dried peat (profile 4). Both profiles were sampled continuously from the surface to the underlying substrate, and a selection of representative spectra is presented. The depth of each sample is indicated adjacent to the spectrum.
Fig. 3.6 Distribution of relative signal intensities (%) of alkyl, O-alkyl, aryl and carbonyl carbon with depth for bog peat profiles (a-e) and dried peat profiles (f-j), derived from $^{13}$C NMR spectra.
The distribution of each carbon type was determined by integration of signal intensity within the 0-45 ppm (alkyl), 45-110 ppm (O-alkyl), 110-165 ppm (aryl) and 165-210 ppm (carbonyl) spectral regions. Changes in the distribution of each type of carbon with depth across the five profiles of bog peat were consistent in direction but varied in extent (Fig. 3.6 a-e). At the surface, the peat was predominantly composed of O-alkyl carbon. With increasing depth, the proportion of O-alkyl carbon decreased, but remained the most abundant type of carbon down to the base of four of the five profiles. Increases in both alkyl and aryl carbon were evident with increasing depth; the increase in alkyl carbon was larger than that associated with aryl carbon. The amount of carbonyl carbon present in the samples remained more constant down the profiles.

Changes in the proportions of each type of carbon with increasing depth in the dried peat (Fig. 3.6 f-j) were similar in direction to those noted for the bog peat. However, at the surface of the dried peat there was less O-alkyl carbon and more alkyl carbon and aryl carbon, than at the surface of the bog peat. The rate of change in carbon composition with increasing depth in the dried peat was greater than the rate of change with depth in the bog peat.

Fig. 3.7 Alkyl:O-alkyl ratios (derived from CP/MAS $^{13}$C NMR spectra) versus depth, for five profiles each of a) bog peat and b) dried peat. Note the different scales on the y axes (depth).

Baldock et al. (1997) found that, assuming a constant vegetational origin, the ratio of alkyl carbon to O-alkyl carbon was a sensitive index of the EOD of organic material. Fig. 3.7 showed that the alkyl:O-alkyl ratio increased with depth for both the bog peat and the dried peat. Near the bottom of bog peat profile 2 there was an anomalously high value, which may have been caused by a layer of material in the
peat profile of different vegetational origin, from the fen plants/moss/algae which preceded the development of the bog proper. Both bog peat and dried peat were less decomposed at the surface, and increased in EOD as depth increased. However, the bog peat was less decomposed at the surface (alkyl: O-alkyl ratio ~ 0.1) than was the dried peat (alkyl:O-alkyl ratio ~ 0.4). At a depth of approximately 60 cm, the EOD of bog peat was similar to that of peat from the surface of the dried peat. The rate of change in EOD with depth in the two peat types was also quite different. In the bog peat, there were two distinct regions. Above 80 cm, decomposition changed only slowly with depth (3x10⁻³ alkyl:O-alkyl units/cm), while below 80 cm, the rate increased to around 8x10⁻³ alkyl:O-alkyl units/cm. In the dried peat, decomposition increased by 31x10⁻³ alkyl:O-alkyl units/cm.
3.3.3 Influence of chemical composition on mineralisation of carbon from peat

Mineralisation of carbon was quantified for five peats of varying chemical compositions, over a 38 day incubation period (Fig. 3.8). In order to define the mineralisability of carbon in the peat, results were expressed in units of CO₂-C mineralised per gram of peat carbon contained in the samples. All peat types showed an initial flush of mineralization, followed by lower rates of CO₂ production. CO₂ production decreased with depth in both the bog peat and the dried peat.
Chemistry had a significant effect upon both the mineralisable carbon pool (p<0.001) and the (transformed) rate constant (p<0.001) (Fig. 3.9). Rate constant data were transformed by multiplying by 0.4 to homogenise variances. In both bog peat and dried peat, the amount of carbon available to be mineralised (the mineralisable carbon pool) decreased with depth. The rate at which the mineralisation occurred (expressed by the rate constant) did not change significantly with depth in either the bog peat or the dried peat.
### 3.3.4 Influence of particle size on mineralisation of peat carbon

There was a significant interaction between peat type and particle size for both the mineralisable carbon pool (p<0.001) and the (transformed) rate constant (p=0.010) (Fig. 3.10). Rate constant data were log transformed to homogenise variances. As particle size increased from 0.2 to 1.5 µm, the mineralisable carbon pool: increased for surface dried peat, decreased for hemic bog peat, increased and then decreased for fibric bog peat, and remained constant for sapric bog peat and base dried peat. The effect of particle size within each peat type was less differentiated for the rate constant than for the mineralisable carbon pool.

![Graph showing influence of particle size on mineralisation of peat carbon](image-url)

**Fig. 3.10 a)** Mineralisable carbon pool and **b)** rate constant for each combination of peat type and particle size in Experiment 2. Error bars are ± the standard deviation of treatment mean values with n=4. Columns labelled with different letters are significantly different from one another (Tukey’s HSD).
3.3.5 Influence of water content on mineralisation of peat carbon

There was a significant interaction between water content and peat type on the mineralisable carbon pool (p<0.001) (Fig. 3.11a). Water content (p<0.001) and peat type (p<0.001) each had a significant effect on the (transformed) rate constant, however, the interaction between water content and peat type was not significant for the rate constant (p=0.066) (Fig. 3.11b, c). Rate constant data were log transformed to homogenise variances. The mineralisable carbon pool decreased as conditions became drier for fibric bog peat (Fig. 3.11a). In the surface dried peat, the mineralisable carbon pool was not significantly different at different water contents. The rate constant was larger for the fibric bog peat than for the surface dried peat (Fig. 3.11b). As water content decreased, the rate constant increased, peaked at a volumetric water content of 0.37 cm$^3$/cm$^3$, and then decreased (Fig. 3.11c).
3.3.6 Comparison of carbon mineralisation from fresh and prepared peat

There was a significant interaction between peat type and preparation for both the mineralisable carbon pool (p=0.003) and the rate constant (p=0.029) (Fig. 3.12). Preparation had most effect on the mineralisable carbon pool in the fibric bog peat; the mineralisable carbon pool was not significantly affected by preparation in the other peat types. The rate constant, on the other hand, was affected by preparation in all peat types.

Fig. 3.12 a) Mineralisable carbon pool and b) rate constant for each combination of peat type and preparation in Experiment 4. Error bars are ± the standard deviation of treatment mean values with n=4. Columns labelled with different letters are significantly different from one another (Tukey’s HSD).
3.4 Discussion

3.4.1 Elemental data (C, N, C/N)

The trends in carbon and nitrogen contents with depth in the bog peat (Fig. 3.1) reflect an increase in EOD. Carbon is preferentially mineralised, and thus, as decomposition proceeds, nitrogen concentrations increase relative to carbon concentrations (Kuhry and Vitt 1996). The lack of change in the carbon/nitrogen ratio in the dried peat, and below 60 cm in the bog peat, indicate that the aforesaid process is most relevant in the initial stages of decomposition.

3.4.2 $^{13}$C Nuclear Magnetic Resonance analyses

The spectra (Fig. 3.5) and distribution of signal intensities (Fig. 3.6 a-e) in the five profiles of bog peat suggest that bog peat becomes gradually more decomposed with depth. The upper samples in the bog peat profile are dominated by O-alkyl carbon, at 74 and 104 ppm, indicative of the presence of cellulose or other carbohydrates. These two peaks decrease in intensity with depth, consistent with a preferential mineralisation of carbon associated with carbohydrate structures, which is commonly seen in peat profiles (Gondar, Lopez et al. 2005; Preston, Shipitalo et al. 1987). As depth in the bog increases, alkyl carbon (32 ppm) increases in contribution to the total, and is likely derived from microbes and/or plants (Wilson 1987). The relative intensity of the aryl (110-165 ppm) and carbonyl (165-210) regions also increase with depth. This may be due to a combination of two factors: an accumulation of lignin and microbially derived proteins, and retention of nitrogen as carbon is mineralised. While lignin does not occur in mosses (Wilson, Sawyer et al. 1989), it would be added to the peat by shrubs growing through the Sphagnum moss. Proteins are incorporated into the peat by the breakdown of plant material and by the death of microbes. The retention of nitrogen is evident in the narrowing of the carbon/nitrogen ratio (Fig. 3.1), and many aryl and carbonyl structures contain nitrogen.

The five dried peat profiles also yielded spectra (Fig. 3.5) and signal intensity distributions (Fig. 3.6 f-j) consistent with an increase in EOD with depth. However, the upper samples of the dried peat lacked a large O-alkyl carbon peak commonly associated with the cellulose of fresh plant material. The alkyl:O-alkyl ratios (Fig. 3.7) indicate that the dried peat is well decomposed at the surface, and comparison of my
results with those of Preston et al. (1987) suggest that the explanation lies in the conditions which the peat is exposed to.

$^{13}$C CP/MAS NMR was applied by Preston et al. (1987) to quantify the effects of cultivation on peat soils. Profiles of peat were analysed from three adjacent fields, one neither drained nor cultivated, and two drained and cultivated for five and twenty-five years, respectively. The uncultivated peat had a high proportion of O-alkyl carbon at the surface, with an increasing contribution from alkyl carbon and a decrease in O-alkyl carbon with depth down to one metre, just as described above for the bog peat. The cultivated peats, similar to my dried peats, had much less O-alkyl carbon at the surface than the uncultivated peat did, and the increase in alkyl carbon occurred over a shorter depth than in the uncultivated peat. This similarity between my results for bog peat and dried peat and Preston et al. (1987)’s results for uncultivated peat and cultivated peat suggested that the dried peat at Wellington Plain has undergone a process with similar effects to cultivation.

The $^{13}$C NMR results for the bog peat (Fig. 3.6 a-e) reflect the process of peatland formation. The slow build up of organic matter, due to its incomplete decomposition under anaerobic conditions, has resulted in an organic soil which gradually increases in EOD with depth (Fig. 3.7). Decomposition in the bog peat, although slow due to the lack of oxygen below the water table, is not hindered by incorporation of organics within an inorganic matrix, as can occur in mineral soils (Skjemstad, Clarke et al. 1996; Tisdall and Oades 1982). Fresh plant material added at the surface of the bog peat is decomposed first aerobically in the acrotelm and then anaerobically in the catotelm. The uni-directional trend in EOD (Fig. 3.7) suggests that there have been no major changes in hydrological conditions since the peatland began forming. Paleobotanical analysis of this site found that the composition of the peatland vegetation has not changed since the peatland began forming (Elwood 2001), supporting the proposition that the hydrological conditions have remained stable since peat initiation. Alternating layers of well decomposed peat and poorly decomposed peat in ombrotrophic bogs in the northern hemisphere have been used as evidence of climatic change (Charman 2002). The Wellington Plain peatland is fed by both groundwater and rainfall, and thus may be less sensitive to climatic change than solely rain-fed bogs.

The progression of EOD with depth in the dried peat profiles (Fig. 3.6 and Fig. 3.7) also reflects the process of their formation. Dried peats are thought to have
originated from bog peats, drained by trampling by introduced livestock (Costin 1954). Channels through the peatland allowed water to flow out, lowering the watertable and drying the peat. Dried peat no longer maintains a permanent watertable (Chapter 2), and is thus subject to the rapid aerobic decomposition associated with cycles of wetting and drying. The similarity between the dried peat spectra and spectra from depth in the bog peat (Fig. 3.5 and Fig. 3.6) indicates that the original vegetation of the two peat types appears to have been the same. Peat formed from different types of vegetation yields different NMR spectra, even when the organic material is very decomposed (Kroshavn, Southon et al. 1992; Norden, Bohlin et al. 1992). Thus the dried peat at Wellington Plain has lost a large proportion of its original material, some of which was likely released into the atmosphere as CO₂.

3.4.3 General incubation characteristics

The shape of the cumulative CO₂-C release curve (Fig. 3.8) for each peat type displayed an initially steep gradient, which leveled off after three to five days. This initial flush of mineralisation is caused by rewetting the oven-dry peat, and has been noticed in other incubations of peat (Stewart 1990). It is partly due to decomposition of the microbial biomass killed by drying.

3.4.4 Influence of chemical and physical properties of peat on carbon mineralisation

The size of the mineralisable carbon pool decreased with depth in both the bog peat and the dried peat (Fig. 3.9). A decrease in CO₂ production with peat depth has been widely reported and is attributed to an increase in the EOD of the organic matter with depth (Hogg, Lieffers et al. 1992; Scalon and Moore 2000; Turetsky 2004; Waddington, Rotenberg et al. 2001). Rather than using CO₂ as an indicator of EOD, as some studies have done (Waddington, Rotenberg et al. 2001), I measured peat chemistry to ascertain how decomposed the peat was (the alkyl/O-alkyl ratio) and compared this with the size of the mineralisable carbon pool and the rate of mineralisation (the rate constant) (Fig. 3.13).
The EOD accounts for over half of the variation in both the size of the mineralisable carbon pool and the rate constant (57 % and 64 % respectively) (Fig. 3.13). As the peat becomes more decomposed (i.e. the alkyl/O-alkyl ratio increases), the size of the mineralisable carbon pool decreases. This is consistent with the findings of Turetsky (2004), who used sequential extractions of organic fractions to look at peat chemistry, and found that the soluble fractions (from fresh organic matter) were positively correlated with CO₂, and the acid-insoluble material (the most recalcitrant fraction) was negatively correlated with CO₂. The rate constant, on the other hand, increases as the EOD increases (Fig. 3.13 b). This could be because the initial flush of mineralisation of dead microbial biomass contributes more, proportionally, to the total mineralisation in well decomposed peat than in poorly decomposed peat. Thus the rate constant is influenced mainly by this easily-mineralised material. However, the conditions under which these incubations were conducted (20 °C, volumetric water content 0.37 cm³/cm³) were more favourable for carbon mineralisation than the cold, waterlogged conditions under which bogs typically form. Thus while substrate quality does appear to be important, it is likely secondary to environmental conditions.

The idea that peat decomposition is dependant upon substrate quality is implicit in the theory of bog formation. However, under field conditions, and in laboratory incubations of peat cores, the confounding factors of depth, aeration and water content, bulk density, and carbon content obscure the clarity of this relationship. In the current work, substrate quality and mineralisation were measured directly in the absence of confounding factors, and found to be, as anticipated, correlated (Fig. 3.13).
Thus, catotelm peat decomposes more slowly than does acrotelm peat, not only because peat in the catotelm is anaerobic, lower in carbon content, colder and denser, but specifically because the carbon chemistry differs from that of peat in the acrotelm. An objective, continuous variable, such as the alkyl:O-alkyl ratio, is a more useful measure of substrate quality than the subjective, discrete ten point scale of the widely used von Post classification.

