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Grape and Wine Research and Development Corporation

What are we putting on the ground? Characterisation of grape marc and other composts used in the Yarra Valley

What are we putting on the ground? Characterisation of grape marc and other composts used in the Goulburn Valley region

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What are we putting on the ground?
Characterisation of Grape Marc Composts from the Goulburn and Yarra Valley Regions of Victoria

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1. Introduction

The appropriate disposal of grape marc is a significant environmental challenge facing the viticulture industry. Composted grape marc is often spread back into the vineyard. Many questions are being raised about what is being put into the ground and what effect it may have on vine performance, fruit quality and whether this is a sustainable long term practice.

Detailed scientific studies into the composition of grape marc compost are limited, particularly where the composting process has been carefully controlled to gain knowledge of how the process affects the quality of the compost produced. Composts, manures and mulches may vary considerably in composition. Generally, the positive benefits of applying these materials to the soil is recognised, however, the variable composition of nutrients present as well as the potential presence of harmful high salt content and heavy metals requires closer monitoring of their composition. High levels of compost inputs into vineyards has the potential to return very high amounts of macronutrients, micronutrients and possible undesirable chemical entities. This can be readily concluded by examining some typical compost chemical compositions including grape marc composts (Robinson, 2001; Wilkinson and Biala, 2001).

Limited studies involving vineyard applications of grape marc containing compost have been undertaken in Australia (Smith, 2002; Beresford, 2002, Wilkinson, 2002). High potassium levels have been identified in grape marc composts and this feature has received particular attention in several overseas investigations (Mundy and Agnew, 2002; Morris et al., 1980). Inbar, Chen and Hadar undertook some detailed scientific studies, focussing on the organic composition of composts from winery wastes in the late eighties and early nineties (Inbar et al., 1988, 1991, 1992).

Information on the nutritional status of marc compost and other characteristics of typical grape marc composts produced in vineyards is required. In this project, composted grape marcs from various wineries and two samples of commercial compost not involving grape marc were analysed. This information will contribute to developing an appropriate quality standard for marc compost to be recommended. Grape marc compost samples were taken from various locations in the Goulburn and Yarra Valleys, including Mitchelton Winery, De Bortoli's Vineyard, Henkell Vineyard, and Yarra Ridge Vineyards. For comparison purposes, a conventional greenwaste compost (ex Mitchell City Council) and a commercial compost ('Coles' supermarket compost, ex 'Collex') were also collected and studied.

It is important to note that there was no input into the production of the compost and that samples were taken "as is" from the paddocks. Different vineyards use different treatments in producing the composted grape marc product. It is not part of the core business of the vineyard and consequently, product composition would be expected to vary considerably, and may not be consistent from year to year depending on the practices employed.

The common practice observed in all the locations where samples were taken involved the use of producing windrows and these were periodically turned, but not necessarily with ongoing regularity. Some vineyards blend the grape marc with other materials such as horse and cow manures, sawdust and diatomaceous earth. (e.g Mitchelton Winery) Other vineyards do not blend in additional materials and simply allow composting to occur in the windrows.

2 Methodology

2.1 Sample Collection

- Yarra Ridge ('racecourse') Grape Marc
- Composite De Bortoli Grape Marc
- De Bortoli Grape Marc "Pale" (no detailed analysis done on this sample)
- De Bortoli Grape Marc "Worm Devoid"
- De Bortoli Grape Marc "Worm Rich"
- Henkell Grape Marc Compost
- Mitchelton Grape Marc compost (one year old)
- Mitchelton Grape Marc 'fresh' (three months old)
- Coles Supermarket compost ex Collex (normally aged 6 weeks)
- Greenwaste compost ex Mitchell City Council: mostly consists of tree trimmings, bushes, and other garden waste.

2.2 Collection Methods

2.2.1 Goulburn Valley - Nagambie

Mitchelton Winery

Compost samples were collected from Mitchelton's Winery in Nagambie (Goulburn Valley) on April 11, 2003. The composted grape marc had been sitting for about 12 months. Most compost had already been removed, so all that remained was a thin layer of compost in the paddock. Samples were extracted from two windrows running parallel, each approximately 150 m in length, 6 meters wide and 10 cm deep. A shovel was used to scrape up compost from the windrows to make small piles (~50 l in size) in 20 different locations (10 piles about 10 m apart for each windrow). Each pile was mixed thoroughly and produced 1 grab sample (~10 l or half a 20 l bucket). The 20 grab samples were bulked together to form another large pile of around 200 l. This pile was mixed and turned over thoroughly before being partially transferred into 2 x 20 l buckets lined with a double layer of plastic waste disposal bags. These two buckets were stored at Monash University at 45 ^{O}C for 24 hours to kill Phylloxera aphids, then stored at room temperature in the storeroom until analysed.

2.2.2 Yarra Valley

Henkell Vineyards

Composted marc was collected on May 7, 2003. The compost pile had been sitting for approximately twelve months. One windrow, (approximately 25 meters long, 5 m wide and 1.2 m high) ran from north to south. A shovel was used to dig into the windrow in 15 different places to take 15 grab samples (~10 l or half a 20 l bucket each). The 15 grab samples were bulked together to form a large pile of around 150 l. This pile was mixed and turned over thoroughly before being partially transferred into 1 x 20 l bucket lined with a double layer of plastic waste disposal bags (Composite sample from whole windrow. The bucket was stored under refrigeration.

De Bortoli's Winery

The composted grape marc was also collected on May 7, 2003. This had also been sitting for approximately twelve months. Three identical windrows, (approximately 50 meters long, 6 m wide and 1.2 m high) ran parallel from north to south. Samples were extracted from the eastern windrow. The southern end was quite moist and contained numerous tiger worms. The northern end was dry and contained no observable worms. A shovel was used to dig into the windrow in 20 different places to take 20 grab samples (~10 l or half a 20 l bucket each). The 20 grab samples were bulked together to form a large pile of around 200 l. This pile was mixed and turned over thoroughly before being partially transferred into 1 x 20 l bucket lined with a double layer of plastic waste disposal bags (Composite sample from whole windrow). One smaller (10 l) bucket was filled with compost from the earthworm end. Another 10 l bucket was filled with compost from the northern dry end. A fourth windrow, only about 15 meters in length. 5 m wide and 1 m high, was located to the east of the others, also running from north to south. The windrow differed in that it was paler in color and seemed fresher than the other three. It was fermenting profusely (very warm and steaming) and contained large quantities of white fungus. A composite sample of this was inserted into a green plastic garbage bag. The buckets and bags were stored under refrigeration.

Yarra Ridge Vineyard

Composted grape marc, which had been sitting for at least 18 months was collected on May 7, 2003. One cone shaped pile (about 5 m diameter, 1.8 m height, was already partially (one quarter) extracted. A shovel was used to dig into the windrow in 10 different places to take 10 grab samples (~10 l or half a 20 l bucket each). The 10 grab samples were bulked together to form a large pile of around 100 l. The compost also contained some tiger worms. This pile was mixed and turned over thoroughly before being partially transferred into two plastic waste disposal bags (Composite samples from whole pile). The bags were stored under refrigeration.

Other

Coles Supermarket compost ex Collex and Greenwaste compost ex Mitchell City Council were collected from the compost piles at the respective composting sites for these two organisations.

2.3 Seed Content

As-received samples (40-50g) were dried to constant weight at 105 ^{o}C. The seeds were then separated manually from the remaining matter, and each fraction was weighed at room temperature. The relative amounts of each were then determined.

2.4 Humic Extractions

The method of extracting the three humic fractions from each sample largely follow that used by Bos-Van der Zalm (private communication, 2003), which is a variation to that of Swift (1996) and Lamar *et al* (2002).

Pre-dried (<40^{o}C) crushed and sieved (< 2mm) samples were accurately weighed (~3g) and mixed with 15 mL H_2O. The pH of the solution was then adjusted to 1-2 (Merck indicator strip) using 1M HCl, and the solution was made up to 30 mL with 0.1 M HCl. This mixture

was ultrasonicated (20 minutes), and then centrifuged (20 minutes @ 4000 rpm). At this point, the supernatant was decanted and filtered (under suction (Advantec GA-SS glass fibre filter paper), washing sparingly with cold water. The acid washings were filtered again (0.45 μm, then a 0.2 μm, nylon filter cartridge fitted onto a plastic syringe) and stored in the fridge away from light, and labelled 'FA1' (fulvic fraction 1).

The residue from this filtration was neutralised with 1 M NaOH, and made to 30 mL with 0.1 M NaOH. This alkaline mixture was then ultrasonicated (30 minutes) The supernatant was decanted and filtered (0.45 μm, 25 mm nylon syringe filter), under N_2(g)). The leftover solid was classed as the 'humin' fraction and freeze-dried and weighed to constant weight.

The filtered supernatants were acidified to pH 1-2 (with 6 M HCl, and Merck pH indicator strips), and left to stand for several days so that the humic acid fraction could have time to precipitate out, checking the pH from time to time ensuring that it remained acidic. The acid mixtures were filtered (0.45 μm Sartorius membrane, and then 0.2 μm syringe filter, and collected as 'FA2' (fulvic acid fraction 2). The solid (humic fraction) was transferred to a dialysis tube and dialysed in ultra pure H_2O until no more chloride ions were detected in the water (using the addition of silver nitrate to observe if any white silver chloride precipitate is formed); during this time the water was changed daily. After this step, the contents of the dialysis tubes (expected to contain pure humic acid and H_2O were transferred to centrifuge tubes (using ultra pure H_2O) and centrifuged (15 minutes @ 4000 rpm). The water was decanted, leaving the humic acid, which was then freeze-dried to constant weight. The acidic fulvic acid fraction solutions obtained (FA1 & FA2) were combined and submitted for TOC (total organic carbon) analyses and the fulvic acid content was then indirectly calculated using the results of these analyses.

2.5 TOC (total organic carbon)

The acidic fulvic acid solutions of each humic separation were combined and forwarded to the Water Studies Centre (WSC) (Monash University, Clayton campus) for analysis of TOC (WSC test method 58). This method involved the use of a carbon furnace method where the carbonaceous material in the sample is burned. The amount of CO_2 produced is measured and used to deduce the level of organic carbon present.

2.6 Nuclear Magnetic Resonance Spectroscopy

2.6.1 Solid state ^{13}C NMR

Solid state ^{13}C NMR spectra of several air-dried grape marc (seed and residue, seed alone, and residue alone) were measured by the Waite Research Institute, at the University of Adelaide by Dr Ron Smernik. Solid-state ^{13}C magic angle spinning (MAS) NMR spectra were obtained at a ^{13}C frequency of 50.3 MHz on a Varian Unity200 spectrometer. Samples were packed in a 7 mm diameter cylindrical zirconia rotor with Kel-F end-caps and spun at 5000±100 Hz in a Doty Scientific MAS probe. Free induction decays were acquired with a sweep width of 40 kHz; 1216 data points were collected over an acquisition time of 15 ms. All spectra were zero filled to 8192 data points and processed with a 50 Hz Lorentzian line broadening and a 0.005 s Gaussian broadening. Chemical shifts were externally referenced to the methyl resonance of hexamethylbenzene at 17.36 ppm.

Cross polarization (CP) spectra were acquired using a 1 ms contact time. Bloch decay (BD) spectra were acquired using a 6.0 ms (90°) ^{13}C pulse. A recycle delay of 90 s was used for

BD spectra. BD spectra were corrected for background signal (Smernik and Oades, 2001). Inversion-recovery experiments (Smernik et al., 2000a, b) were performed using a 1 ms contact time.

Spin counting experiments were performed using the method of Smernik and Oades (2000a, b). Glycine (AR grade, Ajax Chemicals) was used as an external intensity standard (i.e. the glycine spectrum was acquired separately to those of the samples). For CP spin counting experiments, differences in spin dynamics between the sample and the glycine standard were accounted for using the method of Smernik and Oades (2000a), except that a variable spin lock (VSL) rather than a variable contact time (VCT) experiment was used to determine the rate of ^{1}H spin lattice relaxation in the rotating frame (Smernik et al., 2002). Errors in carbon NMR observabilities (C_{obs} values) are estimated to be ±10% in C_{obs}-CP and ±15% in C_{obs}-BD (Smernik and Oades, 2000a). Inversion-recovery experiments were analyzed by statistically comparing one- and two-T_1H component fits to the data, using the method of Smernik et al. (2000a, b).

2.6.2 Solution NMR

Selected fulvic acid fractions obtained from the extraction of the composts samples were freeze dried. Samples for solution NMR (^{1}H, ^{13}C, ^{31}P) were made up by taking the freeze dried solids, mixing with D_2O and transferring to 5 mm nmr tubes. ^{1}H, ^{13}C and ^{31}P nmr were run on a Bruker DPX300 300MHz spectrometer with a 5mm quad probe with Z gradients. ^{1}H spectra were referenced to the HOD signal (4.67 ppm) and the same referencing frequency used for the ^{13}C spectra. ^{31}P spectra were referenced to external 85% H_3PO_4 solution (0 ppm).