Particle size affected the mineralisable carbon pool in poorly decomposed peat but not in well decomposed peat (Fig. 3.10). These incubations used a sand matrix to control physical conditions, and thus smaller particle size was not associated with decreased aeration. The high carbon content of these peats (Fig. 3.1) corresponds with a small mineral component, and thus there is little opportunity for organic material to be protected from mineralisation by association with mineral material. Thus grinding the peat more finely does not expose previously-protected organic material to mineralisation. In contrast to my results, Stewart (1990) found that the most decomposed peat (von Post EOD) emitted the most CO₂, and attributed this to the small particle size of the amorphous deep peat. Overall, Experiment 2 suggested that particle size is not a major factor affecting the mineralisation of peat carbon.

Water content affected both the mineralisable carbon pool (in an interaction with peat chemistry) and the rate constant (independently of chemistry) (Fig. 3.11). Water content thus affected the rate constant more strongly than it affected the mineralisable carbon pool. This is to be anticipated, as the amount of water will affect how fast the mineralisation occurs, rather than the total possible amount of mineralisation. The rate constant increased and then decreased as water content increased (Fig. 3.11). Carbon mineralisation is hindered at high water contents by a lack of oxygen, and at low water contents by a lack of water for the microbes to move in. Other studies of peat decomposition have also recorded an increase and then decrease in CO₂ as water content increased (Hogg, Lieffers et al. 1992; McNeil and Waddington 2003; Saidy 2002; Waddington, Rotenberg et al. 2001).

It is well established that peats decompose more rapidly as temperature increases (Bergman, Lundberg et al. 1999; Hogg, Lieffers et al. 1992; Scalon and Moore 2000; Updegraff, Bridgham et al. 1998; Updegraff, Bridgham et al. 2001). Thus global warming will likely increase CO₂ emissions from peat bogs. However, water content can dampen the effect of temperature (Waddington, Rotenberg et al. 2001). I found that increased water content alone was sufficient to decrease the rate of
carbon mineralisation by more than 50% in surface peats (Fig. 3.11c). Therefore, rewetting areas of dried peat could decrease carbon emissions from peat in the Australian Alps. Restoration work in damaged bogs has focused on installing weirs to increase water retention, and replanting wetland species (Good 2004; Hope, Whinam et al. 2005). The incubations reported in this study suggest that this restoration work may also decrease peat mineralisation. This would be positive in terms of maintaining soil cover and limiting CO₂ emissions to the atmosphere. Further, predictions of a warmer and wetter climate bode more positively for the future of bogs and dried peat soils in the Australian Alps than do predictions of a warmer, drier climate.

Experiment 4 (Fig. 3.12) demonstrated that the preparation of the peat samples and the use of a sand matrix affected, in an interaction with peat chemistry, both the mineralisable carbon pool and the rate constant. The difference in the size of the mineralisable carbon pool for the fibric bog peat (Fig. 3.12) suggests that this peat type is, under natural conditions, somehow protected from decomposition. Various suggestions have been proposed to explain this phenomenon. Bergman et al. (1999) suggested that Sphagnum is composed of unique polymers with chemical properties that make them decay resistant. Turetsky (2004) referred to unique physiological and structural characteristics, in addition to antimicrobial agents and low nitrogen requirements, as factors inhibiting the decay of mosses. Van Breeman (1995) proposed that Sphagnum is particularly resistant to decomposition because its cell walls are chemically protected by polyphenolic network polymers and a lipid surface coating. While these explanations contain some overlap, further research is required to ascertain why Sphagnum is so decay resistant.

Environmental conditions are crucial to the build up of a peat soil. This was demonstrated by the significantly lower rate constant for samples of fresh peat compared with samples of prepared peat (Fig. 3.12). All peat types mineralised more slowly when fresh and intact, than when dried, ground and mixed through a sand matrix. The fresh peat samples were wetter and less aerated than the prepared peat samples, in addition to the chemical resistance of Sphagnum discussed above. Thus, the environmental conditions, more so than the peat chemistry, slowed decomposition. This final experiment points to the importance of field incubations in any attempt to understand the formation, and ongoing function, of a peatland. Field measurements of decomposition are reported in the next chapter.
3.5 Conclusions

The preceding results met the aims of this study, which were to describe the carbon chemistry of peat in the Australian Alps, and to investigate the influence of carbon chemistry, water content, and particle size on carbon mineralisation from these peats.

The carbon chemistry of profiles of bog peat and dried peat indicated an increase in EOD with depth. The similarity between spectra from well decomposed samples of bog peat and dried peat supports the theory that bog peat and dried peat share a common origin. The dried peat was considerably more decomposed at the surface than the bog peat, and increased in EOD over a smaller depth. The relationship between the carbon chemistry of bog peat and dried peat in this research, and the carbon chemistry of uncultivated and cultivated peats (Preston, Shipitalo et al. 1987), indicated that the dried peat has undergone a process with similar effects to cultivation.

Incubation of samples of bog peat and dried peat quantified the effects of chemistry, particle size and water content on the size of the potentially mineralisable pool of carbon and the rate of carbon mineralisation. The five peat types incubated spanned the range of EODs recorded. Carbon chemistry had the greatest effect on the mineralisable carbon pool, while water content had the greatest effect on the rate of carbon mineralisation.
Chapter 4. Carbon cycling II - Field measurements and future emissions

Summary
Carbon dioxide emissions and the mass loss of peat incubated in situ were measured in peat soils in the Australian Alps. The carbon chemistry of incubated peats was characterised with $^{13}$C NMR. In situ decomposition decreased as a function of increasing alkyl carbon content of the initial organic matter, providing direct evidence of the oft-cited link between substrate quality and decomposition rates. More mass loss occurred in the bog peat samples than in the dried peat samples. However, at the peat surface, the amount of CO$_2$ emitted was not significantly different between bog peat and dried peat. The apparently conflicting results from the two methods of measurement of decomposition could be due to recent carbon inputs from surface vegetation and pressurised and occluded gases at depth. Carbon inputs, and therefore the sink or source status, of these peats are yet to be quantified.
4.1 Introduction

Carbon stored and released by peat soils, both natural and human-altered, plays a significant role in the global carbon cycle (Gorham 1991). Peat soils occur where decomposition is hindered, and thus organic matter accumulates. This store of carbon can be released to the atmosphere if the system is disturbed (Page, Wust et al. 2004), and even undisturbed peatlands are predicted to reach a point at which the addition of organic matter at the surface is balanced by decomposition of the peat below (Clymo 1984). The measurement of peat decomposition has recently attracted much attention as researchers try to quantify the role of natural and disturbed peat bogs in the global carbon cycle, and predict the carbon balance response of bogs to higher temperatures (Latter, Howson et al. 1998; Thomas and Pearce 2004; Updegraff, Bridgham et al. 2001; Waddington, Rotenberg et al. 2001). Decomposition can be measured either a) directly, as the loss of mass of the original material (Belyea 1996; Haraguchi, Hasegawa et al. 2003; Limpens and Berendse 2003), or b) indirectly, as the CO\textsubscript{2} produced by microbial respiration which causes the decomposition (Chimner and Cooper 2003b; Koizumi, Kontturi et al. 1999). Further, measurements can be completed either in situ or on samples extracted from the field and incubated in a laboratory. Laboratory incubations allow the many factors influencing decomposition, such as temperature, water content, substrate quality and bulk density, to be controlled and manipulated (Hogg, Lieffers et al. 1992; Scalon and Moore 2000). Field measurements yield results which are a summation of these factors (Buttler, Dinel et al. 1994; Petrone, Waddington et al. 2001).

Field and laboratory measurements of peat decomposition in the northern hemisphere abound (see previous paragraph), and have improved models of global carbon cycling. However, there are comparatively little data on carbon cycling for peat soils in the tropics and southern hemisphere (Earle, Warner et al. 2003; Krull, Thompson et al. 2004; Page, Wust et al. 2004). To my knowledge, no previous studies have directly measured the decomposition of organic matter in Australian peats. Peat soils in the Australian Alps comprise a mosaic of intact bog peats and disturbed dried peats, which occur along valley bottoms and beneath springs and seepage zones. Damage by recent bushfires (1998 and 2003) and an end to cattle grazing in the Victorian Alpine National Park (2005) have lead to an upsurge in bog rehabilitation work (Good 2004; Hope, Whinam et al. 2005; Wahren and Papst 1999). To realise
their full potential, rehabilitation works need to be informed by an understanding of carbon cycling in peat soils.

Undisturbed bog peat in the Australian Alps consists of layers of organic material exhibiting different chemistries, morphologies and extents of decomposition (EOD). The Australian Soil Classification (Isbell 1996; McDonald, Isbell et al. 1990) differentiates three types of peat on the basis of chemistry, morphology and EOD: fibric peat, hemic peat, and sapric peat. Typically the progression through these layers occurs with increasing depth. In dried peat, one or more of the less decomposed layers are absent and the materials present are differentiated in this research by their location within the profile (surface dried peat or base dried peat).

I assessed rates of mineralisation of carbon from bog peat and dried peat using two techniques, one direct and one indirect: quantification of the mass loss associated with the burial and incubation of mesh bags containing the different peat materials; and measurement of carbon dioxide emissions from peat surfaces. Carbon released as CH$_4$ was not measured, as prior studies found that non-CO$_2$ fluxes accounted for less than 1 % of carbon exchange in bogs (Waddington and Roulet 2000). Informed by laboratory incubations of these peats (Chapter 3) and other research (Belyea 1996), the hypotheses investigated in this study were:

1. Mass loss from mesh bags containing peat is influenced by the initial EOD of the peat and the depth of burial within peat profiles.
2. Emission of CO$_2$ from peat surfaces is greater from the bog peat than from the dried peat.
3. Emission of CO$_2$ from peat surfaces is influenced by the environmental conditions associated with the two types of peat.
4.2 Methods

4.2.1 Field incubation of mesh bags

Mesh bags were used to estimate the rates of mineralisation of carbon in different peat types in the field. Two experiments were conducted to test the hypothesis that mass loss will be influenced by the initial EOD of the peat and the depth of burial within peat profiles. Experiment 1 measured rates of carbon mineralisation in situ, as each of the five peat types was reburied at the depth from which it was collected. Experiment 2 measured rates of carbon mineralisation of the three types of bog peat at two different depths: near surface (10 cm) and the zone of watertable fluctuation (40 cm). See Table 4.1 for experiment details and Fig. 2.5 for a map of burial locations.

Table 4.1 Details of mesh bag incubation experiments of peat at Wellington Plain

<table>
<thead>
<tr>
<th>Experiment</th>
<th>Peat type</th>
<th>Collection depth (cm)</th>
<th>Burial depth* (cm)</th>
<th>Blocks / Replicates</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fibric bog peat</td>
<td>5-15</td>
<td>10</td>
<td>10/2</td>
</tr>
<tr>
<td></td>
<td>Hemic bog peat</td>
<td>35-50</td>
<td>40</td>
<td>10/2</td>
</tr>
<tr>
<td></td>
<td>Sapric bog peat</td>
<td>80-85</td>
<td>80</td>
<td>10/2</td>
</tr>
<tr>
<td></td>
<td>Surface dried peat</td>
<td>4-7</td>
<td>5</td>
<td>10/2</td>
</tr>
<tr>
<td></td>
<td>Base dried peat</td>
<td>20-25</td>
<td>20</td>
<td>10/2</td>
</tr>
<tr>
<td>2</td>
<td>Fibric bog peat</td>
<td>5-15</td>
<td>10, 40</td>
<td>5/2</td>
</tr>
<tr>
<td></td>
<td>Hemic bog peat</td>
<td>35-50</td>
<td>10, 40</td>
<td>5/2</td>
</tr>
<tr>
<td></td>
<td>Sapric bog peat</td>
<td>80-85</td>
<td>10, 40</td>
<td>5/2</td>
</tr>
</tbody>
</table>

* bags were buried horizontally

Peat was collected with a spade and a serrated knife from each of three depths in a pit in the bog peat and from each of two depths in a pit in the dried peat (Table 4.1) in April 2004 and stored, sealed, at 4 ºC prior to preparation. The water content (60 ºC, 24 hours) and ash content (550 ºC, 12 hours) were determined for five subsamples of each peat type. The carbon content, nitrogen content and initial chemistry of each peat type was measured, as described in Section 4.2.3. A mass of field-moist peat equivalent to 2 g of oven-dry peat was sewn into a mesh bag (8 x 8 cm) and weighed. These bags were returned to Wellington Plain and reburied in June 2004. The burial locations are shown in Fig. 2.5. Each bag was tied to a bamboo stake with fishing line to facilitate recovery. Four controls for each peat type were
prepared as above, buried and immediately retrieved, to account for mass lost in handling. In June 2005, I retrieved the bags and gently washed them with tap water to remove peat attached to the outside of the bags. Ingrown roots were carefully removed with tweezers before the bags were oven-dried (60 °C, 24 hours) and reweighed. A subsample from each bag was ashed (550 °C, 12 hours), and a composite sample of each peat type was prepared, by bulking all remaining material, for chemical analysis (Section 4.2.3). Results are reported as the change in ash-free dry mass as a proportion of the original ash-free dry mass (%). This accounts for the un-decomposable mineral component.

A potential problem associated with the use of mesh bags to measure the rate of mineralisation of carbon is mesh size: if the holes are large, material falls out, but if they are small, macrofauna are excluded (Limpens and Berendse 2003). The consensus is that bacteria and fungi are the major decomposers of peat (Belyea 1996) and thus I opted for a fine weave mesh of 100 µm, adapting my methodology from Belyea (1996) and Limpens and Berendse (2003).

4.2.2 Surface CO₂ emissions

Emissions of CO₂ from the surface of the bog peat and the surface of the dried peat were measured with chambers. The chambers (basal area 0.66 m²) were buried 2-4 cm into the soil and pegged down, one month before the first measurement was taken, to minimise the impact of soil disturbance. Wire stands in the centre of each chamber supported a soda lime CO₂ trap. Soda lime is a white granular compound, which is a mixture of calcium hydroxide and sodium hydroxide. Soda lime absorbs CO₂, increasing in mass as it does so, thus it is a suitable material for a CO₂ trap. The tight-fitting lids of the chambers were assisted by vacuum grease around the rim, and a brick on the top, to form an airtight seal.

Fifteen chambers were located in each of the bog peat and the dried peat: 12 active chambers and three controls. The control chambers had a Perspex base, so that the internal chamber volume was isolated from the peat below. The location of each chamber is shown in Chapter 2, Fig. 2.5. This equipment was installed in February 2004 and removed after the final measurement, in May 2005.

On 18 occasions, a CO₂ trap was sealed in each chamber for 24 hours, to measure the daily emission of this gas from the surface of the two peat types. The timing of measurements was selected to cover the extremes of temperature and water
content, the two factors anticipated to most affect CO₂ emissions. Temperature and water content were continuously recorded with data loggers in both the bog peat and the dried peat. These data are presented in Chapter 2. In addition, each time CO₂ emissions were measured in the chambers, soil temperature was measured at 10 cm depth with a mercury thermometer and bog peat and dried peat were sampled to determine gravimetric water content. Soda lime (mesh size 4-8, diameter 2.4-4.8 mm) contained in a glass petri dish, was dried at 105 °C for 14-16 hours, cooled in a desiccator and weighed, both before and after residing in a chamber for 24 hours. The CO₂ absorbed during this preparation and en route to the site is accounted for by the control chambers. The methodology followed Keith and Wong (2006). This methodology was limited in temporal resolution and measured CO₂ emissions from both plants and soil. These limitations are considered below.

A comparison of the data from chambers in which CO₂ emissions are measured manually, and automated chambers, found that monthly and annual totals from the two methods were the same (Savage and Davidson 2003). While automated chambers provided better temporal data, the lower cost of manual methods allows a greater number of chambers to be used, which better accounts for spatial variation (Savage and Davidson 2003).

In order to measure only the CO₂ emitted from the soil, and not that emitted by the growing plants, above-ground vegetation is usually removed from chambers. However, clipping the above-ground vegetation in a bog leads to rapid deterioration of the condition of the *Sphagnum* (my observation, and McNeil and Waddington 2003). Thus I left the vegetation intact in all chambers and consequently measured both CO₂ emitted from the peat itself, and CO₂ emitted by the growing plants. This was anticipated to have limited effect on the results, as all chambers contained similar types and amounts of vegetation, aside from the aforementioned lack of *Sphagnum* on the dried peat. To quantify the impact of the vegetation I clipped above-ground biomass from each chamber at the end of the study. *Sphagnum* was separated from the other plant material and both fractions from each chamber were weighed, oven dry (40 °C).

4.2.3 Chemical analyses

All samples for chemical analysis were stored at 4 °C, then oven-dried at 60 °C and ground to less than 0.5 μm with a mortar and pestle.
4.2.3.1 Carbon and nitrogen

Carbon and nitrogen contents were determined in duplicate for the five peat types, both before and after incubation, on a Europa Roboprep carbon and nitrogen analyser.

4.2.3.2 $^{13}$C CP/MAS Nuclear Magnetic Resonance spectroscopy

Solid-state $^{13}$C NMR spectroscopy using a standard cross polarization (CP) pulse sequence (Wilson 1987) was used to characterise the chemical composition of organic carbon in the five peat types from the field incubation, Experiment 1. Each peat type was analysed both before and after incubation in the field for one year. The methodology is described in Chapter 3.

4.2.4 Data analysis

I used ANOVA to identify significant treatment effects and Tukey’s HSD post hoc test to define significant differences between treatments. The first incubation experiment (mesh bags) was analysed with a complete randomised design with five treatments (combinations of peat type and original EOD) and ten replicates of each treatment. In the second mesh bag experiment a complete randomised block design was used with a 3x2 factorial arrangement of the EOD (fibric, hemic, sapric) by depth (near surface and zone of water table fluctuation) treatments. The relationship between mass loss from mesh bags and initial peat chemistry was investigated with scatterplots and regression analysis. Analysis of surface CO$_2$ emission data took the form of a repeated measures analysis to define the influence of peat type, with 12 replicates for each peat type. Multiple regression analysis was used to define the relationship between CO$_2$ emission, and the environmental variables of soil temperature and soil water content. A complete randomised design was used to examine the influence of peat type on live biomass. Normality and homogeneity of variance were investigated with box plots. All data were normally distributed. Where required, transformations (log and squared) were applied to homogenise variances. All analyses were performed with STATISTICA 7.
4.3 Results

4.3.1 Field incubation of mesh bags

There was a significant difference (p<0.001) between the amount of decomposition that occurred in the five peats incubated in situ (Fig. 4.1). Both the chemistry of the decomposing peat material and the environment in which the decomposition occurred were different for each peat type. Decomposition decreased with depth in both the bog peat and the dried peat (Fig. 4.1), although the amount of decomposition measured in fibric bog peat (10 cm) and hemic bog peat (40 cm) did not differ significantly in this experiment. Over one year, the bog peat decomposed more than the dried peat did. The magnitude of proportional mass loss measured in this experiment (18-29 %) is towards the high end of the range of losses measured in studies of *Sphagnum* decomposition in bogs in the northern hemisphere (Clymo 1965, 2-20 %; Lieffers 1988, 15-22 %; Limpens and Berendse 2003, 5-30 %; McNeil and Waddington 2003, 0-30 %).
Peat type and depth both had a significant effect upon the (transformed) amount of decomposition measured in Experiment 2, p<0.001 and p=0.042 respectively (Fig. 4.2). Data were squared to homogenise variances, prior to analysis. The interaction between peat type and depth was not significant. Hemic bog peat lost the most mass, followed by fibric bog peat and sapric bog peat (Fig. 4.2 a). More mass loss occurred in the zone of watertable fluctuation (40 cm) than near the surface (10 cm) (Fig. 4.2 b).
4.3.2 Chemical analyses

Fig. 4.3 Chemistry of peat before and after incubation a) carbon b) nitrogen c) C/N ratio. Results are the average of duplicate measurements.

In the bog peat, both the carbon content and the nitrogen content increased with depth prior to incubation (Fig. 4.3 a, b). The carbon/nitrogen ratio, therefore, initially decreased with depth in the bog peat. After incubation in mesh bags for one year, both the carbon content and the nitrogen content increased and then decreased with depth. The carbon/nitrogen ratio thus still decreased with depth after the incubation (Fig. 4.3 c).

In the dried peat, both carbon content and nitrogen content decreased with depth before and after the incubation, however, the decrease with depth was smaller after the incubation (Fig. 4.3 a, b). The carbon/nitrogen ratio of the dried peat was similar across both depth and time (Fig. 4.3 c). In comparison with the bog peat, the dried peat was low in carbon, high in nitrogen and had a lower carbon/nitrogen ratio (Fig. 4.3).
The spectra of the fibric bog peat, the hemic bog peat and the surface dried peat were dominated by O-alkyl carbon (Fig. 4.4). Alkyl carbon and carbonyl carbon both increased in contribution to the total signal intensity with depth, in both bog peat and dried peat. Aryl carbon was only a minor component (<10%) of all peat spectra (Fig. 4.4). The alkyl:O-alkyl ratio increased with depth in both bog peat and dried peat.
Changes in carbon chemistry after one year’s incubation were small. Significant change (>2%, see Chapter 3, Section 3.2.3) only occurred in the hemic bog peat and the sapric bog peat, in the alkyl, O-alkyl and carbonyl regions, and the O-alkyl and carbonyl regions, respectively (Fig. 4.4). The alkyl:O-alkyl ratio indicated that, after one year’s incubation, the fibric bog peat and the hemic bog peat became more decomposed, however, the sapric bog peat, and both types of dried peat, became less decomposed.

Carbon observability \( (C_{\text{obs}}) \) was low for peat from the base of both profiles (Fig. 4.4). However, additional \(^{13}\)C NMR analyses reported in Chapter 3 suggested that carbon from each spectral region was similarly affected by low observability, and thus the distribution of carbon types remained accurate.
4.3.3 Chambers

Carbon dioxide emitted from the surface of the peat did not vary between peat type (bog peat or dried peat) \((p=0.466)\) but did vary over time \((p<0.001)\) (Fig. 4.5). The data for each peat type were not presented separately because there was no difference between CO\(_2\) emitted from bog peat and CO\(_2\) emitted from dried peat. The lack of a difference between peat types does not support hypothesis 2: emission of CO\(_2\) from peat surfaces is greater from the bog peat than from the dried peat. However, the difference over time may be due to variation in the environmental conditions of temperature and water content, as proposed in hypothesis 3: emission of CO\(_2\) from peat surfaces will be influenced by the environmental conditions associated with the two types of peat. The relationship between CO\(_2\), temperature and water content is presented in Section 4.4.
4.3.4 Chamber biomass

![Graph showing biomass comparison between Bog peat and Dried peat](image)

Fig. 4.6 Average oven-dry (40 °C) biomass from chambers on the bog peat and chambers on the dried peat, collected 27/5/2005, after the final CO₂ measurement. Error bars are ± the standard deviation from 12 replicate chambers.

There was no difference between the (transformed) average biomass of plants other than *Sphagnum* in chambers on the bog peat and chambers on the dried peat (p=0.550) (Fig. 4.6). Data were squared to homogenise variances. However, when *Sphagnum* was included, there was a difference between the (transformed) biomass of chambers on the bog peat and chambers on the dried peat (p<0.001).
4.4 Discussion

4.4.1 Field incubation of mesh bags and chemical analyses

4.4.1.1 Substrate quality

The effect of peat chemistry on decomposition was investigated by using linear regression to determine the existence, and significance, of relationships between the loss of mass of the five different peat types (Fig. 4.1) and their chemistries (Fig. 4.3 and Fig. 4.4). The loss of ash-free dry mass was best predicted by the signal intensity of alkyl carbon. Equation 4.1 described 91 % of the variation in mass loss.

\[
M = -0.39 A + 30.75
\]

Equation 4.1

Where \(M\) = proportional loss of ash-free dry mass of peat
\(A\) = alkyl carbon, 0-45 ppm

The idea that the rate of decomposition decreases with depth is one of the central concepts used to explain peat bog formation (Clymo 1984). It is based on the twin premises that, as depth increases, a) the organic matter available becomes less susceptible to decomposition and b) the conditions become less conducive to decomposition. The organic matter becomes less susceptible to decomposition because substrate quality decreases, i.e. the EOD increases. The conditions become less conducive to decomposition because temperature and oxygen availability decrease. However, few studies have measured decomposition of peat in situ, as most mesh bag studies use surface peat as the decomposition substrate (Lieffers 1988; Limpens and Berendse 2003; McNeil and Waddington 2003). Belyea (1996) reburied peat at the depth of collection and found that, aside from a maximum in the zone of watertable fluctuation, decomposition of in situ peat decreased with depth. However, the EOD of the peat was not measured directly, but equated with ‘source depth’ – the depth that the peat was collected from, based on the understanding that EOD increased with depth. The use of \(^{13}\)C NMR to quantify carbon chemistry yielded a more specific measure of EOD. Equation 4.1 suggests that the rate of decomposition can be predicted from the amount of alkyl carbon initially present in the peat. An increase in alkyl carbon is associated with an increase in the EOD of organic material (Baldock,
While Equation 4.1 was derived from a limited number of data points (five different peat types), this research nonetheless provides evidence that a decrease in the rate of decomposition with depth is directly linked to substrate quality.

4.4.1.2 Environment

The bog peat and the dried peat are two quite different environments for decomposition. The bog peat had less variation in temperature and watertable depth than did the dried peat, and tended to be slightly colder (Chapter 2). Thus, I anticipated that the dried peat would be a more conducive environment for decomposition than would the bog peat. However, more decomposition occurred in the bog peat than in the dried peat (Fig. 4.1), which suggested that the bog peat was the more conducive environment. This result contrasts with the work of Lieffers (1988), who found that decomposition was greater in a drained peatland than that in the adjacent natural site. However, drainage occurred in the year previous to Leiffers’ (1988) study, whereas the dried peat at Wellington Plain was likely drained around 130 years ago (Chapter 6). Thus the difference in physical properties between the two sites in the current study is likely to be much greater than that in Lieffers’ (1988) work. Belyea (1996) suggested that differences in decomposition rates between sites could be due to differences in the suite of invertebrate detritivores, such as protozoans and oribatid mites, present. While the biological characteristics of bog peat and dried peat have not been investigated, it is possible that the wet-adapted fauna of the bog peat may not all survive in the more variable environment of the dried peat.

4.4.1.3 Depth

More decomposition occurred in the zone of watertable fluctuation (40 cm) than in the near-surface (10 cm) in the bog peat (Fig. 4.2). This result supports hypothesis 1: mass loss from mesh bags containing peat will be influenced by the initial EOD of the peat and the depth of burial within peat profiles. Belyea (1996) also observed most mass loss in the zone of water table fluctuation, and suggested that this may be due to the dual requirements of microbes for water and oxygen, or, alternatively, to physical erosion of particles through the holes in the mesh. I used a sufficiently small mesh size (100 μm) that this was not an issue for fibric bog peat or hemic bog peat, but could have affected the results for the well decomposed sapric bog peat. However, as sapric
bog peat yielded the lowest mass loss, it seems that physical erosion of particles out of the mesh bags is not likely to have occurred in this study.

4.4.1.4 Implications for restoration and global warming

Incubation of peat in the field in its original environment (Fig. 4.1) yielded both qualitatively and quantitatively different results from laboratory incubations of the same peat types (Chapter 3). The controlled conditions possible in laboratory incubations allow one to manipulate the conditions that affect decomposition; however, field studies are essential to understand how bogs function and to predict how they might respond to global warming.

I expected that the dried peat, with its more variable temperatures and watertable (Chapter 2), would be an environment of rapid decomposition. The results of this study indicate otherwise, suggesting that the dried peat may be a fairly stable environment, in terms of losing substrate via decomposition. Further, restoration works aimed at rewetting dried peats to improve their suitability as a substrate for wetland plants could actually increase decomposition rates, if the peat becomes only slightly wetter, and not fully saturated. Studies of peatland restoration (Price, Heathwaite et al. 2003) suggested that it could be many decades before drained peatlands regain their function as carbon sinks. Decomposition is only one aspect of the carbon balance of peatlands, and production inputs, and erosion and dissolved organic carbon outputs, have yet to be quantified for bog peats and dried peats in the Australian Alps. Drainage has been found to increase production inputs in Finnish bogs as lower watertables enhances tree growth (Komulainen, Tuittila et al. 1999). Tree incursion into drained bogs is unlikely in the Australian Alps, as bogs, occurring predominantly in subalpine frost hollows, are beyond the climatic limit for tree growth. Global warming, however, could change this situation.