2.7 Analysis conducted by the DPI State Chemistry Laboratory, Werribee

The code numbers alongside parameters that were measured refer to the standard methods used by the State Chemistry Laboratory. Detailed information on each method was not available, but a general description of the principle of the method has been included, where appropriate. Compost analyses also utilised the Australian Standard AS 4454-1999 for composts, soil conditioners and mulches (1999).

2.7.1 Moisture Loss (@ 40 ^{o}C and 105^{o}C), pH, & EC

Moisture loss was determined using method 1047 – DPI State Chemistry Laboratory, Werribee. Electrical conductivity and pH were determined using method 453.

2.7.2 Physical Parameters: Particle Size greater than 16 mm, Wettability, Bulk Density, Water-Holding Capacity and Air-Filled Porosity

These were determined using DPI State Chemistry Laboratory methods 446 (see also Appendix F of AS4454 - 1999), 451 (see also Appendix D of AS4454 - 1999), 448 (see AS4419 - Appendix B for Bulk density), and 447 (see Appendix B of AS3743) respectively.

2.7.3 Germination & Toxicity Index

These were carried out using DPI State Chemistry Laboratory method 456 (equivalent to appendix E of AS4454 - 1999). The germination index is the percentage of seedlings that germinated in the test samples for that product (i.e. sometimes not all seeds germinate). The toxicity index compares the length of these germinated seedlings to a specific "reference" potting mix. (toxicity index equation is in Appendix E of AS4454 - 1999)

2.7.4 Calcium carbonate, total sodium, and chloride

These were conducted using methods IAM04001 (see also Appendix G of AS4454 - 1999), 092, and AS3743 (Appendix D of AS3743) respectively.
DPI State Chemistry Laboratory method 092 was used for total Na, P, K, S, Ca, Mg. This involved a block digestion of the sample followed by analysis of the digest using ICP-OES. $CaCO_3$ is as per the standard method is actually $\underline{\%CaCO_3 \text{ equivalent}}$ and not the true content of $CaCO_3$.

2.7.5 Organic Matter, Carbon:Nitrogen, Total Carbon, Total Nitrogen, Ammonium-N, Nitrate-N, and Nitrogen Drawdown Index

These were conducted using the following methods: 1103 (see also Appendix B of AS4454-1999), Calculated from Leco , Leco (0117), (See also Appendix B of AS4454 - 1999), Leco (0117) (RFA)(083), (see also Appendix A of AS4454 - 1999), (RFA) (083) and 454 (See also Appendix K of AS4454 - 1999) respectively.

2.7.6 Total P and Soluble P

These were determined using DPI State Chemistry Laboratory method 092 and AS4454 - 1999 respectively.

2.7.7 Total K, Total S, and Total Ca, Boron

Total K, S and Ca were determined using DPI State Chemistry Laboratory method 092. Method 110 was used for total B and also involved microwave digestion of the sample with nitric acid, followed by analysis of the digest using ICP-OES.

2.7.8 Other Metals: Total Mg, Cu, Zn, Mn, Mo, Fe, B, Se, Al, & Ni

These were carried out using methods 092, 104, 104, 104, 104, 104, 110 (These involved microwave digestion with nitric acid followed by analysis with ICP-OES), IMKIT08014 (involved block digestion of the sample with nitric/perchloric acids followed by analysis with ICP-MS VGA), 104, and 104 respectively. As with method 092 (for total Na, P, K, S, Ca, Mg), in method 104 (total Cu, Zn, Mn, Mo, Fe, Al, Cd, Cr, Ni, Pb), samples underwent a block digestion with nitric/perchloric acids and the digest was analysed using ICP-OES. Block digestion with nitric/perchloric acids, analysed by ICP-OES.

2.7.9 Heavy Metals: Total Pb, Hg, Cd, Cr and As

These were carried out using methods 104, 1016 (involved microwave digestion of the sample with nitric/sulphuric acids followed by CETAL Hg analysis), 104, 104, and

IMKIT08014 (involved block digestion of the sample with nitric/perchloric acids followed by analysis with ICP-MS VGA) respectively.

2.7.10 Organic Residues

A suite of organic residues including benzene hydrocarbons (BHC), aldrin, lindane and other chlorinated hydrocarbons were determined in samples using method OMNF05029. This involved a solvent extraction, a florisil clean-up, followed by analysis with GC-ECD.

3 Results and Discussion

3.1 Residual Seed

Table 1 shows the amount of seed remaining in the grape marc samples. In all samples, the remaining seed levels were significant, indicating that the grape seed is very resistant to all the composting conditions employed for these samples.

The De Bortoli composite sample containing about 51% seed was representative of the grape marc from all the De Bortoli samples, as it contained both the Worm Devoid and Worm Rich material. The differences observed probably reflect the variability across the compost windrows and cannot be ascribed to any particular factor. Overall the De Bortoli material appeared to be less decomposed and the windrows were still quite biologically active. This may have been caused by the very dry 2002-2003 summer period when the compost heaps dried out. The autumn rains of 2003, which occurred not long before the samples were taken, probably reactivated the biological activity in the windrows.

Table 1. Seed Content of Grape Marc Compost Samples

Sample	% (w/w) Seed
COMPOSITE DE BORTOLI GRAPE MARC	51
DE BORTOLI 'WORM DEVOID' GRAPE MARC	57
DE BORTOLI 'WORM RICH' GRAPE MARC	76
HENKELL GRAPE MARC	35
MITCHELTON 1 YR OLD COMP GRAPE MARC	29
MITCHELTON FRESH 3 MTH OLD GRAPE MARC	41
YARRA RIDGE (RACECOURSE) GRAPE MARC	39

The Yarra Ridge compost sample was more mature in age (2001 vintage) and the lower seed content (39%) is likely to reflect the greater opportunity for seed break-down over time. The Henkell sample was also lower in seed content (35%) and the grape marc appeared to be better degraded than some of the others. There was evidence that some clay material or diatomaceous earth had been added to the composting grape marc. The lower seed content is likely to be related to more efficient composting conditions.

This is supported by the seed content result obtained for the Mitchelton samples. A decrease in seed content from 41% to 29% was measured between the three month old compost

sample and the sample that was twelve months old. A lower initial value of seed can be related to the composting mixture used at Mitchelton, where the grape marc is mixed with horse stable litter and sawdust, hence diluting the initial seed content. The additional materials employed in the Mitchelton procedure also suggest that there is a more active composting process that is biodegrading the seed.

3.2 Physical Parameters, Moisture Content, pH and Conductivity

The data for the moisture content, pH and electrical conductivity for all the composts tested are shown in Table 2. Moisture content measurements, taken by drying the compost under two temperature regimes, indicate that at the time of sampling, all the composts contained between forty and sixty percent water. This water was generally weakly bound as the values did not differ significantly between the two temperatures.

Table 2. Moisture Loss, pH, & Electrical Conductivity (EC) for Composts

Sample	Moisture Loss @ 40°C	Moisture Loss @ 105°C	Dry Matter %w/w	pH_{H2O}	EC (dS/m)
COMPOSITE DE BORTOLI GRAPE MARC	56	58	42	7.5	1.4
DE BORTOLI 'WORM DEVOID' GRAPE MARC	52	54	46	7.5	1.2
DE BORTOLI 'WORM RICH' GRAPE MARC	48	51	49	7.7	1.7
HENKELL GRAPE MARC	50	56	44	8.2	2.1
MITCHELTON 1 YR OLD COMP GRAPE MARC	45	47	53	8	1.7
MITCHELTON FRESH 3 MTH OLD GRAPE MARC	49	51	49	8.1	2.9
YARRA RIDGE (RACECOURSE) GRAPE MARC	59	61	39	7.9	1.5
GREENWASTE COMP EX MITCHELL CITY COUNCIL	45	47	53	7.2	0.8
COLES SUPERMARKET COMPOST EX COLLEX	43	44	56	7.6	2.4

The Dry Matter values shown in Table 2 were calculated by difference and based on the 105° C moisture values. Water content would be expected to vary with seasonal conditions and the general characteristics of the compost heap, nevertheless it is an important parameter to consider when determining applications rates for a compost in the field. Most of the grape marc composts examined have bulk density values between 0.7 and 0.9 kg/L. Hence, a cubic metre of compost, (assuming 1L = 1 dm^3) would weigh between 700 and 900 kg, approximately half of this weight being made up of water.

Electrical conductivity is an important indicator of soluble salts present in a compost. These can potentially contribute to salinisation of the soil if soluble salt levels are too high and

consequently harm plant growth. It should be noted that the electrical conductivity values are normally determined on the moist sample of compost.

The electrical conductivity values for the grape marc samples tested in this study varied between 1.2 dS/m and 2.9 dS/m. These values equate to estimated total soluble salt levels (Brady and Weil, 2003)) ranging from 1200 to 2900 mg/L. The highest conductivity was found in the Mitchelton three month-old sample with a trend towards lower values in the more matured compost samples. The twelve month-old Mitchelton sample gave a lower conductivity value and provided these two compost samples from the same winery, were produced by similar methods, the trend is consistent. The Coles supermarket compost also shows a higher electrical conductivity value (2.4 dS/m) and it was observed that this compost was relatively immature and still very biologically active. The composition of the soluble salts in the grape marc samples is discussed in Section 3.3.

No firm conclusions should be made from these observations without further systematic studies, as the salt levels will be affected by the way the composts were produced and subsequently left in the paddocks. However, the Australian Standard for composts, soil conditioners and mulches (AS4454, 1999) recommends that for plants that are sensitive to salinity, application rates should not exceed 15 L/m^2 of compost with an EC range of 1-2 dS/m. When the electrical conductivity enters the 2-4 dS/m range, the application rate should not exceed 8 L/m^2. (These rates apply to surface applications). Soil electrical conductivity should remain below 2 dS/m for dissolved salts to have no effect on vine growth (White, 2003).

All the composts examined in this study fell in the pH range between 7.2 and 8.2. This is the typical range of pH found in composted materials, including grape marc composts (Inbar *et al*., 1988). Higher pH values may be associated with higher levels of ammonium ion (NH_4^+) and indeed this was found to be the case for both of the Mitchelton grape marc samples, the "Worm Rich" De Bortoli sample and the Coles supermarket compost.

Table 3 lists a range of physical parameters for the composts. Wettability measures the time in minutes for water to soak into the compost samples. It provides a simple measure of hydrophilicity or compatibility of the materials with water. All the grape marc compost samples were equally and readily "wetted" compared with the Mitchell City and Coles supermarket composts, where higher "wetting times" were measured. The Coles supermarket compost was the most resistant to wetting.

The grape marc composts also displayed higher water holding capacities than the non grape marc composts, with values falling in the range of 58-69% water on a volume/volume basis. The Mitchell City Council green-waste compost had the lowest water holding capacity. Water holding capacity and wettability will be influenced by the how the compost has been produced and stored. Composts that have been dried out will be more difficult to rewet. The high water-holding capacity of the grape marc compost has the potential for decreasing water needs, if used as a mulch in the vineyard (Smith, 2002).

The grape marc composts had greater bulk densities (~0.8-0.95 kg/L) than the non-marc derived samples. (<0.7 kg/L). Mitchell City Council green-waste compost gave a particularly low value and it is interesting to note that this compost also had the highest level of particles exceeding 15 mm in size. The percentage of material with particle sizes exceeding fifteen millimeters displayed quite a range across the composts investigated. This parameter is dependent on how the compost was prepared and subject to sampling errors.

Table 3. Compost Physical Parameters: Wettability, Particle Size, Bulk Density, Water-Holding Capacity

Sample	Wettability	Particle Size % Material with Particles > 15 mm	Moist Bulk Density kg/L	Water Holding Capacity % V/V
COMPOSITE DE BORTOLI GRAPE MARC	0.2	28	0.79	63
HENKELL GRAPE MARC	0.2	7	0.78	59
MITCHELTON 1 YR OLD COMP GRAPE MARC	0.2	0	0.79	58
MITCHELTON FRESH 3 MTH OLD GRAPE MARC	0.2	25	0.95	68
YARRA RIDGE (RACECOURSE) GRAPE MARC	0.2	27	0.91	69
GREENWASTE COMP EX MITCHELL CITY COUNCIL	0.6	40	0.65	42
COLES SUPERMARKET COMPOST EX COLLEX	1.5	1	0.69	56

3.3 Total Nutrients

3.3.1 Potassium, Calcium and Magnesium

Potassium, Calcium and Magnesium are essential macronutrients for plant growth. Sodium, however, although generally an abundant element in soil, is not considered an essential plant nutrient but it is known to improve the growth of certain plant species and is readily taken up by plants including grapevines.

Tables 4 and 5 summarise the data for the total levels of these four elements found in all the compost samples. Given that all the composts were produced from plant derived material, the most likely form of these elements will be as cations and these four elements are the major contributors to the soluble salts mentioned in Section 3.1.
As the compost further degrades and/or is modified by natural processes in the environment, these elements are likely to be released to the soil.

The proportions of the exchangeable cations present in the composts are also shown in Tables 4 and 5. In the case of potassium, it can be seen that most of it is in the exchange complex of the composts, hence freely available to plants and not bound up in any complex forms. All the sodium present in the compost samples was also found to be in exchangeable form and hence readily water soluble and mobile. The sodium levels in the grape marc were generally fairly low and no cause for any concern with respect to adverse effects on soil health. Significantly higher levels of sodium were detected in both of the non grape marc derived composts. Nevertheless, sodium levels should always be carefully monitored. Studies on the effects of sodium chloride additions to Cabernet Savignon vines grown in pots (Downton,

1977) indicated that high levels of sodium chloride can adversely affect vine growth. Monitoring of soil electrical conductivity is indicative of any potential problems (see Section 3.2).

A high level of potassium was present in all the grape marc composts, ranging between 2-3% w/w, and was still abundant in the composts not originating from grape marc, though significantly less by a factor of four to six. The potassium issue will be discussed in Section 3.3.2.

Table 4. Total Potassium (K) and Sodium (Na) in Composts

Sample	Total K ppm	% K w/w	% of total K in exchange complex	Total Na ppm	% Na w/w	% of total Na in exchange complex
COMPOSITE DE BORTOLI GRAPE MARC	31000	3.1	100	420	0.042	100
DE BORTOLI 'WORM DEVOID' GRAPE MARC	24000	2.4	100	370	0.037	100
DE BORTOLI 'WORM RICH' GRAPE MARC	26000	2.6	100	410	0.041	100
HENKELL GRAPE MARC	32000	3.2	100	740	0.074	100
MITCHELTON 1 YR OLD COMP GRAPE MARC	27000	2.7	100	400	0.040	100
MITCHELTON FRESH 3 MTH OLD GRAPE MARC	24000	2.4	100	550	0.055	100
YARRA RIDGE (RACECOURSE) GRAPE MARC	23000	2.3	100	530	0.053	100
GREENWASTE COMP EX MITCHELL CITY COUNCIL	5400	0.54	95	1700	0.17	95
COLES SUPERMARKET COMPOST EX COLLEX	5500	0.55	95	2400	0.24	95

Table 5. Total Calcium (Ca) and Magnesium (Mg) in Composts

Sample	Total Ca ppm	% Total Ca w/w	% of total Ca in exchange	Total Mg ppm	% total Mg w/w	% of total Mg in exchange
COMPOSITE DE BORTOLI GRAPE MARC	6200	0.62	Not determined	2100	0.21	n.d
DE BORTOLI 'WORM DEVOID' GRAPE MARC	6500	0.65	Not determined	1600	0.16	n.d.
DE BORTOLI 'WORM RICH' GRAPE MARC	5500	0.55	34	1700	0.17	54
HENKELL GRAPE MARC	9800	0.98	22	2500	0.25	50
MITCHELTON 1 YR OLD COMP GRAPE MARC	5200	0.52	38	1600	0.16	55
MITCHELTON FRESH 3 MTH OLD GRAPE MARC	5400	0.54	29	2200	0.22	33
YARRA RIDGE (RACECOURSE) GRAPE MARC	8800	0.88	28	2200	0.22	49
GREENWASTE COMP EX MITCHELL CITY COUNCIL	5900	0.59	52	5000	0.50	20
COLES SUPERMARKET COMPOST EX COLLEX	11000	1.1	31	1600	0.16	70

After potassium, calcium, an essential plant macronutrient, was the next most abundant element present in all the compost samples. Levels of calcium ranged between 0.5-1% w/w with the highest abundance occurring in the Coles supermarket waste compost at slightly over 1% w/w (Table 5). The elevated calcium level in this sample was likely to have arisen from the addition of some lime to control the pH during the composting process. It was not known whether lime or any other calcium source had been added to any of the grape marc composts. The calcium present in the grape marc samples is beneficial and when applied in the vineyard, would achieve the benefit of replacing what has been removed through the grape crop and any other plant material which might be removed. The total calcium measured was only partially available in exchangeable form in the grape marc composts and the Coles Supermarket compost, ranging between 20 and 35 %w/w of the total. The level was higher in the Mitchell City Council greenwaste compost (52 %w/w).

Magnesium, also an essential plant macronutrient, was present in all the grape marc derived compost samples in the range of 0.1-0.2% w/w. This is in the typical of range of magnesium levels in plant derived material. The fraction of the total magnesium in exchangeable form was around 50 %w/w in all the grape marc composts except the Mitchelton three month old sample. This result is consistent in that an immature compost will still retain cations in plant materila that has not completely broken down. The Mitchell City Council compost gave a lower value for exchangeable magnesium. This compost is derived from more heterogeneous plant material inputs. Further sampling over a time period would need to be done to determine the variability in all the parameters measured for this particular compost. The Coles Supermarket compost gave the highest value for the proportion of total magnesium that was exchangeable, approximately double that of any of the grape marc composts.

Magnesium deficiency in vineyards is possible, particularly in sandy soils, and can be corrected by the appropriate use of fertiliser. As for calcium, grape marc compost applications in the vineyard serve to replace the magnesium removed through biomass taken out. Oversupply of magnesium itself is not likely to be a problem.

3.3.2 Potassium Levels in the Grape Marc Composts

Potassium is an essential plant macronutrient, which concentrates in grape skins and is consequently found in elevated levels in grape marc composts. The potassium in plants occurs in the form of potassium ions (K^+) in the plant cells. It has important functions in activating plant enzymes (Brady and Weil, 2002), controlling osmotic water potential, regulating photosynthesis and a number of other important roles.

Potassium also affects berry size and vine tolerance to disease and stress. It is readily taken up by the vines and may lead to higher levels in the grape juice when higher levels are present in the soil.

There are many reports in the literature (for examples see: White, 2003; Munday and Agnew, 2002; Morris et al., 1980) that discuss the effects of high soil potassium levels on vine growth, grape juice quality and hence wine quality and wine stability. High potassium levels in the juice alter the ratio of malic to tartaric acids, leading to an increase in the pH of the wine. A study in New Zealand (Munday and Agnew, 2002) indicated that soil type must be taken into consideration when disposing of grape marc composts or mulches into the vineyard. In that study, high levels of composted grape marc were applied to different soil types in vineyards and a noticeable elevation in soil potassium levels was measured. Application rates in the order of 120 tonne/ha were used and assuming a 50% moisture content, this amounts to 60 tonne/ha of compost on a dry basis. The compost contained about

1.2% w/w of potassium, and this amounted to an application of 720 kg of K per hectare! This is a very high rate of application of potassium. A similar Australian study (Smith, 2002) also used high rates of application of composted grape marc and positive effects on soil fertility and vine growth were observed.

High potassium levels in the soil can also lead to magnesium deficiency and severe imbalances with nitrogen levels can cause a false K deficiency effect (White, 2003).

The results of this investigation found elevated levels of potassium in all the grape marc composts that were analysed, and were at levels consistent with previous literature reports. Potassium levels ranging between 2-3% w/w (dry basis) were observed in all the grape marc composts tested. Despite the ready solubility of potassium and hence its availability for easy leaching, it still remained at high levels in the oldest grape marc sample tested (Yarra Ridge) where a longer period of exposure to rainfall might have caused considerable potassium losses. The same trend was observed in the Mitchelton grape marc compost samples, where a slight increase in potassium levels was measured in the twelve month-old sample, compared to the 3 month old sample. These observations are consistent with the role of potassium as the significant cation in the exchange complex of the grape marc composts.

Potassium replacement is important, however, when excess potassium is available, plants have a tendency to take up far in excess of their needs. Grapevines have the potential to do so and consequently, the risk of elevated levels in grape juice is real. The close monitoring of potassium levels in the vineyard soil is important for good potassium management. Some potassium will be released from the weathering of soil minerals, so despite losses of potassium through leaching or removal of plant material, only a proportion of what is lost may need to be replaced. The losses will vary depending on soil type, climatic conditions and vineyard management practices.

Grape marc compost can be regarded as a low-grade potassium fertiliser and consequently the way it is used needs careful consideration of the above issues. Beresford (2002) has highlighted this problem and end use decisions about grape marc compost use need to be made according to reliable information on soil characteristics and nutrient content. A typical grape marc compost containing 2% w/w of potassium on a dry basis would supply 200 kg of potassium per hectare if applied at a rate of 20 tonne per hectare, assuming the compost contained 50% moisture.

This level of potassium application is within the range of recommended potassium replacement treatments published in fertilizer technical guides. (e.g see Robinson, 2001; Caspari, 1995; OMAF, 2003; Spectrum Analytic, 2004). As pointed out by Robinson (2001), the actual application rate per hectare may be significantly greater given that the compost is generally applied in a narrow strip between the rows of vines.

3.3.3 Phosphorus and Nitrogen

Total phosphorus and nitrogen levels, as well as the major soluble forms of these elements for all the composts are summarised in Table 6. Total phosphorus levels in all the grape marc composts ranged between 0.2 - 0.3 % w/w (2000-3000 ppm). The plant available form was significantly lower with most of the grape marc composts falling between 50-100 ppm. The non grape marc derived composts contained significantly lower amounts of available phosphorus. Coles supermarket compost, despite its relatively high total phosphorus content (~0.2% w/w), only released 18 ppm in the available form.

The pH of the compost and the nature of the cations present significantly influence available phosphorus levels. Henkell grape marc compost gave the lowest proportion of available P relative to the total phosphorus present (~2.6%). This compost also had the highest calcium content of the grape marc composts and the highest pH. Plants take up phosphorus in the form of phosphate anions (PO_4^{3-}, HPO_4^{2-} and $H_2PO_4^-$). At higher pH, the PO_4^{3-} form will predominate and this anion forms a relatively insoluble calcium phosphate salt ($Ca_3(PO_4)_2$). The Henkell grape marc compost contained a higher level of calcium and had the highest pH of all the composts examined. This explanation is supported by the relatively low proportion of total P measured as available in the Coles supermarket compost (~0.9%) where the highest calcium content was observed.

The phosphorus available in the grape marc composts is likely to be released if applied to more acidic vineyard soils, such as those of the Yarra Valley.

Table 6. Phosphorus (P) and Nitrogen (N) in Composts

Sample	Total P (ppm)	Soluble P (ppm)	Total N (% w/w)	Ammonium N (mg/L)	Nitrate-N (mg/L)
COMPOSITE DE BORTOLI GRAPE MARC	2900	120	2	<5	3.1
DE BORTOLI 'WORM DEVOID' GRAPE MARC	3100	100	2.2	<5	3.3
DE BORTOLI 'WORM RICH' GRAPE MARC	2700	120	2.2	10	<5
HENKELL GRAPE MARC	3100	82	1.9	<5	21
MITCHELTON 1 YR OLD COMP GRAPE MARC	1900	72	1.5	13	1.4
MITCHELTON FRESH 3 MTH OLD GRAPE MARC	2500	97	1.2	21	<5
YARRA RIDGE (RACECOURSE) GRAPE MARC	1700	68	1.7	<5	4.4
GREENWASTE COMP EX MITCHELL CITY COUNCIL	750	9	0.45	<5	<5
COLES SUPERMARKET COMPOST EX COLLEX	2000	18	0.93	7.1	21

The total nitrogen levels in the grape marc composts were approximately in the 1-2 % w/w range. Slightly lower nitrogen levels were measured in the Mitchelton composts (1.2 %w/w and 1.5 %w/w for 3-month and 1-year old respectively) compared with the Yarra Valley samples where nitrogen levels were around the 2 %w/w value. The lower level for the Mitchelton samples may reflect the manner in which the compost was prepared, particularly where other components have been blended into the mix (e.g sawdust has a lower level of total nitrogen than grape skins). The Mitchell City Council greenwaste compost had the lowest level of nitrogen of all samples. It is likely that the greenwaste compost contains more "woody" input material and this also lowered the total nitrogen level. This Mitchell City Council compost also gave the highest C:N ratio and greatest nitrogen drawdown effect (See Section 3.3.4). Coles Supermarket compost, however, gave a total nitrogen level of about 0.9 %w/w. While this compost has some sawdust blended into it, a significant amount of non-woody biomass (vegetable and fruit waste) makes up the biomass input.