The greater magnitude of decomposition that I measured in the bog peats (Fig. 4.1), combined with their considerably greater depths (Chapter 2), suggest that emissions of CO₂ from the bog peat surface will be higher than emissions from the surface of the dried peat.
4.4.2 Chambers

4.4.2.1 Environmental properties

Carbon dioxide emissions from the peat surface were influenced by the temperature and the water content of the peat (Fig. 4.7). An increase in temperature resulted in an increase in CO$_2$ emissions, except on one occasion. In December, unseasonal snow lowered air and surface temperatures, and hence CO$_2$ emissions, but not soil temperature at 10 cm depth (Fig. 4.7 a), due to the insulating properties of soil. The influence of gravimetric water content on CO$_2$ in Fig. 4.7 b) is not clear. However, stepwise multiple regression yielded a significant relationship between CO$_2$, temperature and water content, which explained 75% of the variation in CO$_2$ (Equation 4.2). The CO$_2$ data were log transformed to homogenise variances.

\[
\ln (\text{CO}_2) = 0.114 \, T + 0.022 \, \theta_g - 0.653 \\
\text{Equation 4.2}
\]

Where $T$ = soil temperature at 10 cm

$\theta_g$ = gravimetric water content at 10 cm

Equation 4.2 was applied to soil temperature and soil water content continuously measured in the bog peat and the dried peat (Chapter 2) to yield a prediction of the annual CO$_2$ emission from the peat surface.
4.4.2.2 Predicted decomposition

Fig. 4.8 Daily CO$_2$ emissions from the surface of bog peat and dried peat, predicted from measured soil temperature and soil water content (Chapter 2) and Equation 4.2.

Predicted daily emissions of CO$_2$ from the bog peat and from the dried peat are similar for most of the year, apart from in winter and early spring (late May to early September) (Fig. 4.8). The increased CO$_2$ emissions predicted for the dried peat are driven by the high temperatures recorded in the dried peat at this time (Chapter 2). A possible explanation for the higher winter temperatures in the dried peat than in the bog peat may be found in the hydrologic properties of the two peat types. The high hydraulic conductivity of the upper layer of the bog peat (Chapter 5) allows water to move rapidly through the upper layer of the peat. The dried peat has low hydraulic conductivity (Chapter 5) and thus water is more likely to move over the surface as surface runoff. Surface runoff may melt snow, exposing the dark surface of the dried peat to the winter sun. The bog peat, in contrast, remains covered by a layer of insulating, radiation-reflecting, snow. Thus, day-time winter sun may have more impact on the temperature of the dried peat than on the temperature of the bog peat. The daily CO$_2$ emissions in Fig. 4.8 were summed to annual totals, weighted to account for the areas covered by bog peat and dried peat in the whole peatland (44 % and 56 % respectively), and presented in Table 4.2. This model of peatland carbon emissions was subsequently run under four possible future climate scenarios for the
An increase in temperature was predicted to result in an increase in CO\textsubscript{2} emissions from peatlands in the Australian Alps (Table 4.2). This finding is in line with predictions of the impact of climate change on carbon emissions from peatlands in the northern hemisphere (Gorham 1991). However, the effect of a change in water inputs to the peatland system is less straightforward to predict. This issue will be considered further in Section 4.2.5.

Table 4.2 Annual CO\textsubscript{2} emissions from peat at Wellington Plain, predicted from Equation 4.2 and measured soil temperature and water content data (Chapter 2), under current environmental conditions and under four possible future climate scenarios of increased temperature and decreased soil water content, from Hennessey \textit{et al.} (2003)

<table>
<thead>
<tr>
<th>Environment condition</th>
<th>Predicted annual CO\textsubscript{2} emissions (g/m\textsuperscript{2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Current</td>
<td>698</td>
</tr>
<tr>
<td>Temperature +0.6</td>
<td>745</td>
</tr>
<tr>
<td>Temperature +1.0</td>
<td>782</td>
</tr>
<tr>
<td>Temperature +2.9</td>
<td>971</td>
</tr>
</tbody>
</table>

I also predicted annual CO\textsubscript{2} emissions from the results from the mesh bag incubation. The peat was incubated in mesh bags at discrete depths, and thus additional data (from Chapter 3) were used to integrate the results over the whole profile. These additional data were bulk density, carbon content, and carbon chemistry of whole peat profiles. The ensuing results were 41 times larger for the bog peat and 11 times larger for the dried peat than the annual totals predicted from the chamber, soil temperature and soil water content (Table 4.3). Possible explanations are explored in 4.2.4 below.

Table 4.3 Annual CO\textsubscript{2} emissions from Wellington Plain peatland, predicted from chamber and soil temperature results (March 2004-February 2005), and from mesh bag results integrated over depth using carbon chemistry, bulk density and carbon content (June 2004-May 2005)

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4.4.2.3 Controls on decomposition

Temperature, soil water content or watertable height, and substrate quality are the main factors affecting peat decomposition, but their relative importance differs depending on local conditions (Chimner and Cooper 2003b). In the bog peat and the dried peat at Wellington Plain, I found a positive relationship both between CO$_2$ and temperature, and between CO$_2$ and water content (Equation 4.2). This positive relationship between CO$_2$ and temperature has been widely reported in the northern hemisphere (Chimner and Cooper 2003b; Tuittila, Vasander et al. 2004; Waddington and Roulet 2000). The positive relationship between CO$_2$ and water content is more unusual. Some research found that CO$_2$ emissions increased and then decreased as peat became drier (Chimner and Cooper 2003b; Tuittila, Vasander et al. 2004), while other studies found that CO$_2$ emissions increased as the watertable fell or soil water content decreased (Koizumi, Kontturi et al. 1999; Komulainen, Tuittila et al. 1999; Tuittila, Komulainen et al. 1999), i.e. a negative relationship between CO$_2$ and water content. The daily CO$_2$ emissions measured in this study were within the range of CO$_2$ emissions from peatlands measured by researchers in the northern hemisphere (Table 4.4).

<table>
<thead>
<tr>
<th>Study</th>
<th>Minimum</th>
<th>Maximum</th>
</tr>
</thead>
<tbody>
<tr>
<td>This study</td>
<td>0.84</td>
<td>1.97</td>
</tr>
<tr>
<td>(Waddington, Rotenberg et al. 2001)</td>
<td>0.023</td>
<td>0.087</td>
</tr>
<tr>
<td>(Hogg, Liefers et al. 1992)</td>
<td>0.44</td>
<td>11.4</td>
</tr>
<tr>
<td>(Buttler, Dinel et al. 1994)</td>
<td>0.98</td>
<td>5.24</td>
</tr>
<tr>
<td>(Chimner and Cooper 2003b)</td>
<td>2.4</td>
<td>14.4</td>
</tr>
</tbody>
</table>

In this study, substrate quality varied greatly between the bog peat and the dried peat and, thus, the effect of substrate quality is best considered by comparison of CO$_2$ emissions from the bog peat with CO$_2$ emissions from the dried peat.

4.4.2.4 Comparison of bog peat and dried peat

I anticipated that more CO$_2$ would be released from the surface of the bog peat than from the surface of the dried peat, based on three other findings from my research. Firstly, the bog peat is deeper than the dried peat (Chapter 2, average peat depth 0.76 m bog peat, 0.26 m dried peat) and has a higher carbon content (Chapter 3), thus
there is more organic matter available for decomposition in the bog peat. Second, the bog peat contains peat of a higher substrate quality (fresher organic material) than does the dried peat (Chapter 3, $^{13}$C NMR results), and fresh organic matter is more readily decomposed by microbes. Finally, in situ decomposition measured with mesh bags indicated that more decomposition occurred in the bog than in the dried peat (this Chapter, Section 4.3.1). However, there was no significant difference between the CO$_2$ emissions measured in chambers on the surface of the bog peat and on the surface of the dried peat (Section 4.3.3).

I speculate that two factors contributed to this unexpected result, occluded and pressurised gases and surface vegetation. Buttler et al. (1994) found that surface CO$_2$ emissions were less than 1 % of the gas concentrations measured at 45-60 cm below the peat surface. They attributed this finding to the presence of occluded and pressurised gases trapped within the peat matrix. Thus decomposition is occurring, but the gases are not being released at the surface. This proposition is supported by the occurrence of gases thousands of years old at depth in peat (Aravena, Warner et al. 1993). Therefore, more decomposition could be occurring in the bog peat than in the dried peat, but not resulting in more CO$_2$ release at the surface, as the gases produced are stored within the peat matrix in the catotelm of the bog peat. Gases could not be similarly stored within the dried peat because the watertable regularly falls to the base of the profile (Chapter 2).

Surface vegetation in the chamber respires, contributing to the measured CO$_2$. I found no significant difference between the mass of non-Sphagnum vegetation in chambers on the dried peat and chambers on the bog peat (Section 4.3.4), so this would not be biasing the results. However, studies have found that new carbon from fine roots and root exudates accounts for half of the measured peat respiration (Komulainen, Tuittila et al. 1999; Moore, Bubier et al. 2002). Thus the contribution from surface vegetation could dilute differences in decomposition of the peat itself. Further, the bog peat also has a layer of Sphagnum moss (Table 2.3). This layer of Sphagnum is important for many reasons, one of which being that it refixes some of the CO$_2$ produced by the peat beneath it (Turetsky and Wieder 1999). Thus, the measured emissions from the bog peat may be an underestimate of the amount of decomposition occurring in the bog. This will not be the case for the dried peat, which lacks a layer of Sphagnum (Table 2.3).
4.4.2.5 Implications for climate change and restoration

The positive correlation between temperature and CO$_2$ emission from peat surfaces that I measured (Equation 4.2) suggests that global warming could increase CO$_2$ emissions from peat soils in the Australian Alps. However, peat accumulation is dependant upon both carbon input and carbon output. Higher summer temperatures are likely to increase plant growth, which could result in net carbon accumulation in peat soils (Waddington and Roulet 2000). Higher winter temperatures may result in more frequent freeze-thaw events, particularly in the marginal alpine environment of the Australian Alps. Freeze-thaw cycles have been found to increase CO$_2$ emissions from peat (Bubier, Crill et al. 2002). The basal age of the peatland at Wellington Plain (Chapter 6) and the stability of the vegetational composition (Elwood 2001) indicate that the peatland has survived previous changes in climate. The rate of change in temperature and accompanying changes in rainfall regime are likely to determine the response of peat soils in the Australian Alps to climate change.

Rewetting is the basis of peatland restoration practices worldwide. Several studies have found that rewetting drained peatlands can decrease CO$_2$ emissions and even result in net carbon accumulation in only a few years (Tuittila, Komulainen et al. 1999; Tuittila, Vasander et al. 2004; Waddington, Warner et al. 2002). While I measured a positive relationship between CO$_2$ emissions and water content in the field (Equation 4.2), the range of water contents was limited. Over a larger range of water contents applied in the laboratory, I found that CO$_2$ emissions increased and then decreased as water content increased (Chapter 3). Further, I measured only carbon output, not carbon inputs. The greater total (Sphagnum and non-Sphagnum) biomass that I measured in chambers on the bog peat (Fig. 4.6) indicates that carbon inputs to the bog peat are greater than carbon inputs to the dried peat. Carbon inputs to bog peat and dried peat ecosystems is an avenue that requires further research. Nonetheless, rewetting facilitates the re-establishment of wetland plants, particularly Sphagnum, and thus restoration will have a positive impact on the net carbon balance of peatlands in the long term.
4.5 Conclusions

The results presented in this Chapter support hypotheses 1 and 3, but do not support hypothesis 2. The initial EOD of the peat and the depth of burial both influenced mass loss from mesh bags. Temperature and water content both influenced CO₂ emissions from peat surfaces. However, CO₂ emissions from the surface of the bog peat were not greater than CO₂ emissions from the surface of the dried peat. While more decomposition occurred within the bog peat than within the dried peat, emissions from the surface did not reflect this, possibly due to the impact of surface vegetation, and pressurised and occluded gases. Further research is required to quantify carbon inputs into these systems, and to provide a definitive answer as to their status as carbon sinks or carbon sources. Increased temperatures are likely to increase carbon emissions from peat soils in the Australian Alps.
Chapter 5. Water dynamics

Summary

The importance of peat soils in the catchment hydrology of the Australian Alps has been long recognised, however, the details of water movement and storage in these soils are not well understood. I measured the water retention and the hydraulic conductivity of profiles of bog peat and dried peat from Wellington Plain peatland, in the Victorian Alps. The water retention properties of the two peat types differed: the bog peat released water very easily, while the dried peat retained more water under all suctions. Hydraulic conductivity differed between two groups of peats: surface, fibric and hemic bog peat and surface dried peat all had rapid hydraulic conductivity, while hydraulic conductivity was several orders of magnitude slower in sapric bog peat and mid and base dried peat. From these results, I developed a conceptual model of the hydrology of bog peat and dried peat soils. This model can be applied to peat soils throughout the Australian Alps, to inform the management and restoration of these ecosystems.
5.1 Introduction

Peat soils exist because of water. The anaerobic conditions caused by waterlogging slow decomposition such that plant production is greater than organic matter decay, and an organic soil accumulates. Genesis aside, the relationship between water and an organic soil differs from the relationship between water and a mineral soil. In addition to free water, up to three kinds of bound water have been detected in peat (Culligan and Sinfield 2001; Holmgren, Wikander et al. 1990; Mc Brierty, Wardell et al. 1996). Consequently, it is difficult to drain peat (Armstrong and Castle 1999), and drainage results in irreversible physical change in the peat (Charman 2002).

Bog peats have long been considered important in the catchment hydrology of the Australian Alps (Cambell 1983; Costin 1952; Costin 1954; Good 1992). However, intentional and unintentional drainage has caused widespread contraction of bogs, and dried peat soils are extensive throughout the Australian Alps (Costin, Wimbush et al. 1959).

The structural differences between bog peat and dried peat might be expected to alter catchment hydrology. Bog peats have an open, porous, layered structure and are permanently saturated at depth, while dried peats have a fine crumb structure and are not permanently saturated (Chapter 2, and Costin 1954). Dried peats are shallower and have a higher bulk density than do bog peats (Grover 2001). These structural differences are likely to affect water movement through the soil. Consequently, change on a large scale from bog peats to dried peats could affect the hydrological functioning of Alps catchments, including timing and yield of outflow.

Restoration works aimed at rewetting damaged areas of bogs and dried peats have been stimulated following extensive bushfires in the Alps in 1998 and 2003 (Hope, Whinam et al. 2005; Wahren and Papst 1999), and an end to cattle grazing in the Victorian Alpine National Park in 2005. Extensive research into the restoration of peatlands drained for mining and forestry in Canada and Finland all point towards hydrology as the key factor (Komulainen, Tuittila et al. 1999; McNeil and Waddington 2003; Price and Whitehead 2004; Tuittila, Komulainen et al. 1999; Van Seters and Price 2002; Waddington, Rotenberg et al. 2001; Waddington, Warner et al. 2002). A better understanding of the hydrological functioning of bog peats and dried peats in the Australian Alps could thus aid local peatland restoration.
Studies of water movement through peat in the Australian Alps have yet to result in integrated models of bog peat hydrology and, particularly, dried peat hydrology. Wimbush (1970) used the water-balance approach to describe the input and output variables of a *Sphagnum* bog in Kosciuszko National Park. He found that bogs increase streamflow in winter, reduce streamflow in summer, and have more value in maintaining water quality than in regulating streamflow (Wimbush 1970). This seminal study (Wimbush 1970) clarified the role of bogs in catchment hydrology; however, the study did not address how water moves through peat within the bog, nor did it investigate dried peat hydrology. Two recent studies (Grover 2001; Growcock 1999) that attempted to compare water movement through bog peat and through dried peat were inconclusive, due to differences both between bog peat and dried peat, and between different layers within the bog peat. No single field technique is suitable for measuring a) the slow saturated flow in deep bog peat, b) the rapid saturated and unsaturated flow in surface bog peat, and c) the slow saturated and unsaturated flow in the dried peat. Yet to improve understanding of peat hydrology, we need to compare how water moves, both within, and between, whole peat profiles.

In this chapter I aimed to describe water movement in profiles of bog peat and dried peat. Laboratory measurements of water retention and hydraulic conductivity shed light on how water moves through these two different soils. These data have been used to develop basic models of the hydrology of bog peat and of dried peat, which can be used to inform practical restoration works, and from which further research can proceed.
5.2 Methods

5.2.1 Sample collection

Samples were collected from soil pits in three profiles of bog peat and six profiles of dried peat on the Wellington Plain peatland. The location of each profile was chosen, after an extensive survey of the entire peatland, to be representative of bog peat and dried peat. Intact peat cores were collected in brass rings (diameter 7.3 cm, height 5.7 cm) compatible with the apparatus used to measure hydraulic conductivity and water retention. Peat structure was minimally disturbed during sampling, as I carefully worked the ring into the peat by hand, with the aid of a serrated knife. Adjacent peat was cut away, and the sample was removed from the base of the soil pit. The core was trimmed, two end caps were fitted, and water from an adjacent stream was added, to buffer the peat structure from jolting during transport to the laboratory. Samples were stored at 4 °C until required for analysis. Sampling followed the scheme in Table 5.1. The dried peat was sampled at the surface, mid profile and at the base of the profile.

The profiles of bog peat were sampled at the surface (defined as the closed surface of the moss capitula, after Ingram (1978)) and in each of the peat types recognised in the Australian Soil Classification (McDonald, Isbell et al. 1990), fibric hemic and sapric.

Table 5.1 Sampling scheme for hydraulic conductivity and water retention

<table>
<thead>
<tr>
<th>Peat type</th>
<th>Profiles (#)</th>
<th>Defining layer</th>
<th>Depths (cm)</th>
<th>Replicates</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bog peat</td>
<td>3</td>
<td>Surface</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>Bog peat</td>
<td>3</td>
<td>Fibric</td>
<td>15, 20, 24</td>
<td>4</td>
</tr>
<tr>
<td>Bog peat</td>
<td>3</td>
<td>Hemic</td>
<td>38, 48, 50</td>
<td>4</td>
</tr>
<tr>
<td>Bog peat</td>
<td>3</td>
<td>Sapric</td>
<td>85, 90, 95</td>
<td>4</td>
</tr>
<tr>
<td>Dried peat</td>
<td>6</td>
<td>Surface</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>Dried peat</td>
<td>5*</td>
<td>Mid profile</td>
<td>8, 10, 14</td>
<td>4</td>
</tr>
<tr>
<td>Dried peat</td>
<td>6</td>
<td>Base</td>
<td>10, 15, 17, 20</td>
<td>4</td>
</tr>
</tbody>
</table>

* at one location, the dried peat could only be sampled at two depths before the underlying substratum was reached

5.2.2 Water retention, bulk density and specific yield

The ability of the peat to retain water under suction was measured in order to better understand how water drains from peat as the watertable falls. Thus this study focused on suctions at the low end of the scale of suctions normally applied in the study of the water retention properties of soil. Water retention was measured on samples from all three profiles of bog peat, and from four of the six profiles of dried peat, totaling
92 samples, after the method in Topp et al. (1993). Suctions of 0, 2, 3, 4, 5, 6, 8 and 10 kPa were applied to the peat cores with presoaked ceramic pressure plates (10 kPa) above hanging columns of water (of 0, 20, 30, 40, 50, 60, 80 and 100 cm length, respectively). Cores were weighed after equilibration at each suction, and after 10 kPa, cores were oven-dried (105 °C, 24 hours) and weighed to determine bulk density. Water retention results are presented as volumetric water contents, \( \theta_v \) (cm\(^3\)/cm\(^3\)).

At saturation, the volumetric water content is theoretically equal to the total porosity of the sample. However, because the core is not infinitely thin, a suction is applied over the height of the core. Water was observed to drain from the saturated core before it could be weighed, in samples of bog surface peat, bog fibric peat, bog hemic peat and dried surface peat. Consequently, total porosity for these samples was calculated from bulk density and particle density according to Equation 5.1. For bog sapric peat, dried mid peat and dried base peat, measured values of total porosity were used.

\[
TP = 1 - \left( \frac{\rho_b}{\rho_p} \right) 
\]

Where \( TP = \) total porosity
\( \rho_b = \) bulk density
\( \rho_p = \) particle density

Particle density was measured, in quadruplicate, on a sample of peat from each layer of each peat type, following the pycnometer method in Flint and Flint (2002).

The application of greater suction results in long equilibration times for large cores. Thus, a sub-core (diameter 2.7 cm, height 1 cm) was carefully removed with a serrated knife from each core. These smaller cores were placed on presoaked ceramic pressure plates (1500 kPa) in sealed pressure vessels and subjected to consecutive suctions of 500 kPa, 1000 kPa, and 1500 kPa. Cores were weighed after equilibration at each suction, and, after 1500 kPa, cores were oven-dried (105 °C, 24 hours) and weighed to determine bulk density. Water retention results are presented as volumetric water contents \( \theta_v \) (cm\(^3\)/cm\(^3\)).

Specific yield of water was calculated for each core. Specific yield has been defined for peat soils as the change in volumetric water content between saturation
and 10 kPa, and is a property, similar to field capacity for mineral soils, used to compare the water retention of different peats (Ingram 1983). Large pores (defined as pores which drain at less than 10 kPa) as a proportion of total porosity, were also calculated for each core.

5.2.3 Hydraulic conductivity

Hydraulic conductivity is a measure of the movement of water through soil. The concept of hydraulic conductivity is based on Darcy’s Law, which states that fluid moving through a porous medium will reach a steady state, at which time outflow is proportional to the rate of water movement. There has been some debate as to the applicability of Darcy’s Law, and hence hydraulic conductivity, to peat (Dai and Sparling 1973; George 1975; Hemmond and Goldman 1985; Rycroft, Williams et al. 1975a). The presence of gas bubbles in catotelm peat may explain observations of non-Darcian behaviour (Beckwith and Baird 2001; Reynolds, Ann Brown et al. 1992). However, as long as small pressure gradients (cm rather than dm) are applied, hydraulic conductivity remains a useful measure of water movement through peat (Armstrong and Castle 1999). Preliminary testing found that no single method of measuring hydraulic conductivity in the field could accommodate the diverse conditions of whole profiles of bog peat and dried peat (this study, data not shown, and Grover 2001). Thus, in order to compare water movement through different types of peat, I chose a laboratory-based method, the mini-disc permeameter, and followed the method in Cook et al. (1993). Hydraulic conductivity was measured on each core collected (Table 5.1), without pretreatment. The mini-disc permeameter applied a suction of 0.1 kPa to the top of the soil core. Beneath the core, a saturated sand stand applied the same suction (0.1 kPa) to the base of the core, and a layer of sand over a piece of muslin cloth ensured good contact between the permeameter and the top of the core. Timed measurements of water height allowed calculation of saturated hydraulic conductivity (k) from Equations 5.2 and 5.3:

\[ k = \frac{Q. (h/\gamma)}{A.g.t} \]  \hspace{1cm} \text{Equation 5.2}

\[ Q = \frac{V}{A.g.t} \]  \hspace{1cm} \text{Equation 5.3}
Where \( h \) = height of core (m)
\( \psi \) = water potential (m)
\( V \) = volume of water passing through core per time \( t \) (m\(^3\))
\( A \) = area of core (m\(^2\))
\( t \) = time (s)

5.2.4 Carbon chemistry

Solid-state \(^{13}\)C NMR spectroscopy was used to characterise the chemical composition of organic carbon in a core from each depth from one profile of bog peat and two profiles of dried peat. The method is described in Chapter 3. Instrument malfunction prevented the collection of spectrum from further peat profiles.

5.2.5 Data analysis

The results from the four replicate cores at each sampling location were averaged prior to analysis. Sampling depths varied at each location, due to differences in morphology and chemistry. This difference in the depths at which the peat was sampled at each location precluded the use of a factorial analysis. Therefore, one way ANOVA was used, to identify differences between different layers in the two peat types. Where significant differences were identified by ANOVA, Tukey’s HSD was used to identify which layers differed from one another, at \( \alpha = 0.05 \). Homogeneity of variances was investigated with plots of residuals versus predicted values, and Levene’s test. Data that displayed unequal variances were log transformed.

Linear regression analyses were completed to identify the influence of bulk density, total porosity, specific yield and proportion of large pores, on hydraulic conductivity. A homogeneity of slopes analysis was used to determine whether a single relationship existed across peat types, or whether a unique relationship existed for each peat type. Linear regression was then used to define the appropriate relationships. A correlation matrix was used to gain an indication of the potential role of peat chemistry, as defined by solid-state \(^{13}\)C NMR, on the peat’s hydrologic properties.
5.3 Results

5.3.1 Water retention and specific yield

Volumetric water content in the bog peat at saturation was close to one, for peat from all depths (Fig. 5.1 a, b, c). Bog peat from each depth lost most water between saturation and the first suction, 2 kPa, as Boelter (1964) also found. As suction increased, the relationship between samples within a profile changed (i.e. sapric peat had the lowest volumetric water content at saturation but the highest volumetric water content at 1500 kPa).

In the dried peat, the volumetric water content at saturation was around 0.7 (Fig. 5.1 d, e, f, g). As suction was increased, the volumetric water content of the surface peat changed more than did the volumetric water content of peat below the surface. Thus, while the surface peat was initially the wettest, by 1500 kPa, it was the driest sample in each profile (Fig. 5.1 d, e, f, g).

Comparison of the water retention curves from profiles of bog peat and dried peat showed that the bog peat had a greater change in volumetric water content than the dried peat, over the applied range of suctions.
Fig. 5.1 Water retention curves (volumetric water content versus log (suction) from 0 to 1500 kPa suction) for each of three profiles of bog peat (a-c) and each of four profiles of dried peat (d-g). Error bars are ± the standard deviation from 4 replicate cores. The depth that each sample was collected from is indicated in the individual graph keys. The bog peat was sampled at the surface and in the fibric, hemic and sapric layers, and the dried peat was sampled at the surface and one or two subsequent depths, see Table 5.1 for details.
ANOVA showed a difference between peat layers for volumetric water content at saturation and at 100 cm suction, for specific yield and for bulk density (p<0.001 for each property) (Fig. 5.2). Across all four properties, peat from the upper three layers of the bog was always different from all layers of the dried peat. However, the sapric bog peat did not differ from the surface dried peat in any of the four properties, nor did the sapric bog peat differ from the mid dried peat in volumetric water content at saturation or at 100 cm (Fig. 5.2). Boelter (1975) reported comparable specific yields of 0.86 to 0.48 for undecomposed *Sphagnum* peats, and 0.08 for a dried peat, and also found that bulk density increased with depth.

![Fig. 5.2 Comparison of the properties of the seven different peat layers: surface bog peat, fibric bog peat, hemic bog peat, sapric bog peat, surface dried peat, mid dried peat and base dried peat.](image)

a) volumetric water content at saturation (0 cm), b) volumetric water content at 100 cm suction, c) specific yield and d) bulk density. Columns labelled with different letters are significantly different from one another (Tukey’s HSD). Error bars are ± the standard deviation from 4 replicate cores.
5.3.2 Hydraulic conductivity

Fig. 5.3 Comparison of the hydraulic conductivity (k) of the seven different peat layers: surface bog peat, fibric bog peat, hemic bog peat, sapric bog peat, surface dried peat, mid dried peat and base dried peat. Columns labelled with different letters are significantly different from one another (Tukey’s HSD). Error bars are ± the standard deviation from 4 replicate cores. Note that hydraulic conductivity is on a log scale.

ANOVA showed a difference between peat layers for (transformed) hydraulic conductivity (p<0.001) (Fig. 5.3). Data were log transformed to homogenise variances. Post hoc tests divided the seven peat layers into two distinct groups. The first group contained surface bog peat, fibric bog peat, hemic bog peat and surface dried peat. The second group contained sapric bog peat, mid dried peat and base dried peat (Fig. 5.3). The results for the bog peat concur with Ingram’s (1978) definition of the acrotelm - the upper layer of a bog with high hydraulic conductivity - and the catotelm - the lower layer of the bog with negligibly small hydraulic conductivity, and a later review, which suggested that, on average, there is a difference of four orders of magnitude between the hydraulic conductivities of the acrotelm and the catotelm (Ingram 1983).
5.3.3 Relationships between hydrologic properties and physical properties

Regression yielded significant relationships between (log transformed) hydraulic conductivity and the four physical properties of bulk density, total porosity, specific yield and proportion of large pores (Fig. 5.4). For bulk density ($\rho_b$), an analysis of homogeneity of slopes indicated that a distinct relationship existed for each peat type (Equations 5.4 and 5.5).

Bog peat  \[ \ln(k) = -21.10\rho_b - 7.68 \quad r^2 = 0.52 \quad \text{Equation 5.4} \]

Dried peat  \[ \ln(k) = -4.36\rho_b - 8.67 \quad r^2 = 0.44 \quad \text{Equation 5.5} \]
For total porosity (TP), specific yield (Y) and proportion of large pores (LP), analysis of homogeneity of slopes indicated that only one relationship existed across both peat types (Equations 5.6, 5.7 and 5.8)

\[
\ln(k) = 8.46TP - 16.76 \quad r^2 = 0.51 \quad \text{Equation 5.6}
\]

\[
\ln(k) = 5.55Y - 12.38 \quad r^2 = 0.53 \quad \text{Equation 5.7}
\]

\[
\ln(k) = 5.49LP - 12.64 \quad r^2 = 0.49 \quad \text{Equation 5.8}
\]

Thus regression indicated that approximately half of the variation in hydraulic conductivity can be explained by the physical properties of the peat.