An important result obtained for all the composts, including those not containing grape marc, was that ammonium and nitrate levels were very low. No Yarra Valley grape marc compost

exceeded 10 mg/L in ammonium ion (NH_4^+). Nitrate levels (NO_3^-) were all less than 5 mg/L in the Yarra Valley samples except for the Henkell grape marc compost (21 mg/L). The Mitchelton one year old grape marc compost was slightly lower in nitrate than the three month old sample (13 mg/L and 21 mg/L respectively) and both Mitchelton samples were below 5 mg/L in nitrate.

The ammonium and nitrate forms of N in the soil, are those utilised by plants and microorganisms. Of the total nitrogen present in the compost samples, these "available" forms are very low. This suggests that most of the total nitrogen is bound into the organic matter, which can be slowly released over time. As such, there is less likelihood of a nitrogen oversupply unless a flush in mineralisation occurred due to favourable climatic conditions (Robinson, 2001). Estimates of nitrogen fertiliser requirements for vineyards are in the range of 20-30 kg per hectare of actual nitrogen (White, 2003; Robinson, 2001). Hence, assuming an application of 10 tonne/ha (= 20 tonne/ha on a dry matter basis) of a typical grape marc compost taken from this study, the actual nitrogen applied would be 150 kg/ha (1.5 %w/w N). This exceeds the recommended levels of nitrogen applied through a fertiliser. However, the important factor is the availability of the nitrogen in the total nitrogen applied. This value is low (5-10% estimated as available) compared to the total nitrogen present in the grape marc composts examined in this study. Nevertheless, nitrogen input and balances must be carefully considered when returning grape marc composts into the vineyard.

3.3.4 Organic Matter, Carbon and the C:N ratio

Table 7. Organic Matter, Carbon:Nitrogen Ratio, Total Carbon, Total Nitrogen, Nitrogen Drawdown Index for Composts

Sample	Organic Matter (%Loss on Ignition @ 550 °C)	C/N Ratio (calc. From Leco)	Total Carbon % (w/w)	Total Nitrogen (% w/w)	Nitrogen Drawdown Index (150 mg N/L)
COMPOSITE DE BORTOLI GRAPE MARC	74	19	37	2	0.5
DE BORTOLI 'WORM DEVOID' GRAPE MARC	70	19	42	2.2	0.6
DE BORTOLI 'WORM RICH' GRAPE MARC	75	18	40	2.2	1.6
HENKELL GRAPE MARC	54	15	28	1.9	0.7
MITCHELTON 1 YR OLD COMP GRAPE MARC	62	21	32	1.5	0.2
MITCHELTON FRESH 3 MTH OLD GRAPE MARC	44	21	25	1.2	0.1
YARRA RIDGE (RACECOURSE) GRAPE MARC	70	21	35	1.7	0.5
GREENWASTE COMP EX MITCHELL CITY COUNCIL	55	40	18	0.45	<0.1
COLES SUPERMARKET COMPOST EX COLLEX	50	26	24	0.93	0.1

The percentage of organic matter and proportion of total carbon in all the composts tested is summarised in Table 7. Total nitrogen figures have been repeated in this table for comparison with the Carbon:Nitrogen ratio. As mentioned previously, a large proportion of the nitrogen present in the composts is likely to be in organic forms.

The highest levels of organic matter in the grape marc composts was found to be around 70 %w/w in the Composite De Bortoli and Yarra Ridge samples from the Yarra Valley. The mature Mitchelton grape marc compost consisted of about 60 % w/w organic matter and the Mitchelton immature three month old marc was lower in organic matter at 44 %w/w. Organic matter contents of grape marc compost reflect the blend of ingredients used to produce the compost, as well as the loss of fresh organic matter through carbon mineralisation during composting. Apart from the Henkell grape marc compost (55 %w/w organic matter), the non grape marc derived composts gave lower organic content values ranging from 50-55 %w/w organic matter. Inbar and co-workers (1988) obtained organic matter contents of around 90% w/w for composted grape marcs. The discrepancy in values is likely to be related to the inputs to the composting process and the method of analysis of the organic matter. Incomplete breakdown of the organic matter through charring (the analysis method used in this study) would lead to a lower loss on ignition.
In general, the carbon content measured in all the grape marc compost samples amounted to 50-60% w/w of the total organic matter measured. The lowest carbon content was found in the Mitchell City Council Greenwaste compost. Without knowledge of how the greenwaste was treated, no plausible explanation can be offered for this observation.

The carbon to nitrogen ratio is an important parameter to consider with respect to applications of compost onto soil. Soil microbes require an appropriate balance between available carbon sources and nitrogen in order to metabolise carbonaceous materials (Brady and Weil, 2003). Typical carbon:nitrogen (C:N) ratio in the range of 20-25:1 are required in order to maintain optimum microbial activity. If the C:N ratio exceeds 25:1, the microbes will deplete the nitrogen in the soil solution, leading to a nitrogen deficiency in higher plants. Conversely, a low C:N ratio has the potential of providing too much nitrogen, leading to unwanted growth flushes, when conditions are right.

The C:N ratio of six out of the seven grape marc compost samples investigated showed a remarkable consistency with all values falling in the range 19-21. Even the two Mitchelton samples of different maturity gave the same C:N ratio. The exception to these observations was the Henkell sample which gave a C:N ratio of 15. Previous mention was made of the fact that the Henkell sample was also lower in seed content (35%) and the grape marc appeared to be better degraded. The non grape marc derived composts, in contrast, gave higher C:N ratios of 26 and 40 for the Coles Supermarket compost and Mitchell City Council compost respectively.

The C:N ratio found for most of the grape marc compost samples in this study are remarkably consistent with the figures reported in other studies (Inbar, 1988 and 1991; Mundy and Agnew, 2002) where C:N values in the range of 20-23 were observed. Ideally, the C:N ratio of the compost should not exceed 20:1 (White, 2003; Small and Somers, 2002-2003) and slightly lower values are preferable. Under carefully controlled composting conditions the C:N ratio will decrease as the compost matures (Inbar, 1988).

If C:N ratios exceed 25,the risk of nitrogen drawdown increases considerably. The nitrogen drawdown indices for the compost samples investigated are shown in Table 7. The nitrogen drawdown index was determined by charging the sample with a solution of potassium nitrate

and then determining the proportion of applied nitrate remaining after 96 hours of incubation. The non grape marc derived composts gave the lowest values, particularly the Mitchell Council Greenwaste compost with a value below one. This would be expected given the high C:N ratio for this compost. The very low values in these samples indicated that the nitrate (and hence available nitrogen) was readily immobilized by microbial activity. Excessive use of these composts can cause nitrogen deficiency in soil for a period of time.

The Mitchelton grape marc composts also gave fairly low nitrogen drawdown values with the three month old marc compost (0.1), slightly lower than the one year old sample (0.2). This result would be expected, given the greater biological activity in the younger compost. The Mitchelton grape marc composts have considerable potential to immobilise nitrogen.

All the Yarra Valley compost samples fell in a nitrogen drawdown index range of 0.5-0.7 except for the De Bortoli "Worm Rich" sample (1.6). A value exceeding one indicates that more nitrogen is being released or mineralised than the amount that was added through the treatment. This is likely to be associated with high biological activity in that part of the compost pile where this sub-sample was collected. The earthworm activity, not observed in any other sample collected is a likely contributor to this mineralisation. The results for the other Yarra Valley grape marc compost samples indicate ongoing biological activity with the potential to immobilise some nitrogen.

Compost maturity and prevailing conditions will ultimately determine the nitrogen dynamics. Eventually, a significant part of the nitrogen that is immobilised into complex organic forms through microbial activity, will be released.

3.3.5 Total Sulphur (S), Chloride (Cl^-) and other anions

Sulphur is an essential plant nutrient and S-deficient soils have been reported in parts of Gippsland and on the South Australian border. Generally sulphur occurs in organic forms and is mineralised to sulphate anion (SO_4^{2-}) through microbial activity. Plants take up sulphur as the sulphate anion. Sulphur deficiency is generally not an issue in vineyards and may be easily addressed by applications of gypsum (calcium sulphate). The total sulphur content of all the grape marc composts examined in this study ranged between 0.1-0.2 %w/w (Table 8). The sulphur was likely to be partly in organic forms and partly as sulphate anion.

Table 8. Total Sulphur and Chloride (Cl^-)

Sample	S (mg/kg)	Cl^- (mg/L)
COMPOSITE DE BORTOLI GRAPE MARC	2000	52
DE BORTOLI 'WORM DEVOID' GRAPE MARC	1800	50
DE BORTOLI 'WORM RICH' GRAPE MARC	2000	38
HENKELL GRAPE MARC	1700	73
MITCHELTON 1 YR OLD COMP GRAPE MARC	1300	<10
MITCHELTON FRESH 3 MTH OLD GRAPE MARC	1400	42
YARRA RIDGE (RACECOURSE) GRAPE MARC	1600	24
GREENWASTE COMP EX MITCHELL CITY COUNCIL	800	130
COLES SUPERMARKET COMPOST EX COLLEX	2500	2200

Chloride ion levels in the grape marc composts were all relatively low, the highest concentration being 73 mg/L in the Henkell sample. This is equivalent to approximately 93 mg/kg. Chloride ions are associated with higher levels of sodium (Na^+) ion. Chloride is taken up by vines and higher levels are detrimental to plant growth and wine quality (White, 2003). Chloride levels in the soil should not exceed 1050 mg/L (measured in a saturation extract). The levels in all the grape marc compost samples are well below the levels considered to present a problem in the soil of a vineyard (White, 2003). The Coles Supermarket compost, however, displays a high level of chloride (and sodium -see Section 3.3.1) and its applications onto soil could pose a risk of generating salinity problems.

The other significant cation present in all the compost samples was carbonate (CO_3^{2-}). This was measured indirectly by treatment of the compost sample with acid and titration of the unreacted acid with sodium hydroxide (See document AS4454-1999, Appendix G in Appendix 2). A calcium carbonate equivalent is determined. The presence of the carbonate anion is reflected in the pH values of the compost, which are all above 7.

3.3.6 Micronutrients - Manganese (Mn), Iron (Fe), Zinc (Zn), Copper (Cu) and Boron (B)

Essential micronutrients required by grapevines include copper, zinc, manganese, molybdenum, iron and boron. Apart from iron, which is relatively abundant in soil, the other elements occur in trace levels. Soil pH plays an important function in regulating the availability of the trace elements to the plant. Manganese, iron, zinc and copper deficiencies can occur in vineyards when soil pH is above 7 (White, 2003).

Table 9. Micronutrients: Total Copper (Cu), Zinc (Zn), Manganese (Mn), Molybdenum (Mo), Iron (Fe), Boron (B)

Sample	Cu mg/kg	Zn mg/kg	Mn mg/kg	Mo mg/kg	Fe mg/kg	B mg/kg
COMPOSITE DE BORTOLI GRAPE MARC	49	26	43	<10	5100	43
DE BORTOLI 'WORM DEVOID' GRAPE MARC	50	23	38	<10	3000	53
DE BORTOLI 'WORM RICH' GRAPE MARC	65	25	38	<10	3200	47
HENKELL GRAPE MARC	95	34	55	<10	4200	38
MITCHELTON 1 YR OLD COMP GRAPE MARC	52	34	86	<10	4000	23
MITCHELTON FRESH 3 MTH OLD GRAPE MARC	83	62	130	<10	6400	25
YARRA RIDGE (RACECOURSE) GRAPE MARC	58	23	56	<10	2000	25
GREENWASTE COMP EX MITCHELL CITY COUNCIL	20	92	210	<10	37000	<3
COLES SUPERMARKET COMPOST EX COLLEX	32	77	52	<10	3900	8

The levels of micronutrients found in the compost samples are shown in Table 9. The problem with micronutrients is the danger of applying excess amounts where more damage can be done (OMAF, 2003).
Copper levels in the grape marc composts were in the range of 50-100 mg/kg, with the highest level found in the Henkell grape marc compost. Mitchelton three month old grape marc compost was also in the high end of the range (83 mg/kg) and the value was lower in the Mitchelton one year old grape marc compost (52 mg/kg). The copper levels were lower in the non grape marc derived composts. The higher copper levels in the grape marc samples is likely to have resulted from a contribution of copper due to the use of copper containing fungicides. Copper is not very mobile in the soil, particularly where organic matter levels are high and can thus persist for a long time. Optimum levels of copper in grapevines have been reported in the range of 5-35 ppm (mg/kg), depending on time of the year and the part of the plant that is analysed (Caspari, 1995). The level of copper present in the grape marc samples tested is relatively low, however, assuming this was all available to the vines, a 10 tonne/ha (dry basis) compost application should adequately replace the copper removed through the crop.

Zinc levels in all the grape marc composts ranged between 20-30 mg/kg except for the . Mitchelton three month old grape marc compost where an elevated level of 62 mg/kg was measured. The level dropped into the normal range quoted for the mature Mitchelton grape marc compost. It is likely that the zinc, in the form of zinc cations (Zn^{2+}) is released and leached away as the compost matures. The zinc levels were approximately 2-3 times higher in the non grape marc derived composts, with the Mitchell City Council compost giving the highest level. The total zinc levels observed in the grape marc composts were typical of zinc levels (20-50 mg/kg) reported as optimum in grapevines (Caspari, 1995).

The highest manganese level was again found to be in the Mitchelton three month old grape marc compost (130 mg/kg) and was still higher than all the remaining grape marc composts in the Mitchelton one year old compost (86 mg/kg). All the other grape marc composts gave manganese levels in the range of 40-60 mg/kg. The total manganese levels observed were also typical of levels reported as optimum in grapevines (Caspari, 1995). Coles supermarket compost gave a manganese level in the same range as the majority of the grape marc composts. Mitchell City Council compost was notable in that it gave a somewhat higher value than all the compost samples (210 mg/kg). It is possible that some anthropogenic source is the cause of this higher level.

Molybdenum levels in all the compost samples were below 10 mg/kg. Molybdenum availability to plants is controlled by soil pH and molybdenum toxicity is rare (Peverill, 1999). The levels present in the grape marc compost would serve to replenish the soil and not cause any problem.

The levels of iron in all the compost samples were between 0.4-0.5 %w/w except for the Mitchell City Council greenwaste compost where the total iron was 3.7 %w/w. Iron chlorosis (a deficiency) can be a problem in grapevines on calcareous soils (pH > 7). The grape marc composts would all contribute some iron to the soil, how its availability is controlled by soil factors including pH, soil organic matter content and cation exchange properties.

Boron deficiency is one of the more common micronutrient deficiencies found in grapevines. (Caspari, 1995; OMAF, 2003; White, 2003). Boron has an important role in controlling fruit set. It is also fairly readily leached form the soil and becomes unavailable in dry conditions. Boron also displays a narrow tolerance between deficiency and excessive toxic levels.

Higher levels of boron were found in the De Bortoli grape marc composts (43-53 mg/kg). Levels in the other grape marc composts were lower, (20-40 mg/kg) and there was no obvious trend that could be related to the age of the compost. The non grape marc derived composts were lower in boron by a factor of 3-6, with the Mitchell City Council compost giving the lowest value (< 3 mg/kg). Boron levels in the grape marc composts were typical or even below levels reported as optimum in grapevines (Caspari, 1995) and for vineyard soils (OMAF, 2003). The grape marc composts are likely to serve a useful purpose in replenishing soil boron, with little risk of oversupply.

In all cases of fertilising grapevines, soil analysis results and correlation with inputs and outputs of nutrients should be considered when applying any nutrient source to the soil (White, 2003).

3.4 Forms of Carbon in Grape Marc Compost

3.4.1 Humic Substances

The natural transformations of decaying plant materials in composting and soil processes, driven primarily by microbial processes, lead to the formation of humic substances. Generally, the fraction of the carbon from the original biomass, that does not end up lost as carbon dioxide, will be incorporated into the humic fraction. Other important elements such as nitrogen, phosphorus, sulphur and trace elements will also be bound up in the humic fraction. The quantity of humic materials in a compost can be a measure of the effectiveness of the composting process. Humic substances are complex organic molecules with no specific defined structure, characterised or defined according to the solubility of the organic material in acid and alkali (Brady and Weil, 2003). Humic acids are the organic component, which is base soluble, but acid insoluble. Both humic and true fulvic acids are known to contain higher proportions of carboxylic acid functional groups and phenolic groups. The fulvic acid fraction is the organic material that is acid and base soluble. Unless the extraction procedure was conducted to remove other non-acidic, soluble components, this fraction will also contain other compounds and not simply organic acids (e.g. carbohydrates, amino acids). The humin fraction is that component of the organic material that is not soluble in either acid or base.

Table 10 gives the results of humic acid extraction on the composts examined in this study. All the grape marc composts gave very low values for humic acid and fulvic acid content. The quantity of humic acid extracted correlated with the total carbon values present in the compost with the Henkell grape marc compost, which had the lowest carbon level, also giving the lowest humic acid content. These values were very low compared with the results obtained on grape marc composts by Inbar et al. (1992) where up to 40% of the organic material was measured as humic acid. This value decreased during the composting period. It should be noted that the grape marc composts collected for this study were not prepared under the strictly designed experimental design conditions reported in the literature.

Several explanations can be offered for the differences observed. It is possible that organic material was lost through leaching in the early stages of composting, before the compost is mature when a greater fraction of soluble organic matter is present. Coles Supermarket compost gave a low humic acid value but high fulvic acid result. As mentioned previously, this material was still biologically active and composting was still occurring. This supports the hypothesis concerning the grape marc composting process. Conversely, it is also possible that the composting had produced a high humin fraction, again linked to the different processes employed and "maturity" of the products. The presence of carboxylic acid

functional groups was detected in the spectral data (see Section 3.4.2), thus there is good evidence that some humification had occurred.

Table 10 Humic Acid, Fulvic Acid and Humin Content of Composts

Sample	%Humic Acid	%Fulvic Acid	%Acid/Base Insolubles (includes Humin)
COMPOSITE DE BORTOLI GRAPE MARC	1.3	0.6	88
DE BORTOLI 'WORM DEVOID' GRAPE MARC	1.7	0.5	79
DE BORTOLI 'WORM RICH' GRAPE MARC	1.4	0.7	90
HENKELL GRAPE MARC	0.4	0.6	63
MITCHELTON 1 YR OLD COMP GRAPE MARC	1.2	0.6	80
YARRA RIDGE (RACECOURSE) GRAPE MARC	0.9	0.5	93
COLES SUPERMARKET COMPOST EX COLLEX	0.7	35	~60
DE BORTOLI 'PALE'	1.5	1.2	85

Fulvic acid quantities quoted are best estimates only. They were determined indirectly by pooling the fulvic fractions and analysing for Total organic carbon. Calculations of fulvic acid content were then carried out on the basis that the total volume of fractions analysed was 35 mL, and that fulvic acid contained 60 % organic carbon.

The acid/base insoluble fraction also includes inorganic material. The carbon content in that fraction or residue was not determined.

Good levels of humic substances in composts are beneficial and desirable. The lower molecular weight fraction of this material (mainly the fulvic fraction) provides a carbon source for microbial activity. The higher molecular weight or more aggregated component (i.e the humic and humin fraction) provides useful organic matter to soil, which improves the soil physical properties, improves soil cation exchange capacity, assists in nutrient cycling and also provides a carbon source for microbial activity. The levels of humic materials in grape marc composts can be increased by systematic management of the composting process, however, more scientific studies are required to establish the best conditions.

3.4.2 Solid-state ^{13}C CP NMR spectra of selected whole grape marc composts and non grape marc derived composts

(This section is reproduced from a report provided by Dr Ron Smernik, Waite Research Institute, University of Adelaide. Some additions have been by Dr Patti)

The "standard" solid-state ^{13}C NMR spectra of a selection of whole grape marc composts and the Mitchell City Council green-waste compost are shown in Figure 1. These spectra were acquired using the cross polarization (CP) technique that is usually used for acquiring ^{13}C NMR spectra of organic matter. The spectra of the grape marc composts are fairly similar to each other, with a number of strong and sharp resonances for carbohydrates in the 60-110 ppm range (O-alkyl region) and a substantial contribution from aryl (110-140 ppm) and, particularly O-aryl carbon (140-160 ppm). There are some differences in the relative size of resonances in the carboxyl (160-190 ppm) and alkyl (0-45 ppm) regions. The Mitchell City Council compost sample is clearly quite different, with broader resonances, although the same types of carbon appear to be present, and in similar proportions.

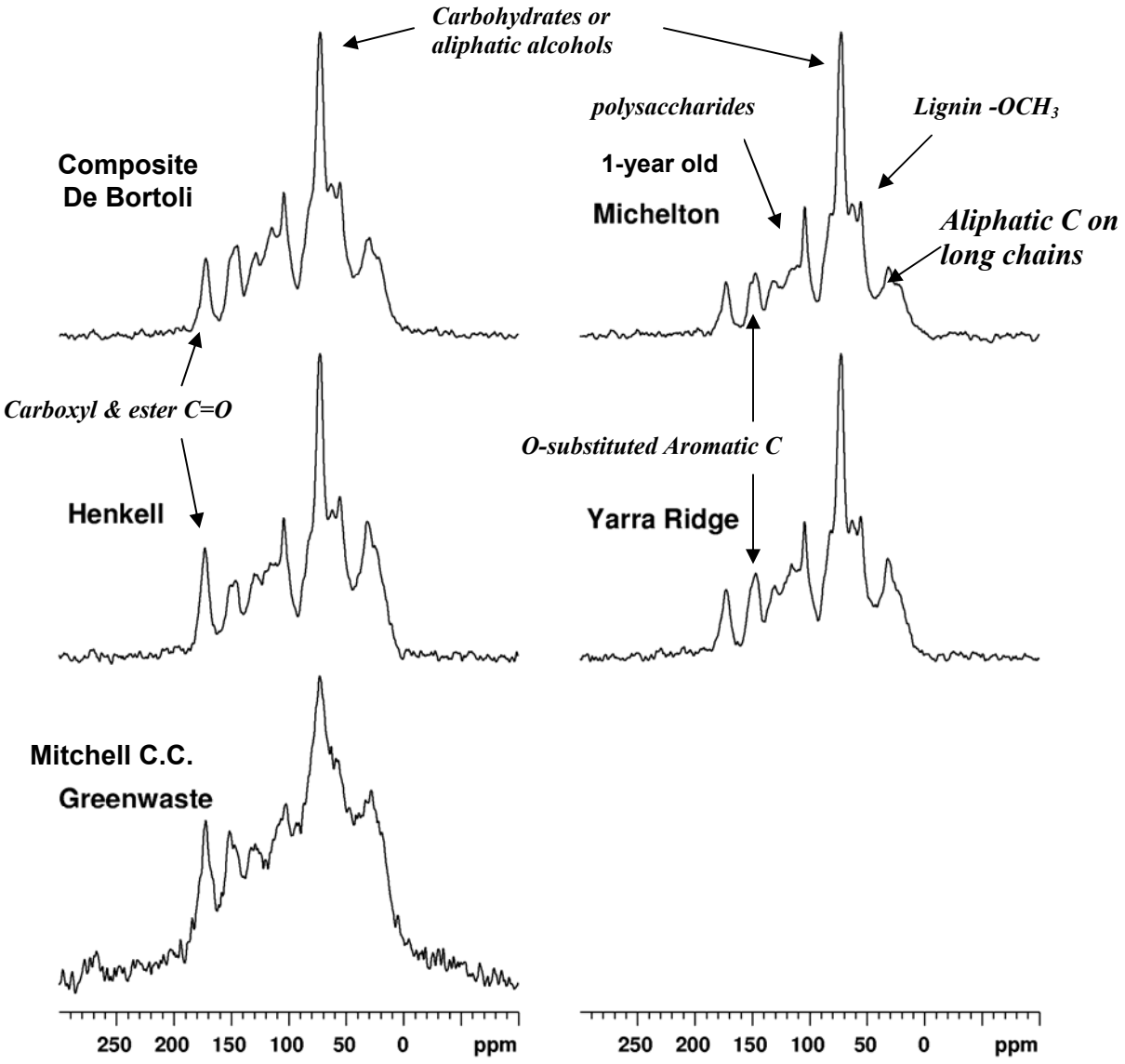


Figure 1: Solid-state ^{13}C CP NMR spectra of whole grape marc composts and Mitchell City Council greenwaste compost.

The grape marc compost spectra shown in Figure 1 bear remarkable similarity to those published by Inbar and co-workers (1991) who examined the changes in the carbon forms over time, during the composting of grape marc. The peak assignments labeled in Figure 1 were according to those published by Inbar and co-workers (1991). The broad peaks in the 20-45 ppm region are due to aliphatic carbon chains, most likely associated to fatty acid, long chain alcohol and ester compounds. The very prominent strong and sharp signals for carbohydrates in the 60-110 ppm range (O-alkyl region) result from cellulose and other polysaccharide material present in the grape marc compost. Tannins have also been reported to contribute in this region with a sharp peak at 108 ppm. The humic/fulvic extraction indicated that only a small part of these carbohydrates were water soluble (see Section 3.4.1). The carbohydrate fraction of the grape marc compost would provide an ongoing carbon source for microbial activity and undergo further transformations when applied in the vineyard.

Aromatic carbons attached to oxygen gave a prominent broad peak in the 140-160 ppm region of the spectra. The remaining aromatic carbon is accounted for by signals between 110 and 140 ppm. The aromatic signals in the spectra are associated with lignin material and this is also correlated by the O-methyl signal at about 58 ppm. Lignin is more resistant to degradation and transformations during composting (Inbar et al., 1991) and is also a higher component in the grape seed.