5.3.4 Relationships between hydrologic properties and chemical properties

Significant correlations existed between hydraulic conductivity and chemistry, and between specific yield and chemistry (Table 5.2). Alkyl carbon explained the most variation in hydraulic conductivity, while O-alkyl carbon explained the most variation in specific yield. However, these results were based upon the chemistries of only one profile of bog peat and two profiles of dried peat, and thus further data are required to confirm these relationships.

Table 5.2 Partial correlation coefficients (r) for the relationships between hydraulic conductivity (log transformed, ln k), specific yield (Y) and chemical properties. Significant relationships are shown in bold

<table>
<thead>
<tr>
<th>Chemical property</th>
<th>ln k</th>
<th>Y</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkyl:O-alkyl ratio</td>
<td>-0.79</td>
<td>-0.95</td>
</tr>
<tr>
<td>Alkyl C</td>
<td>-0.88</td>
<td>-0.94</td>
</tr>
<tr>
<td>O-alkyl C</td>
<td>0.77</td>
<td>0.96</td>
</tr>
<tr>
<td>Aryl C</td>
<td>-0.70</td>
<td>-0.97</td>
</tr>
<tr>
<td>Carbonyl C</td>
<td>-0.61</td>
<td>-0.94</td>
</tr>
<tr>
<td>C</td>
<td>0.61</td>
<td>0.89</td>
</tr>
<tr>
<td>N</td>
<td>-0.22</td>
<td>0.19</td>
</tr>
<tr>
<td>C/N ratio</td>
<td>0.77</td>
<td>0.93</td>
</tr>
</tbody>
</table>
5.4 Discussion

Peat is composed primarily of organic matter and thus its physical structure, and hence its ability to hold and store water, are largely determined by how decomposed that organic material is. Thus porosity is not influenced by the grain size of the mineral component, but rather by the botanical composition and extent of decomposition of the organic component of the soil. The first Section of the Discussion addresses bog peat, the second Section compares bog peat and dried peat, and the third Section develops hydrologic models for each peat type.

5.4.1 The effect of decomposition on pore size distribution and binding of water

Undecomposed *Sphagnum* peat has an open structure with many large pores between plant parts (Ingram 1983). Water can move rapidly through these large pores, and this is reflected in the high hydraulic conductivity of the surface peat and fibric peat from the bog (Fig. 5.4). In the intact *Sphagnum* plant material, water is held in both a) ‘capillary pores’ - between the stem and downward hanging branches - and b) intracellular pores - large water-storing hyaline cells (Ingram 1983). The large pores between plant parts are too large to store water (Ingram 1983), and thus surface bog peat and fibric bog peat lost most of their water between saturation and the first suction, 2 kPa (Fig. 5.1 a, b, c). There are few very small pores in undecomposed *Sphagnum* peat, which explains the small decrease in volumetric water content at high suctions shown by the surface and fibric peats in comparison with the hemic and sapric peats (Fig 5.1). As the peat becomes more decomposed, the relationship between solid plant material and liquid water becomes more complex, as water is bound by physical and chemical forces to the organic matter. The large pores between plant parts disappear due to compression by the ever-increasing mass of overlying peat. Decomposition of the organic matter can result in organic compounds of high molecular weight. Compounds of high molecular weight actively adsorb water to their surfaces, with hydrogen bonds and Van der Waals forces (Volarovich and Churaev 1968). Thus, while sapric bog peat has a high volumetric water content at saturation (0.75 to 1, Fig. 5.1 a, b, c), it has low hydraulic conductivity \(3 \times 10^{-6} \text{ m/s, Fig. 5.3}\). The water present in the sapric bog peat moves only slowly and cannot easily drain away.
Between the large pores between plant parts that transmit but cannot store water, and the decomposition products with high molecular weight that bind water to their surfaces, there are a range of structures in peat that both store and transmit water. Peat in all stages of decomposition contains water held within cells, on surfaces and in pores (Volarovich and Churaev 1968). Much of this water is very loosely held, which is reflected in the fact that all peat samples experienced the greatest decrease in volumetric water content between 0 and 2 kPa (Fig 5.1 a, b, c); subsequent increases in suction all resulted in smaller decreases in volumetric water content.

5.4.2 The effects of irreversible changes upon drying on hydrologic properties

The structure of peat changes irreversibly when it dries. Total pore volume is decreased, and the pore size distribution is altered, by a combination of shrinkage and compression forces, such that there are more small pores and fewer large pores. Shrinkage occurs above the water table, caused by high capillary pressures near the surface, and compression occurs below the water table, caused by changes in effective stress due to fluctuations in pore water pressure (Kennedy 2004). Therefore, after drying, peat will have lower total porosity and fewer large pores. This is reflected in my results for dried peat. In comparison with bog peat (the upper layer), the dried peat had lower total porosity, lower specific yield and higher bulk density (Fig. 5.2). Dried peat retained more water under suction (Fig 5.1) and had slower hydraulic conductivity (Fig. 5.3) than did bog peat. This change in hydrologic properties has implications for plant growth, and thus for attempts to revegetate drained peatlands and regenerate intact bogs from dried peat.

Dried peat is a very different medium, hydrologically speaking, for plants to establish themselves in, compared with bog peat. Infiltration, which I did not measure, is positively related to hydraulic conductivity. Consequently, it is reasonable to infer from the hydraulic conductivity results (Fig. 5.3), that infiltration of water into the dried peat will be slower than infiltration into the bog peat. The low hydraulic conductivity of the surface of dried peat (Fig. 5.3), in combination with low infiltration, is likely to lead to frequent overland flow (rarely seen in intact bogs (Ingram 1983)) and thus erosion. Erosive forces are not typically encountered by bog plants, as the acrotelm of an intact bog is an erosion-reducing structure (Ingram 1983). In addition to physical stresses, water availability may also be a problem. At saturation, the dried peat had lower volumetric water contents than did the bog peat.
(Fig 5.1). However, under all suctions, the dried peat retained more water than the bog peat, and the surface dried peat had a significantly smaller specific yield than the surface bog peat (Fig. 5.1 and Fig. 5.2). These results suggest that, in the dried peat, plants may have to exert greater suction to acquire the water they need, than they would in the bog peat. *Sphagnum*, in particular, has no vascular system for the internal transport of water (Ingram 1983), and thus requires a shallow and constant watertable. Finally, the higher bulk density of dried peat (Fig. 5.2 d) is likely to hinder root growth and, after rainfall, aeration.

5.4.3 Conceptual model of peat hydrology and implications for catchment hydrology

I combined the results from this study to develop a simple conceptual model of peat hydrology. This model (Fig. 5.5) can be applied to peatlands throughout the Australian Alps, and may assist land managers in understanding the diverse properties and functions of peat soils. The model demonstrates that a change from bog peat to dried peat can alter the hydrology of the catchment, via the three mechanisms of erosion, temporary water storage, and water filtration and aeration.

5.4.3.1 Erosion

Rapid water movement through the upper layer of bog peat results in predominantly subsurface flow. The slow water movement through the dried peat favours overland flow. This change from subsurface flow to overland flow is likely to increase erosion. The erosion of particulate peat into streams has a number of adverse effects. Increased concentrations of organic matter in streams will increase microbial activity, which may decrease the oxygen content of the water. Carbon will be released to the atmosphere as CO₂, contributing to the acceleration of global warming. Particulate matter not consumed by microbes may end up in dams, decreasing their useful lifespan. Dried peat may be eroded down to the underlying substratum. The complete removal of peat results in loss of habitat for plant and animal species, and leaves a medium that is unconducive to plant growth.

5.4.3.2 Temporary water storage

The upper layers of the bog peat have high total porosities and high specific yields (Fig. 5.2), and thus provide temporary short-term storage (hours) of rainfall from storms. Wimbush (1970) found that bogs delayed the flow of rainfall into streams by several hours. Dried peat has high total porosity at the surface, but not in the lower
layers, and all layers of dried peat have low specific yields (Fig. 5.2). Thus dried peat has less capacity to provide temporary short term storage. This decrease in the available volume of temporary short term storage may increase the severity of floods. However, the greater water retention of dried peat under suction (Fig. 5.1) may increase the duration of temporary short term storage.

5.4.3.3 Water filtration and aeration

It is groundwater, which passes through bogs, rather than water released from storage in the bog, that maintains summer stream flow. The stability of the watertable in bog flat peat (Chapter 2) demonstrated that water stored in the catotelm is not released to streams. However, while passing through the surface layer of bog peat, the water is thought to be filtered (Wimbush 1970) and aerated (Legoe 1981). This function cannot be provided by the surface of the dried peat, as the slow water movement through this peat favours overland flow.

Fig. 5.5. Conceptual model of the hydrology of bog peat and dried peat. The rate of water movement is hydraulic conductivity and the volume of water released is specific yield.
5.5 Conclusions

Dried peat and bog peat are hydrologically quite different soils. Bog peat has two distinct layers: a) an upper layer (surface, fibric and hemic peats) with high total porosity, high specific yield and low bulk density, and consequently high hydraulic conductivity; and b) a lower layer (sapric peat) with lower total porosity, higher bulk density and disproportionately slower hydraulic conductivity. While specific yield is also high in the lower layer of bog peat, under natural conditions this water is not released, and thus the lower layer of bog peat stores large amounts of water in the medium to long term. In dried peat, the upper layer has several properties in common with the lower layer of the bog peat: total porosity, volumetric water content at 100 cm suction, specific yield and bulk density. The hydraulic conductivity of the upper layer of the dried peat, however, is not different from that of the upper layer of bog peat. The lower layer of the dried peat has the lowest total porosity and specific yield, the highest bulk density, and an hydraulic conductivity not different from that of the lower layer of bog peat. Over the whole profile, the bog peat has a larger capacity to store water over both the short and long terms. Consequently, a change from bog peat to dried peat will alter both the growing environment for plants and the water regime of the catchment.
Chapter 6. Accumulation and attrition of peat soils in the Australian Alps

Summary

Bog peat soils have been accumulating at Wellington Plain peatland for the last 3300 years. Now, dried peat soils are common adjacent to bog peats. The $^{14}$C basal age of dried peat is not different from the $^{14}$C basal age of bog peat, which supports the theory that dried peat formed from bog peat. $^{210}$Pb dating links the timing of this change with the introduction of livestock to Wellington Plain. Physical loss of material appears to have been the dominant process removing material as bog peats drained to form dried peats, as indicated by the mass balances of carbon and lead. This research has implications for the post-fire and post-grazing restoration of bogs in Victoria’s Alpine National Park, and the contribution of peat soils to Australia’s carbon emissions.
6.1 Introduction

Peat soils form where decomposition is hindered, often by a combination of cold and wet conditions, such that production of organic matter outweighs decomposition. Such conditions are rare in the hot, dry continent of Australia. Consequently, peat barely features on a map of Australian soils, though small areas are noted to occur in the Alps and along the humid east coast (McKenzie, Jacquier et al. 2004). While lowland peats have largely been drained for agricultural use, much of the Alps is within National Parks. Small areas of peat are locally common in alpine and subalpine catchments, as peat-forming bog vegetation is adapted to the wet conditions beneath springs and seepage zones. Shallow, dried peat soils are also extensive, sometimes adjacent to bogs and elsewhere surrounded by mineral soils.

These soils were first described by Costin (1954), who proposed that dried peat formed from a parent material of bog peat, drained either by past climatic warming, or by recent trampling by introduced livestock. Livestock were grazed over summer in the Alps from the mid 1850s (Cabena 1980). Dried peats formed recently are thought to occur adjacent to bog peats, while dried peats formed by past climatic warming are thought to occur independently of bog peats, surrounded by mineral soils (Costin 1954). This theory of the origin of dried peat is based on field observations, environmental history research and an understanding, based primarily upon European research, of how bogs function (Costin 1954; Costin, Wimbush et al. 1959). Alternatively, dried peat adjacent to bog peat could be the result of two periods of bog formation (David Ashton, pers. comm. 2003). Under this scenario, dried peat is the remnant of an earlier period of bog formation, and the entire bog drained due to climatic warming. Subsequent wetter conditions initiated a second period of bog formation, on top of the dried peat (David Ashton, pers. comm. 2003).

Peat soils in the Australian Alps have received renewed attention following the extensive fires of 1998 and 2003, and the cessation of cattle grazing in the Victorian Alpine National Park in 2005. Peatland restoration works, involving weirs and planting/transplanting, are underway in Victoria, New South Wales and the Australian Capital Territory (Hope, Whinam et al. 2005; Wahren and Papst 1999). Any attempt to restore an ecosystem ought to be based on a sound knowledge of the original state of that ecosystem. This research investigates the origin, accumulation and attrition of peat soils on Wellington Plain in the Victorian Alps.
I aimed to investigate the rate of peat formation, whether or not bog peat is the parent material of dried peat, and how and when dried peat formed. I applied techniques of isotopic dating and mass balances of carbon and lead to investigate these questions.
6.2 Methods

6.2.1 Sample collection

I surveyed Wellington Plain peatland extensively to choose representative locations of bog peat and dried peat to collect cores for analysis. Continuous profiles of peat, from the surface to the underlying mineral material, were collected; four profiles of bog peat and six profiles of dried peat. Profiles of bog peat were collected in two sections. PVC pipe (8.5 cm diameter) was carefully inserted into the surface peat, to minimise compaction, and a Russian D-section corer (3.5 cm diameter) was used to collect cores from the deeper, less fibrous peat below 20 cm. The dried peat profiles were sampled with a hemispherical peat corer (2.8 cm diameter). All samples were collected in the summer of 2003/2004, immediately returned to the laboratory and frozen until required for analysis. Frozen cores were sawn into slices and freeze-dried or oven-dried at 60 °C.

6.2.2 $^{14}$C dating

AMS radiocarbon dating was carried out at ANSTO, Sydney. Ten profiles of peat were selected for radiocarbon dating, with the surface and basal sections dated. Of these, the four bog peat profiles were selected for high resolution dating through the core. All new plant material growing through the dried peat was carefully removed prior to grinding. An acid-alkali-acid pretreatment removed humic and fulvic acids, leaving the fibrous fraction. The samples underwent combustion at 900 °C in sealed evacuated silica tubes in the presence of excess copper oxide, copper wire and silver wire. The resulting carbon dioxide was purified, then reduced to graphite by heating overnight to 900 °C with excess hydrogen in the presence of an iron catalyst (Hua, Jacobsen et al. 2001). The resulting graphite/iron mix was then measured at the ANTARES AMS facility (Fink, Hotchkis et al. 2004). The $^{14}$C/$^{13}$C isotopic ratio was measured relative to the internationally accepted HOxI standard material (Stuiver 1983). Corrections were then applied for the preparation and spectrometer background and for the isotopic fractionation. Conventional radiocarbon ages were calculated from the corrected ratios. I used OxCal (Bronk Ramsey 1995; Bronk Ramsey 2001) to transform the radiocarbon age into a probability distribution of calendar ages, and assigned a calendar age based on this probability distribution, with the dates of adjacent samples in mind. This is the common practice for developing peat core
chronologies, and while it has limitations (see Blaauw and Christen 2005), it yields sufficient precision for this study. Results are presented as years BP (before present).