The carbonyl group region (160-190 ppm) gives a prominent broad peak in all the spectra. This is assigned to the carbonyl component in carboxylic acid and ester functional groups. These would partially result from the humification process during composting, but there would also be a contribution from naturally occurring esters and fatty acids present in the compost as remnants of grape seed oil.

The Mitchell City Council greenwaste compost contains the same peaks but gave a more complex spectrum, particularly in the aromatic-C region (110-145 ppm) and carbohydrate region (60-110 ppm). This reflects a more complex mixture of C-substituted and O-substituted aromatic rings, likely to result from lignin residues as well as a greater mixture of carbohydrates from complex polysaccharides. The greater complexity of carbon forms in this compost is to be expected, given that a greater mixture of woody plant materials are likely to be contributors to the greenwaste compost. The Coles Supermarket compost, on the other hand (Fig. 2) was dominated by carbohydrate signal in the range 60-110 ppm. The presence of some lignin material is supported by the shoulder at 57 ppm ($O\text{-}CH_3$ of lignin) and aromatic carbon signals in the range 110-160 ppm, particularly the broad peak at 153 ppm (O-substituted aromatic C).

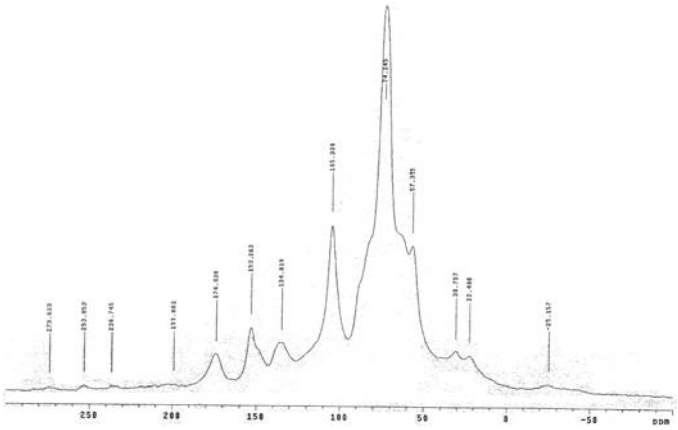


Figure 2: Solid-state ^{13}C CP NMR spectrum of Coles Supermarket compost

The addition of some sawdust to the vegetable waste before composting explains the presence of the lignin. The carbonyl signal due to carboxylic acids and esters appears at 174 ppm. This agrees with the significant quantity of fulvic acid that was detected in the Coles supermarket compost, indicating that the carboxylic acids are the major contributor to this signal. The weak aliphatic signal in the Coles Supermarket compost was also consistent with a raw material input (vegetable waste) that has little aliphatic material in it (e.g. oils and fatty acids).

3.4.3 Seed and No-seed Comparison in ^{13}C CP NMR spectra of grape marc composts

The solid-state ^{13}C CP NMR spectra of the whole and fractionated De Bortoli and Mitchelton grape marc composts are shown in Figure 3. The whole and seed only fractions appear quite similar, whereas the no seed fraction is much richer in alkyl and carboxyl-C for the De Bortoli grape marc only. The result was surprising in that the seed might be expected to produce a stronger alkyl signal due to the presence of grape seed oil. It is possible that all the alkyl signal is not being detected (see Section 3.4.4). In addition, a significant aliphatic component in the grape marc composts is arising from other sources in the parent plant material (Inbar, 1992). The difference between the two "no seed" samples cannot be explained and may be linked to how the compost was produced.

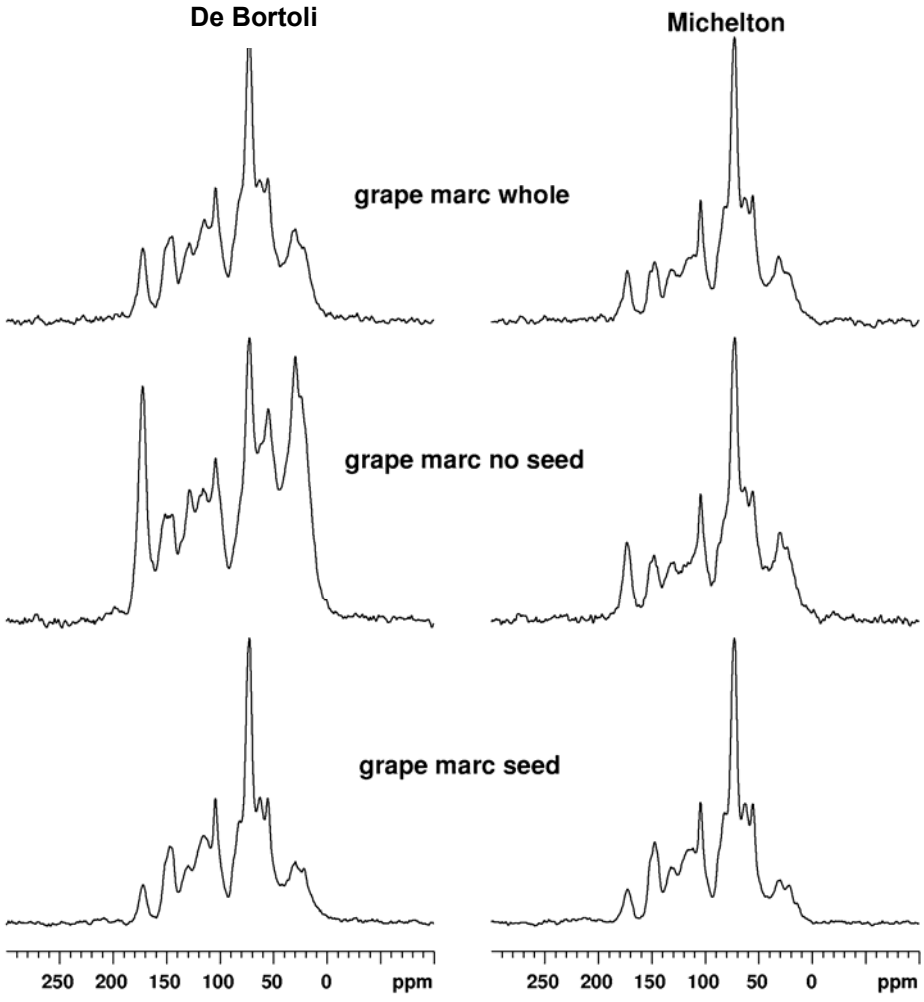


Figure 3: Solid-state ^{13}C CP NMR spectra of whole and fractionated (no seed and seed) De Bortoli and Mitchelton grape marc composts.

3.4.4 Quantitation issues in Solid-State ^{13}C CP NMR spectra

Changes in the proportion of signals in the different regions of the spectrum, are often used to assess properties of organic matter, in particular, changes that may occur over time or under different conditions. Various studies have found that increasing degradation increases the proportion of aryl C, carboxyl C or the alkyl-C: O-alkyl C ratio. These can be calculated once a set of integral regions is defined. The spectra are divided into a set of regions according to the type of carbon that absorbs and the area under the peaks of each region is determined.

There are a number of issues with the quantitative interpretation of solid-state ^{13}C CP NMR spectra of organic matter samples. Indeed, the technique is often described as "qualitative" or "semi-quantitative". Quantitation issues can be dealt with using a technique known as spin counting. This simply involves calibrating the strength of the NMR signal of the sample against that of a reference known to give a quantitative signal. Glycine is an example of a reference compound that can be used for this purpose. The details of the technique were described by Smernik and Oades (2000a, 2000b).

The output is an "NMR observable C content", which is the amount of carbon signal that was detected for the sample, per unit mass. If the actual C content is known then this can be expressed as an "NMR observability" (i.e. "NMR observable C content"/ actual C content). All of the sources of quantitation problems in solid-state ^{13}C NMR spectra of organic matter involve under-detection of signal. Therefore, if the NMR observability is close to 100%, then it can safely be assumed that the NMR spectrum is quantitative, and that the distribution of signal in various NMR chemical shift regions accurately reflects the distribution of carbon types. If the NMR observability is considerably less than 100%, then some potential NMR signal is not being detected. How this affects the reliability of NMR to determine the distribution of carbon types depends on whether the signal under-detection is selective (only some carbon types are under-detected) or non-selective (all carbon types are under-detected to the same extent).

Table 11. Spin counting results for grape marc compost samples

Sample	Total C content (%)	$T_{1\rho}H$ (ms)	NMR observable C content (CP) (%)	C_{obs}(CP) (%)	NMR observable C content (BD) (%)	C_{obs}(BD) (%)
Composite De Bortoli whole	38.6	5.46	24.1	62	35.4	92
Composite De Bortoli no seed	33.7	3.86	20.2	60	28.9	86
Compositie De Bortoli seed	49.4	5.69	32.6	66	45.6	92
Henkell	25.4	5.46[a]	15.3	60		
Yarra Ridge	28.4	5.46[a]	16.9	60		
1-year old Mitchelton whole	29.8	5.46[a]	17.4	58		
1-year old Mitchelton no seed	24.8	3.86[a]	14.6	59		
1-year old Mitchelton seed	46.1	5.69[a]	31.8	69		
Mitchell CC Greenwaste	11.0	4.00[b]	3.5	32		

Coles Supermarket compost not analysed. CP - Cross Polarisation. BD -Bloch Decay

Cross Polarisation (CP) refers to the technique used to acquire the spectra. This technique involves the transfer of the magnetization from ^{1}H to the ^{13}C nuclei. Bloch Decay (BD) involves direct polarization (or excitation) of the ^{13}C nuclei directly.

The results of spin counting are shown in Table 11. For the ^{13}C CP spectra, spin counting results included a correction for differences in the $T_{1\rho}H$ relaxation rate between the sample and glycine. This relaxation rate is a parameter that is measured on the instrument and will be characteristic of the sample and the environment of the nuclei under study. The significance of this was discussed by Smernik and Oades (2000a, 2000b, 2001). $T_{1\rho}H$ was not determined directly for all the samples, as this required running additional NMR experiments that would take considerable time and expense (Dr R. Smernik, personal communication). The $T_{1\rho}H$ relaxation rates were measured for the three De Bortoli samples, and these results were used to estimate relevant values for the other samples. The value of 4.00 ms for the greenwaste sample was an educated guess. The NMR observable C contents are in fact not very sensitive to differences in $T_{1\rho}H$, so these estimations are unlikely to cause big errors. Details of the correction are described in the detailed studies of this approach conducted by Smernik and Oades (2000a, 2000b, 2001).

Interpretation of the spin counting results is best considered alongside the actual carbon contents in the sample. The NMR observable carbon contents for the grape marc compost samples were generally around 60% with the Mitchelton one year old seed sample giving the highest value for observable carbon at 69%. These values indicate that some signal is being under-detected, however, if all the undetected carbon is equally representative across all the carbon forms, then this is not a problem. If there is some selectivity in the detection of carbon, comments about the relative quantities of different forms of organic matter must be treated with caution.

The NMR observable C content of the Mitchell City Council greenwaste was particularly low (32%). This is almost certainly due to interference of paramagnetic inorganic impurities. Mitchell City Council greenwaste had the highest total iron content (3.7 % w/w) and iron is paramagnetic. This would also explain the broadness of resonances in the ^{13}C spectrum of this sample (Figure 1).

There is an alternative NMR technique that avoids many of the problems inherent with CP. It is variously called Bloch decay (BD), direct polarization (DP) or single pulse excitation (SPE). Whereas the CP technique involves magnetization transfer from ^{1}H to ^{13}C nuclei, BD involves direct polarization of ^{13}C nuclei. The CP technique gives greater sensitivity, with each scan producing up to four times more signal. CP also allows much more rapid acquisition of scans, as it requires relaxation of ^{1}H nuclei, a process that is much more rapid than ^{13}C relaxation that controls the repetition rate in BD spectra. BD spectra were acquired for the three De Bortoli samples and are shown in Figure 4, beside the corresponding CP spectra.

There are clear differences between the CP and BD spectra. In particular, the alkyl (0-45 ppm), aromatic (110-160 ppm) and carboxyl (160-190 ppm) resonances appear larger in the BD spectra, whereas the carbohydrate or O-alkyl resonances (60-100 ppm) appear smaller. Spin counting on the BD spectra (Table 11) shows that more carbon is detected in the BD spectra, so these differences must be due to under-representation of alkyl, aromatic and carboxyl carbon by the CP technique. Approximately 90% of the carbon is observable in the BD spectra. The most likely explanation of under-representation of alkyl C is the presence of grape seed oil. The CP technique will only detect structures with limited (solid-like)

mobility. Cross polarization breaks down for molecules with liquid-like molecular mobility. The grape seed oil appears to be unsaturated, based on the appearance of extra resonances in the "aromatic" region of BD spectrum of the seed fraction. Alkene carbons also resonate in this region. Under-estimation of carboxyl and aromatic C by CP is fairly common (Smernik and Oades (2000a, 2000b, 2001).

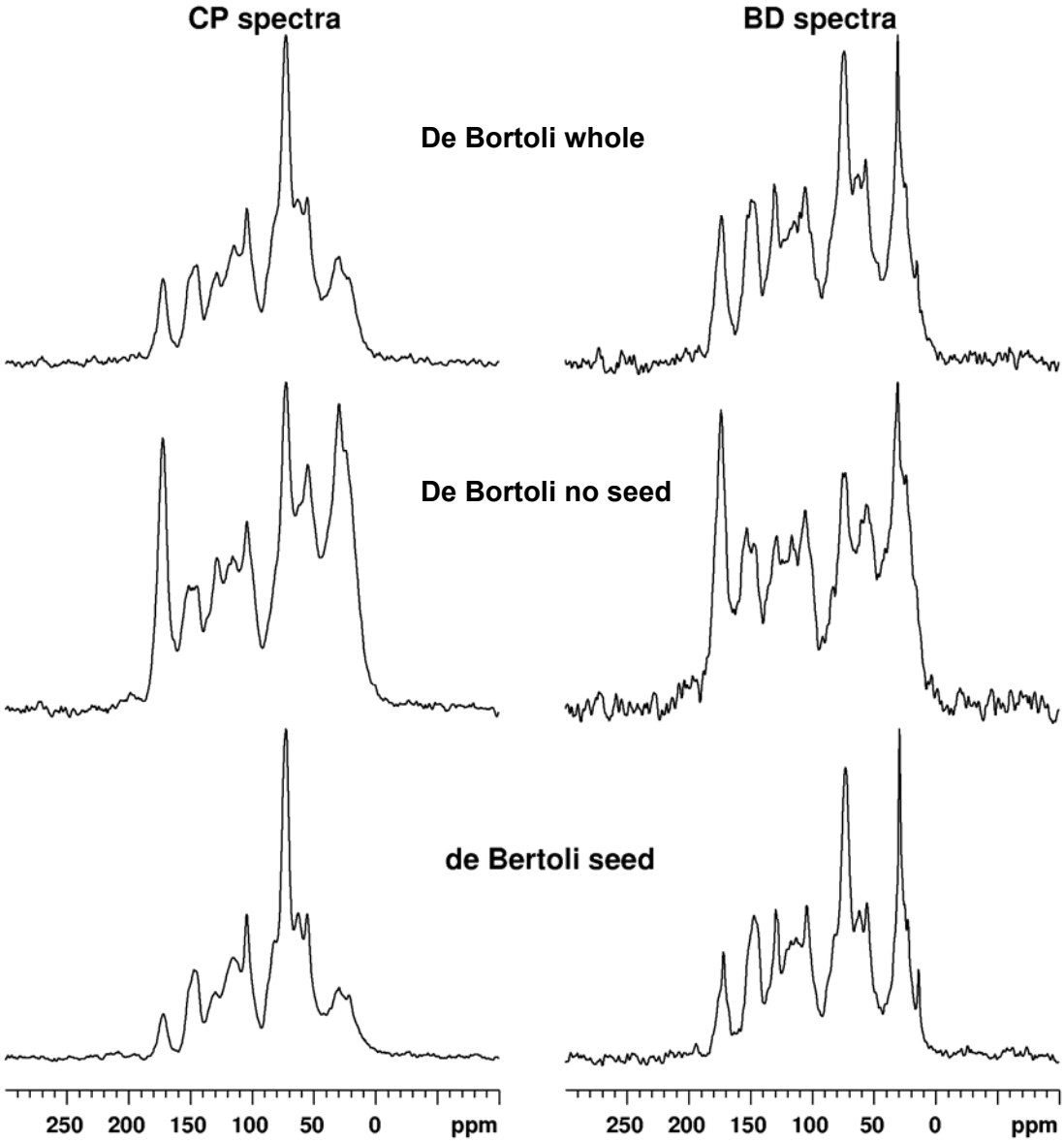


Figure 4: Solid-state ^{13}C CP and BD NMR spectra of whole and fractionated (no seed and seed) De Bortoli grape marc compost.

3.4.5 Relaxation rates

Another potential cause of quantitation problems in CP (and, indeed, BD) spectra is signal "saturation" caused by an inadequate recycle delay between consecutive pulses (This relates to how the spectra were generated on the instrument). Before acquiring each CP spectrum, the relevant T_1H relaxation rate is estimated in order to determine the appropriate recycle delay. The T_1H values were not uniform for most of the samples, and this required undertaking more detailed inversion-recovery experiments to measure this parameter more carefully for the three De Bortoli samples. All the De Bortoli samples exhibited non-uniform T_1H relaxation rates. The average (1-component) T_1H value was much lower for the no seed

fraction (16.2 ms) than for the seed fraction (283 ms), with the value for the whole grape marc falling in between (103 ms). Two-components fits indicated more rapid relaxation rates (10.1 and 134 ms) and a greater proportion of rapidly relaxing component (74%) for the no seed than the seed fraction (22.0 and 539 ms, and 67%, respectively).

This information indicates that the sample is heterogeneous and that there are chemically distinct domains. Applying another type of spectral acquisition technique (proton spin relaxation editing-PSRE) the nature of these domains can be determined. PSRE sub-spectra for the three De Bortoli samples are shown in Figure 5. The PSRE technique is described in detail in Smernik, Skjemstad and Oades (2000)

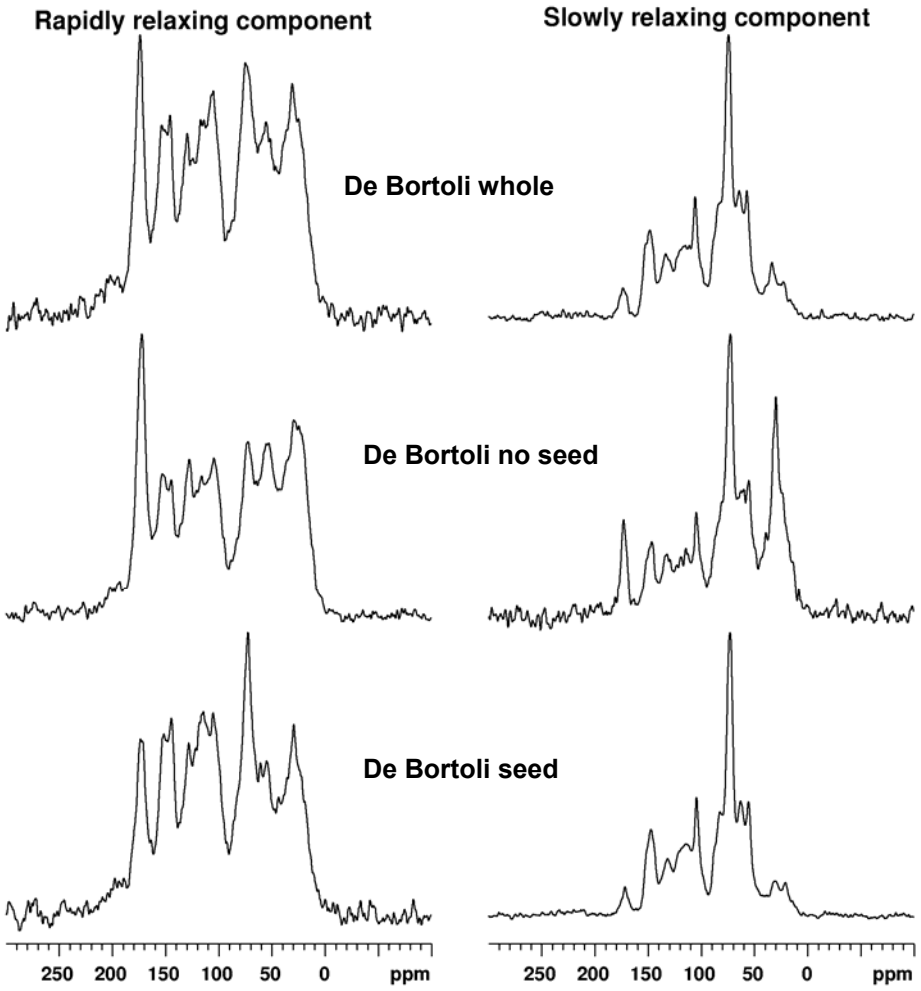


Figure 5: Solid-state ^{13}C PSRE sub-spectra of whole and fractionated (no seed and seed) De Bortoli grape marc compost.

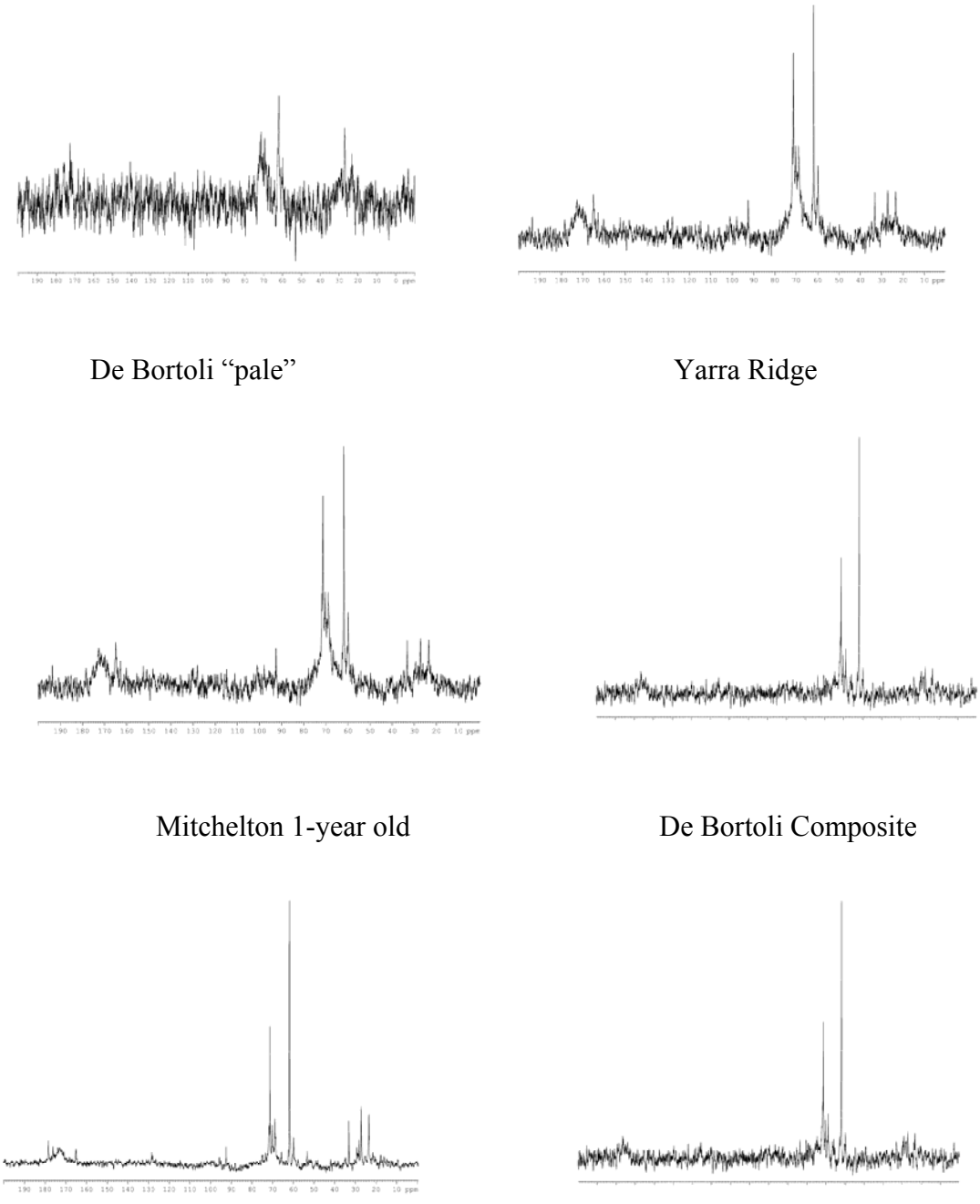
In each case, the slowly relaxing PSRE sub-spectrum is dominated by carbohydrate signals. This suggests that the cellulose component is relatively crystalline and separate from much of the lignin, although there are some small lignin signals in the slowly relaxing sub-spectra. The slowly relaxing sub-spectrum for the no seed fraction differs from the other two slowly relaxing sub-spectra in that it contains much stronger alkyl signal.