6.2.3 $^{210}$Pb dating

$^{210}$Pb dating of peat is an established technique (Appleby, Shotyk et al. 1997; Espi, Boutron et al. 1997; Holynska, Ostachowicz et al. 1998; Vile, Kelman Weider et al. 1999), which I carried out at ANSTO, Sydney. One profile each of bog peat and dried peat was selected for $^{210}$Pb dating. The whole of the dried peat core, and the top 20 cm of the bog peat core, were divided into 1 cm slices. Low sample weight required some samples to be combined (i.e. more than 1 cm of peat was analysed in one sample). The analysis was completed in two batches. The excess $^{210}$Pb activities from the first batch indicated that, in the bog peat, background levels of excess $^{210}$Pb activity had not been reached by 20 cm depth. Thus I included samples down to 50 cm depth, which were each composed of greater than 1 cm of peat, in the second batch of analysis.

Excess $^{210}$Pb activity was measured as total $^{210}$Pb activity (measured via the granddaughter isotope $^{210}$Po) minus supported $^{210}$Pb activity (measured via $^{226}$Ra). Ground samples of 0.5 to 1.5 g were spiked with $^{209}$Po and $^{133}$Ba yield tracers and leached with hot concentrated acids to release $^{210}$Po and $^{226}$Ra. $^{210}$Po was auto plated onto Ag disks after reduction of Fe$^{3+}$ with ascorbic acid. $^{226}$Ra was co-precipitated with BaSO$_4$ on to a filter source. The activities of $^{209}$Po, $^{210}$Po and $^{226}$Ra were counted with high resolution alpha spectroscopy at 4.882, 5.305 and 4.785 MeV, respectively. $^{133}$Ba was measured on a gamma ray detector at the 356 keV peak. The analyses followed ANSTO’s standard methodology (Seen, Townsend et al. 2004).

$^{210}$Pb dating is usually applied to stratified sediments. Radioactive $^{210}$Pb is deposited, from the atmosphere, on the surface and decays in situ. A continual build up of sediment results in an exponential decline with depth in the activity of excess $^{210}$Pb in the undisturbed sediment profile. Measurements of the activity of excess $^{210}$Pb with depth thus enables the creation of a model relating depth to age (Oldfield and Appleby 1984). This standard application of $^{210}$Pb dating was used for the bog peat profile. My application of $^{210}$Pb dating to the dried peat, a disturbed sediment profile, is, to my knowledge, a novel use of this technique. If dried peat formation had been initiated by livestock, it would have occurred between the 1850s, when livestock were first introduced to the area (Cabena 1980), and the 1950s, when extensive dried peats were first recorded (Costin 1952). At the current peat surface, excess $^{210}$Pb activity

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was anticipated to be similar in the bog peat and the dried peat (as the surface of both peats is currently exposed to the atmosphere). However, the dried peat has not been accumulating material since it drained, so below the surface I anticipated an abrupt decrease in excess $^{210}\text{Pb}$ activity. Comparison of the subsurface $^{210}\text{Pb}$ activity with the model developed for the bog peat profile enabled me to determine when the drainage occurred.

6.2.4 Mass balance of carbon and lead

To investigate the contributions of biological and physical loss of material in the formation of dried peat, I determined mass balances of carbon and lead for profiles of bog peat and dried peat. In physical loss of material, both lead and carbon are lost, in equal proportions, from the peat profile. However, in biological loss of material, carbon is lost from the peat as $\text{CO}_2$, but lead is retained. Determination of mass balances for carbon and lead required data on the concentrations of these two elements, and bulk density, for continuous profiles of peat. Carbon contents were determined in duplicate for all samples from one profile each of bog peat and dried peat with a Europa Roboprep carbon and nitrogen analyzer. Lead contents were determined on the same samples by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP OES) with a Spectroflame Modular instrument made by Spectro Instruments, Kleve, Germany.

6.2.5 Data analysis

One way ANOVA was used to look for differences in basal ages between bog peat and dried peat. The analysis was performed with STATISTICA 7.
6.3 Results

6.3.1 $^{14}$C dating

6.3.1.2 Bog peat

![Graph showing calibrated age versus depth for four profiles of bog peat.](image)

Fig. 6.1 Calibrated $^{14}$C age versus depth for four profiles of bog peat. Each profile is indicated by a different colour. Logarithmic trend lines are associated with the data points of the same colour.

The four profiles of bog peat from Wellington Plain peatland all displayed a convex age versus depth curve, best described by a logarithmic trend line (Fig. 6.1). The variation between the four profiles from within the one peatland is testament to the complex nature of the bog ecosystem and the impact of the uneven underlying topography. The data in Fig. 6.1 highlight the danger of making generalisations from one profile. Outliers, such as in the green data set in Fig. 6.1, are a common occurrence in radiocarbon chronologies (Blaauw and Christen 2005). While a logarithmic equation best fits the data, comparison with earlier work on peat accumulation in Australian bogs requires simplification to a linear model. This yields an average peat accumulation rate of $0.04 \pm 0.01$ cm/year, within the range of results found by Dodson (1987) and general values for Australian bogs quoted by Hope (2003). Blaauw and Christen (2005) suggest that, globally, bogs accumulate at $0.05 \pm 0.025$ cm/year, and my results also fall within this range.
6.3.1.2 Dried peat

The dried peat was less than 200 years old at the surface (and thus could not be dated with $^{14}C$), and the base of each profile was between 1360 and 4830 years old (Table 6.1). The average basal age was 3323 years BP. As in the bog peat, the range of basal ages reflected the complexity of the peatland and the variation in topography of the substratum beneath the peat.

<table>
<thead>
<tr>
<th>Surface $^{14}C$ age</th>
<th>Delta $^{14}C$</th>
<th>ANSTO Code</th>
<th>Basal $^{14}C$ age (error)</th>
<th>ANSTO Code</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modern</td>
<td>-26.9</td>
<td>OZG966</td>
<td>2640 (60)</td>
<td>OZG963</td>
</tr>
<tr>
<td>Modern</td>
<td>-25.0</td>
<td>OZG961</td>
<td>4830 (70)</td>
<td>OZG964</td>
</tr>
<tr>
<td>Modern</td>
<td>-26.9</td>
<td>OZH529</td>
<td>1980 (40)</td>
<td>OZH530</td>
</tr>
<tr>
<td>Modern</td>
<td>-25.8</td>
<td>OZH531</td>
<td>4680 (50)</td>
<td>OZH532</td>
</tr>
<tr>
<td>Modern</td>
<td>-25.2</td>
<td>OZH533</td>
<td>1360 (35)</td>
<td>OZH534</td>
</tr>
<tr>
<td>Modern</td>
<td>-26.1</td>
<td>OZH535</td>
<td>4450 (130)</td>
<td>OZH536</td>
</tr>
</tbody>
</table>
6.3.2 $^{210}\text{Pb}$ dating

6.2.3.1 Bog peat

The excess $^{210}\text{Pb}$ activity for the bog peat core is shown in Fig. 6.2. These results enabled calculation of an accumulation rate of 0.25 cm/year below 10 cm. Above 10 cm depth, excess $^{210}\text{Pb}$ activity did not decrease exponentially, likely due to mixing in the continually growing moss layer, analogous to the mixed surface layer often seen in lake sediment $^{210}\text{Pb}$ profiles (Oldfield and Appleby 1984). Belyea and Warner (1994) suggest that incoming lead may fall through the open structure of the living moss at the bog surface before binding to cation exchange sites on the more decomposed material below. The open structure of this growing moss layer yielded a higher accumulation rate, of 0.32 cm/year, resulting in a two-part model of peat bog growth, shown in Fig. 6.3. The down-profile increase in $^{210}\text{Pb}$ activity at 17 cm depth could be caused by the influx of material with a different initial $^{210}\text{Pb}$ activity (Harle, Britton et al. 2002).
Fig. 6.3 Model of age versus depth derived from $^{210}$Pb results for the bog peat.

The model in Fig. 6.3 suggests that 15 cm of peat has accumulated in the past 50 years, and 27 cm in the past 100 years. These results are well within the range of growth rates for $^{210}$Pb dated bogs presented by Turetsky et al. (2000).

6.3.2.2 Dried peat

The activity of excess $^{210}$Pb in the profile of dried peat is shown in Table 6.2. The values decreased rapidly with depth: background levels of $^{210}$Pb were reached by 9 cm. These results will be compared with the results from the bog peat in Section 6.4.3 below.

**Table 6.2 Activity of excess $^{210}$Pb in the dried peat**

Associated errors are in brackets

<table>
<thead>
<tr>
<th>ANSTO code</th>
<th>Depth (cm)</th>
<th>Activity of excess $^{210}$Pb (Bq/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H490</td>
<td>0-2</td>
<td>323 (8)</td>
</tr>
<tr>
<td>H958</td>
<td>2-3</td>
<td>192 (5)</td>
</tr>
<tr>
<td>H959</td>
<td>4-5</td>
<td>97 (3)</td>
</tr>
<tr>
<td>H491</td>
<td>6-8</td>
<td>57 (3)</td>
</tr>
<tr>
<td>H960</td>
<td>9-10</td>
<td>29 (2)</td>
</tr>
<tr>
<td>H492</td>
<td>12-14</td>
<td>27 (1)</td>
</tr>
<tr>
<td>H961</td>
<td>14-15</td>
<td>23 (1)</td>
</tr>
<tr>
<td>H962</td>
<td>15-16</td>
<td>25 (2)</td>
</tr>
</tbody>
</table>
6.3.3 Mass balance of carbon and lead

The mass balances of a profile of bog peat and a profile of dried peat are shown in Table 6.3. The ratio of carbon to lead in each of the two profiles is similar, which suggests that equal amounts of carbon and lead have been lost from the dried peat.

<table>
<thead>
<tr>
<th>Peat type</th>
<th>C (g/m²)</th>
<th>Pb (g/m²)</th>
<th>C/Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bog peat</td>
<td>3932.33</td>
<td>175.25</td>
<td>22.4</td>
</tr>
<tr>
<td>Dried peat</td>
<td>508.92</td>
<td>20.68</td>
<td>24.6</td>
</tr>
</tbody>
</table>
6.4 Discussion

6.4.1 The rate of peat formation

Peat appears to have begun forming at Wellington Plain just over three thousand years ago. The average age of basal peat from the bog peat profiles was 3315 years BP (Fig. 6.1). Numerous other peat bogs in the Australian Alps also began forming at this time (Dodson 1987; Kershaw, Reid et al. 1997). Pollen analyses suggest that the peat forming vegetation at Wellington Plain peatland has remained stable for several thousand years, and is the same for both bog peat and dried peat (Elwood 2001).

Peat accumulation is a slow, non-linear process, which is best understood within the context of bog growth. Models of peat bog growth, building on the seminal ideas of Clymo (1984; 1978) have conceptually and mathematically developed our understanding of how bogs function (Belyea and Warner 1996; Wieder 2001; Yu, Campbell et al. 2001). Central to all these models is the idea that sediment in a growing peat bog is not static, but rather undergoing a continual process of addition (new plant material is added at the surface), compression (material is compacted by the ever-increasing mass of peat above) and subtraction (material is removed via decomposition). This is reflected in the superior fit of a logarithmic equation over a linear equation to the data in Fig. 6.1. Indeed, ‘the majority of published peat profiles show concave peat age-depth curves, suggesting that decay in deep peat is an ongoing process’ (Yu, Campbell et al. 2001, p 208).
6.4.2 The parent material of dried peat

Dried peat and bog peat appear to have begun forming at the same time. The average ages of peat from the base of the bog peat profiles and dried peat profiles were 3315 and 3323 years BP, respectively (Fig 6.1 and Table 6.1). There was no significant difference (p=0.99) between calibrated $^{14}$C ages from the base of four bog peat profiles and six dried peat profiles.

6.4.3 The timing of the change from bog peat to dried peat

The surface of the dried peat had a higher $^{210}$Pb activity than did the surface of the bog peat (323 cf. 227 Bq/kg, Table 6.2 and Fig. 6.2). This build up of lead on the dried peat surface suggests that the dried peat is eroding more slowly than the bog peat is growing. At 2-3 cm depth, the activity of excess $^{210}$Pb in the dried peat was comparable with that in the bog peat at the same depth. Below 3 cm, the $^{210}$Pb activity declined rapidly in the dried peat, reaching background levels by 9 cm depth. It is the dried peat sample from 4-5 cm depth (bold in Table 6.2) with $^{210}$Pb activity lower than that at comparable depth in the bog, but above background levels, that hold the key to when the dried peat was originally drained.

The $^{210}$Pb activity of the dried peat at 4-5 cm (97 Bq/kg) fits into the $^{210}$Pb activities of the bog peat profile just below 35 cm (Fig. 6.2, 105 Bq/kg). The growth model developed for the bog peat (Fig. 6.3) suggests that the dried peat below 3 cm depth was thus 131-139 years old. This peat was likely at the surface some time between 1865 and 1873. Cattle were first taken to Wellington Plains in 1855 (Cabena 1980), thus the erosion seems to have occurred shortly after grazing began. These $^{210}$Pb results suggest that the drainage of bog peat to form dried peat at Wellington Plain coincided with the introduction of livestock to the area.
6.4.4 The mode of the change from bog peat to dried peat

Dried peat could have formed by a) physical loss of material, where whole peat including carbon and lead leaves the system, b) biological loss of material, where rapid aerobic decomposition (microbial respiration) removes carbon and oxygen but leaves lead in the remaining peat, or c) by a combination of physical and biological processes. The mass balances of carbon and lead suggest that physical loss of material was the dominant process (Table 6.3). However, these results are from only one profile each of bog peat and dried peat, and thus further data are required to substantiate the proposition that dried peat formed primarily by a physical loss of material from a drained bog peat.
6.5 Conclusions

The results presented in this chapter met my stated aims, which were to investigate the rate of peat formation, whether or not bog peat is the parent material of dried peat, and how and when dried peat formed. My results suggest that the peatland at Wellington Plain began forming about 3300 years ago and has been accumulating at about 0.04 ± 0.01 cm/yr. The radioisotope results support the hypothesis that bog peat is the parent material of dried peat. Dried peat formation at Wellington Plain appears to have begun about 131-139 years ago, and the data show initial support for the proposition that physical loss of peat was the dominant process of dried peat formation.
Chapter 7. General Discussion

Summary
In this final chapter, the results of this thesis are combined to yield an overview of the past, present and future of peat soils in the Australian Alps. The new contributions of this research to the understanding of peatlands in Australia are highlighted, and models of bog peat and dried peat are presented. These models incorporate both properties measured in this study and properties yet to be quantified. Important avenues of further research are discussed, and the thesis concludes with a summary of how the objectives of this research have been met.

7.1 Peatlands Past

7.1.1 Peat initiation

The timing of peat initiation has been determined by radiocarbon dating for many peatlands in the Australian Alps (Dodson 1987; Hope 2003; Kershaw, Reid et al. 1997; McKenzie 1997). While there is considerable variation in the onset of peat formation, the following scenario has garnered broad agreement. Following the last period of glaciation (26-16000 years ago), conditions in the Alps ameliorated and plant growth trapped sediment in valley floors. The build up of gravel, sand and clay preceded peat development in wet, low lying areas. Peat initiation is associated with a decrease in temperature, an increase in cloudiness, a change in rainfall or a combination of these factors. Reported ages occur in each thousand years, however, there appear to be three peaks in peat initiation, around 10000, 5000 and 3000 years ago (Kershaw, Reid et al. 1997). There does not appear to be a correlation between altitude and peat initiation, and the reasons for the variation in the timing of peat initiation are not yet understood (Hope 2003).

Peat began forming, on average, 3320 years ago at Wellington Plain peatland, 1480 m. The peat formed on top of a gravelly clay, which was dated at 9800 years BP. These data are consistent with the scenario described above, and in particular with the work of Dodson (1987). Dodson (1987) found that peat accumulation began, over clay, around 3300 years ago, at sites of similar altitude to Wellington Plain.

Only one profile of peat from each peatland was dated in most of the studies cited above. I dated four profiles of bog peat and six profiles of dried peat from within the one peatland at Wellington Plain. Basal dates ranged from 1360 to 4830 years BP,
and the average age of 3320 years BP had a standard deviation of 1232 years. Therefore, my results emphasise the importance of dating multiple cores, and the need for caution in the use of basal peat ages to determine past climatic change.

7.1.2 Bog growth

Bogs grow vertically as peat accumulates. Peat accumulation represents the net outcome of plant production minus organic matter decay. This study did not measure plant production in bogs. *Sphagnum* has been recorded to increase in length by up to 30 cm in a growing season at Ginini bog in the Australian Capital Territory (Hope 2003). However, the productivity of other plants has not, to my knowledge, been quantified in Australian peatlands. Plant production in peatlands in the Australian Alps is an area that merits further study. I did measure the decay of organic matter in Wellington Plain peatland, and these data are discussed in Section 7.2.1. Here, suffice to say that the net outcome of plant production and organic matter decay at Wellington Plain peatland has been positive over the past three thousand years. Paleobotanical analyses found that the vegetation at Wellington Plain peatland had remained stable since peat formation began (Elwood 2001). However, due to decay, peat accumulation is not linear; although a rough estimate of the rate of peat accumulation can be determined from the basal age and the depth of the peat.

Linear approximations of peat accumulation in the Australian Alps include 0.03-3 cm/100 years, 0.7-3.3 cm/100 years and 0.1-10 cm/100 years (Dodson 1987; Hope 2003, respectively; Kershaw, Reid *et al.* 1997). My value of 4 cm/100 years for Wellington Plain peatland is thus within the range of previously published rates.

This is the first study to apply high resolution dating to determine a non-linear rate of peat accumulation in the Australian Alps. Peat growth at Wellington Plain was described by Equation 7.1.

\[
d = 16.8 \ln(a) - 13.3 \quad r^2 = 0.73 \quad \text{Equation 7.1}
\]

Where \(d\) = depth of the peat deposit

\(a\) = age

This logarithmic model is a more realistic approximation of peat growth than a linear model, as it incorporates decay. However, the model does not account for hiatuses in
peat growth, which may result from changes in hydrology, temperature or nutrient input, fire or human-induced drainage, or loss of peat by erosion (Hope 2003).

7.1.3 Dried peat formation

Dried peat formed from bog peat. This was first proposed in the initial description of soils in the Australian Alps, where Costin (1954) identified bog peat as the parent material of dried peat. The changes in carbon chemistry with depth that I described (Chapter 3) support Costin’s analysis. The carbon chemistry of the dried peat resembled the carbon chemistry of the lower layer of bog peat. In particular, the similarity of the relationship between the chemistries of bog peat and dried peat in my work, and uncultivated peat and cultivated peats in Canada (Preston, Shipitalo et al. 1987), suggested that dried peat had formed from bog peat via a process with effects similar to those of cultivation.

Beyond Costin’s (1954) initial description, dried peat in the Australian Alps has received little research attention. When and how dried peat formed has been the subject of speculation only. Paleobotanical studies have avoided dried peat, as the historic record is clearly truncated. Elwood (2001) failed to recognise this, sampled the peat at insufficiently high resolution, and thus the study was inconclusive. I used $^{14}$C and $^{210}$Pb dating to investigate when dried peat formed at Wellington Plain peatland (Chapter 6). Both techniques suggested that, at this location, dried peat formed within the past two hundred years. This finding, while based on limited data, has implications for the management of peatlands in the Australian Alps. Restoration of peatlands that dried within the past two hundred years is likely to be both more achievable and more warranted than restoration of peatlands that dried several thousand years ago. Radioisotope dating of several peatlands throughout the Alps could enhance our understanding of the long term processes at work in the Australian Alps.

Drainage is the critical factor that turns bog peat into dried peat. This has been recognised for centuries and is the basis of the extensive northern hemisphere literature on ‘reclaiming’ bogs for agriculture and forestry (Armstrong and Castle 1999). Drainage inevitably leads to loss of peat, by biological and/or physical processes. If drainage is slow, peat may be lost gradually by oxidation, while if drainage is rapid, peat is more likely to be lost by erosion. Costin (1954) alluded to both biological and physical loss of peat in discussing the effects of land use on bog
peat in the Australian Alps. I used an element mass balance approach to investigate the relative contributions of physical and biological loss of peat at Wellington Plain peatland (Chapter 6). Physical loss of peat appeared to have been the dominant process. This finding supports the hypothesis that catastrophic loss of peat occurred soon after bogs were damaged by trampling by introduced livestock. It is inconsistent with a gradual, purely oxidative, loss of peat from Wellington Plain peatland. The resultant dried peat is a very different soil from its progenitor, and in Section 7.2 models of the current functioning of bog peat and dried peat are presented.
7.2 Peatlands Present

The present condition and functioning of peat soils in the Australian Alps, as determined in this study, are summarised in two models. These models draw primarily upon the results presented in this thesis. However, additional properties are also included, to give a more complete picture of peat function, and also to highlight areas that require further research. The models are best understood in light of the flow chart in Fig. 7.1. This flow chart outlines the interrelated nature of carbon and water in peat soils.

Fig. 7.1 Flow chart of carbon and water in peat soils. Processes in bold constitute a cycle of increasing carbon accumulation. When interrupted by drainage (indicated by the X), a cycle of carbon loss is initiated (plain text).
7.2.1 Bog peat model

The interrelated nature of the carbon and water properties of peat outlined in Fig. 7.1 is evident in the model of bog peat developed from the results of this study (Fig. 7.2). An increase in the extent of decomposition of the organic matter coincided with an increase in the proportion of small pores, and correspondingly an increase in water retention and a decrease in the rate of water movement. Variation in the depth of the watertable was buffered by three properties of the acrotelm: a) the rapid rate of water movement and b) the high proportion of large pores, both of which decrease with depth, and c) the increase in water retention with depth (Fig. 7.2 and Van Seters and Price 2001).

The peat described in Fig. 7.2 is, in many ways, typical of bog peat as it is understood in the literature from the northern hemisphere. There are two distinct layers, the acrotelm and the catotelm, which display the characteristic properties of these layers, as described by Ingram (1978) and outlined in Chapter 1, Table 1.3. The peat becomes more decomposed with depth, and the rate of decomposition also decreases with depth, as Clymo (1983) described in his treatise on peat accumulation. The hummocks and hollows of the Sphagnum-dominated surface of the bog peat at Wellington Plain resemble the topography of European Sphagnum bogs (author pers. obs. 2003). However, the input of water from surface run-on and from groundwater is inconsistent with the northern hemisphere definition of a bog, as a system receiving water and nutrients predominantly from rain. This incongruity was noted in Chapter 1, Section 1.5. I suggest that a) further research is required to quantify the water sources and chemistries of peatlands in Australia and b) classification systems developed in the northern hemisphere need to be applied with caution elsewhere.
Fig. 7.2 Model of bog peat, developed from the properties measured in this study. Terms in italics were not measured in this study.
7.2.2 Dried peat model

The dried peat in Fig. 7.3 displays the characteristics typically associated with drainage. Drainage results in shrinkage, an increase in bulk density, a decrease in permeability and in the proportion of pores that drain under low suctions, and increased variation in the watertable (Charman 2002). In comparison with the bog peat from which it formed (Fig. 7.2), the dried peat was shallower and had: higher bulk density, slower hydraulic conductivity (at the surface), a smaller proportion of large pores, and a larger zone of watertable fluctuation. As indicated in Fig. 7.1, drainage interrupts the carbon accumulating cycle of a waterlogged peatland, and thus the future of the dried peat may be unstable.
Dried peat

Fig. 7.3 Model of dried peat, developed from the properties measured in this study. Terms in italics were not measured in this study.
7.3 Peatlands Future

7.3.1 Predictions

Peat soils in the Australian Alps are likely to be sensitive to climate change. The increased temperatures and altered rainfall regimes predicted for the Australian Alps (Hennessy, Whetton et al. 2003) may alter the interrelated carbon and water cycles in peat soils (Fig. 7.1). While increased temperatures may lead to increased rates of decay, rates of plant growth will likely also increase, and thus the net effect of an increase in temperature on peat accumulation is uncertain. Increased rainfall could lead to the expansion of peatlands in the Alps, or contribute to the erosion of peats. Bog peats have some capacity to accommodate increased rainfall, as the acrotelm moderates variation in the watertable. Dried peat, however, is likely to be further eroded if rainfall increases.

Increased frequency of fire is also predicted for Australia as the climate warms. Peat soils are very susceptible to fire (Hope 2003), particularly when already drained. Restoration works aimed at rewetting dried peat may aid peatlands in the Australian Alps to survive climate change.

7.3.2 Future research

This study has developed a solid base for understanding the carbon and water dynamics of peat soils in the Australian Alps. However, the terms in italics in Fig. 7.2 and Fig. 7.3 all remain to be quantified. In particular, water chemistry and plant growth rates warrant attention. The former is essential to further our knowledge of peat soils and their role in catchment hydrology, and how bogs in Australia fit in with world-wide peatland classifications. The latter is required to ascertain the net effects of both peatland restoration and climate change on peat accumulation and attrition.

Drained peats are hydrophobic and difficult to rewet. The nature of this hydrophobicity and possible methods to reverse it are topics that could have direct application in peatland restoration projects. How water binds to organic matter in catotelm peat is incompletely understood, yet central to the function of bogs. Therefore, molecular scale soil-water relations of both bog peat and dried peat deserve further research.
7.4 Conclusions

This research has improved our understanding of bog peat and dried peat in the Australian Alps, by investigating carbon dynamics, water dynamics and peat formation. The objectives of this thesis, presented in Chapter 1, have been met, and the ensuing results are outlined below.

The carbon chemistries of both bog peat and dried peat displayed changes with depth consistent with an increase in the extent of decomposition of the organic material. Representative changes in the alkyl:O-alkyl ratio down the profile were 0.14 to 0.96 for bog peat and 0.28 to 1.07 for dried peat. Laboratory incubations on the influence of chemistry, particle size, water content and sample preparation indicated that, in the absence of confounding factors, peat chemistry was most important factor in determining the size of the mineralisable carbon pool. Water content was the most important factor in determining the rate of carbon mineralization. In the field, both bog peat and dried peat emitted an average of 2 g CO$_2$/m$^2$/d from the surface. Carbon mineralisation was related to both soil temperature and soil water content, and this relationship was used to model peat mineralisation under a range of possible future climate change scenarios. Below the surface, however, I measured lower rates of decomposition in the dried peat than in the bog peat.

The water-holding capacity of peat was measured in the laboratory, as was the rate of water movement through peat. Specific yield decreased down the profile in both bog peat (0.88 to 0.45 cm$^3$/cm$^3$) and dried peat (0.36 to 0.11 cm$^3$/cm$^3$). Hydraulic conductivity also decreased down the profile in both peats: $5.1 \times 10^{-4}$ to $3.0 \times 10^{-6}$ m/s in bog peat, and $1.0 \times 10^{-4}$ to $7.0 \times 10^{-6}$ m/s in dried peat. Relationships between the hydrologic properties of peat and its physical and chemical properties were identified. In the field, fluctuations in the watertable were monitored in concert with rainfall. These laboratory and field measurements enabled me to develop models of the hydrology of bog peat and dried peat.

Both bog peat and dried peat began forming around 3300 years ago. The bog peat appeared to have drained to form dried peat between 131 and 139 years ago. Since that time, erosion appears to have contributed more to the loss of organic material from dried peat than carbon mineralisation has.
References


Cambell CD, Chapman SJ, Cameron CM, Davidson MS, Potts JM (2003) A rapid microtiter plate method to measure carbon dioxide evolved from carbon substrate amendments so as to determine the physiological profiles of soil microbial communities by using whole soil. Applied and Environmental Microbiology 69, 3593-3599.


Charman DJ (2002) 'Peatlands and Environmental Change.' (John Wiley and Sons: Chichester)


Costin AB (1954) 'A study of the ecosystems of the Monaro region of NSW with special reference to soil erosion.' (Government Printer: Sydney)

Costin AB (1957) 'High mountain catchments in Victoria in relation to land use.' (Government Printer: Sydney)


Glob PV (1977) 'The bog people.' (Faber: Chatham)


Hahn C (2004)'Hydrological study of a subalpine, valley side bog in the Snowy Mountains, NSW, after drought and fire.' Australian National University, School of Resource and Environmental Science, Canberra.


Isbell RF (1996) 'The Australian Soil Classification.' (CSIRO Australia: Melbourne)


Rosengren N (2002) 'Mountain areas of eastern Victoria: topography, geology and geomorphology.' La Trobe University and Victorian Department of Natural Resources and Environment, Melbourne.

Rowe RK, Downes RG (1960) 'Reconnaissance survey of the ecology and land-use in the catchment of the Glenmaggie Reservoir.' (Soil Conservation Authority: Melbourne)


White RE (1997) 'Principles and Practice of Soil Science.' (Blackwell Science: Oxford)