3.4.6 Solution NMR: Fulvic Acid from grape marc compost samples

The fulvic acid fraction was measured as a very minor proportion of the overall grape marc compost sample, (see Table 10), however, the solution spectra indicated the nature of the soluble organic material released from the compost. The results of the solution NMR spectra indicated that carbohydrates and carboxylic acids were the major chemical components released in soluble forms.

Carbon-13 Spectra

The spectra of a selection of fulvic acids isolated from the grape marc composts are shown in Figure 6. Some samples are not shown here due to poor spectra, caused by lack of sample.



De Bortoli "pale" | Yarra Ridge

Mitchelton 1-year old | De Bortoli Composite

Henkell | De Bortoli "Worm Rich"

Figure 6: Selected Grape Marc Compost Fulvic Acid fractions - ^{13}C NMR in Solution

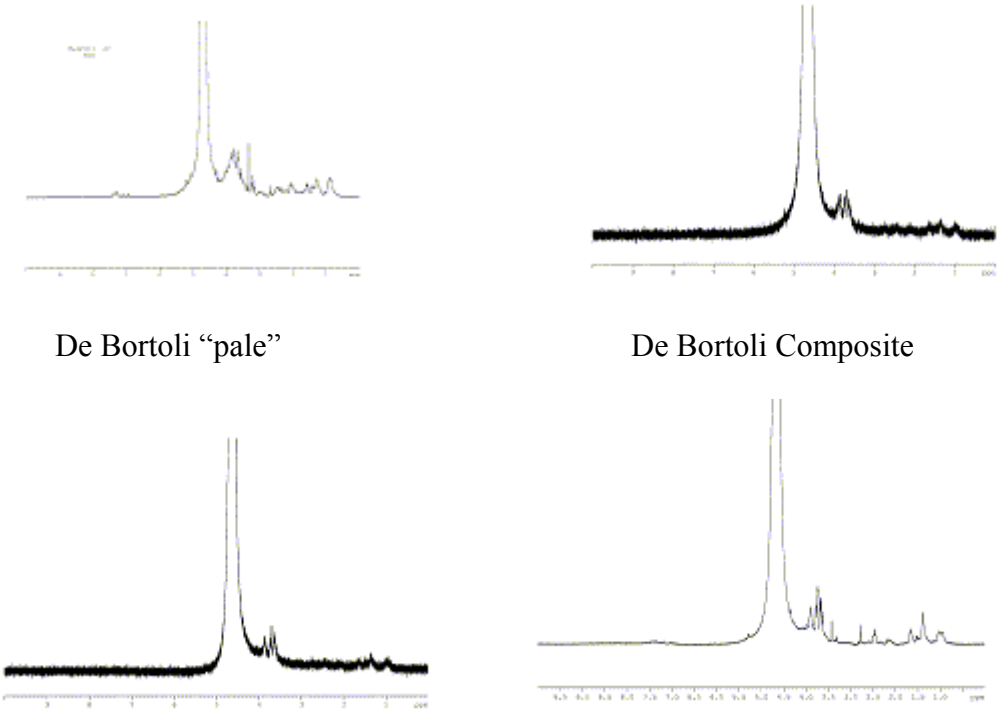
All samples were run in D_2O solvent

A striking feature of all the samples is the remarkable similarity between the spectra. They are also relatively simple spectra compared with those of fulvic materials from soil and sediments, reported in the literature (Thorn, 1987; Frund and Ludeman, 1989). The spectra indicate the presence of carbohydrate material, aliphatic alcohols and carboxylic acids. The three peaks at 24, 28 and 34 ppm are due to alkyl groups attached to carboxylic acid and alcohol functionality. The prominent peaks at 62 and 71 ppm (with other associated peaks in the same part of the spectrum) are consistent with carbons directly attached to oxygen atoms. These are likely to come from carbohydrate material. A small peak at 93 ppm, which occurs in all the spectra, can be attributed to the anomeric carbon of a carbohydrate molecule. The presence of carboxylic acids is evidenced by the broad peak at about 173 ppm.

Proton NMR spectra of Fulvic Acid fractions

The proton nmr spectra of the same fulvic acid solutions examined for carbon-13 are shown for selected composts in Figure 7. All the grape marc composts (both Mitchelton and Yarra Valley samples) gave the same pattern, but the signal:noise intensity was weak, so only a selection of spectra have been illustrated.

The dominant off-scale peak at 4.5-5.0 ppm in all the spectra is due to the residual HDO from the solvent.



De Bortoli "pale" De Bortoli Composite

Henkell De Bortoli "Worm Rich"

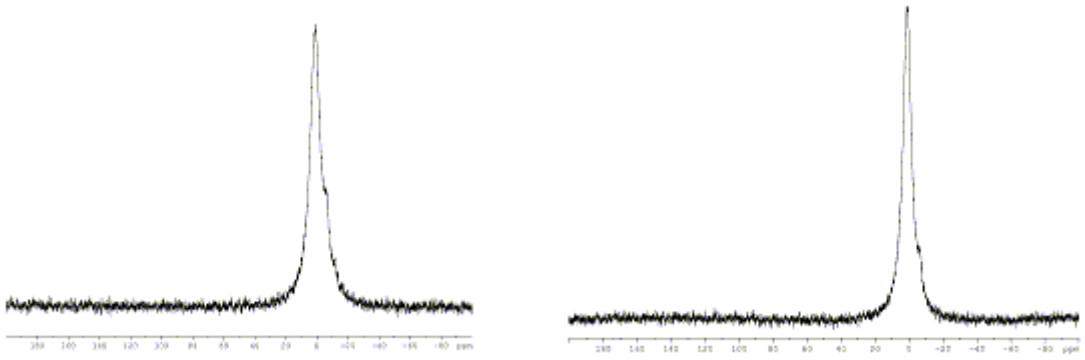
Figure 7: Selected Grape Marc Compost Fulvic Acid fractions - ^{1}H NMR in Solution

The cluster of peaks in the range 3-5-4 ppm were consistent with protons on carbons bearing oxygen and confirm the presence of carbohydrate material detected in the ^{13}C spectra. A number of broadened signals in the range 0.08-2 ppm were attributed to alkyl groups, probably associated with carboxylic acids. The signals in the range 2-3 ppm are also attributed to these carboxylic acids where the methylene (-CH_2-) and methine (CH) groups directly attached to the carboxylic acid (-COOH) group would be found. The ^{1}H spectra for the De Bortoli "pale" and De Bortoli "Worm Rich" fulvic samples also showed a trace of

signal in the aromatic region (~ 7.3 ppm). This can be attributed to polar aromatic phenolic or carboxylic acid compounds, which can be found in fulvic acid materials.

Phosphorus (^{31}P) NMR spectra of Fulvic Acid fractions

Phosphorus-31 NMR spectra were measured for selected samples on the same solutions used to measure the carbon-13 and hydrogen spectra. All spectra were externally referenced to 85% phosphoric acid. All the spectra of the grape marc compost fulvic fraction, both Yarra Valley and Goulburn Valley derived, gave a dominant broad signal, centred at around 6 ppm (Figure 8). This is characteristic of the signal for orthophosphate, the common form of inorganic phosphate and this result was expected from the independent analysis of phosphorus (Section 3.3.3). A shoulder on the major signal peak at approximately -5 ppm is also noticeable. This is normally attributed to pyrophosphate ($P_2O_7^{2-}$) and has been reported by others in phosphorus-31 NMR spectra of natural organic matter (Moller et al., 2000).



De Bortoli composite Henkell

Figure 8: Selected Grape Marc Compost Fulvic Acid fractions - ^{31}P NMR in Solution

3.5 Levels of Aluminium and Heavy Metals

The total amounts of aluminium and heavy metals found in all the composts investigated are shown in Table 12. Aluminium is not a heavy metal, but has been included in this section as it is an element that could be of concern in acidic soils.

Table 12. Other Metals: Total Arsenic (As), Cadmium (Cd), Lead (Pb), Mercury (Hg), Selenium (Se), Aluminium (Al), Chromium (Cr) & Nickel (Ni)

Sample	As mg/kg	Cd mg/kg	Pb mg/kg	Hg mg/kg	Se mg/kg	Al mg/kg	Cr mg/kg	Ni mg/kg
COMPOSITE DE BORTOLI GRAPE MARC	1.5	<0.5	<10.0	0.096	0.089	9100	14	<5
DE BORTOLI 'WORM DEVOID' GRAPE MARC	0.56	<0.5	<10.0	0.076	0.068	4000	7	<5
DE BORTOLI 'WORM RICH' GRAPE MARC	<0.020	<0.5	<10.0	0.065	0.031	4800	7	<5
HENKELL GRAPE MARC	0.74	<0.5	<10.0	0.055	0.088	7800	15	<5
MITCHELTON 1 YR OLD COMP GRAPE MARC	1.3	<0.5	<10.0	0.074	0.066	7200	10	<5
MITCHELTON FRESH 3 MTH OLD GRAPE MARC	2.4	<0.5	<10.0	0.079	0.14	11000	16	6
YARRA RIDGE (RACECOURSE) GRAPE MARC	0.43	<0.5	<10.0	0.084	0.064	4400	7	<5
GREENWASTE COMP EX MITCHELL CITY COUNCIL	4.2	<0.5	87	0.057	0.25	35000	62	43
COLES SUPERMARKET COMPOST EX COLLEX	9.5	0.6	12.9	0.33	0.62	15000	22	9

3.5.1 Aluminium Levels in the Composts

Aluminium is not a plant nutrient and occurs naturally in soil in almost all clay minerals. Soluble aluminium levels in the soil solution and exchange sites become significant at lower soil pH (<5) and is toxic to plants (Peverill et al., 1999).

The highest levels of aluminium occurred in the Mitchell City Council (3.5 %w/w) and Coles Supermarket composts (1.5 %w/w). The Mitchelton three month-old marc compost had the highest amount of aluminium (1.1 %w/w) amongst all the grape marc compost samples followed by the composite De Bortoli grape marc compost with 0.9% w/w of aluminium. All the other grape marc compost contained lower levels of aluminium ranging between 0.4 and 0.8 % w/w. The separate De Bortoli grape marc compost samples labeled "Worm Devoid" and 'Worm Rich" gave lower levels of total aluminium than the composite sample. This was ascribed to sample variability and the composite sample value should taken as the typical De Bortoli value.

The Yarra Ridge grape marc compost sample contained the lowest aluminium level and this was the oldest grape marc sample tested. This sample was likely to have been leached to the highest degree through exposure to rain. This is consistent with the observation that the Mitchelton three month-old marc compost had a higher amount of total aluminium (1.1 %w/w) compared with the twelve-month old Mitchelton sample (0.7 %w/w), however, the fact that these two compost were produced at different times needs to be considered.

The aluminium measured in the compost samples originates from soil minerals and any additives provided to or accidently mixed with the compost mixture (e.g. clay, diatomaceous earth). Any aluminium in mineral form would effectively be unavailable and no cause for concern. In addition, the natural pH of all the composts was between 7 and 8 and in this pH range, any free aluminium will form insoluble hydroxides, which are not harmful to plants. The exchangeable aluminium was measured for all the grape marc compost samples, as well as the Mitchell City Council greenwaste compost. (data not shown). For all the grape marc composts, the highest exchangeable aluminium was found to be 0.6 %w/w of the total aluminium present in the Henkell sample. The other grape marc compost samples gave values below 0.4 %w/w of the total aluminium present and in the greenwaste compost, it was below 0.1% w/w.

Aluminium can be solubilised from its mineral forms or insoluble hydroxides over time, if the pH becomes too low. However, the amount of aluminium supplied in any grape marc composts would become insignificant compared with natural levels of aluminium released from an acidic soil.

3.5.2 Heavy Metals

Normally, any consideration of heavy metals also includes manganese, iron, zinc and copper, but these have been discussed previously in Section 3.3.6.

The highest levels of heavy metals were found in the non grape marc derived composts, with Mitchell City Council compost having the highest values for lead, chromium and nickel (87 mg/kg Pb, 62 mg/kg Cr, 43 mg/kg Ni). Coles supermarket compost had lower levels of these same metals than the Mitchell compost except for arsenic (9.5 mg/kg in Coles compared with 4.2 mg/kg in Mitchell), but still somewhat higher than any of the grape marc composts.

The heavy metals in the grape marc composts are likely to have come from the soil in the vineyards in the first place. Chromium and arsenic occur naturally at higher levels in certain soils (e.g basalt derived soils can have higher chromium levels). Cadmium can come from phosphate fertilisers, however, the levels measured were generally very low (<0.5 mg/kg).

The compost levels for all the heavy metals listed in Table 12 all fall within the background levels for soils, published by the Victorian Environmental Protection Authority (1995). It can be concluded that the residual levels of heavy metals in the grape marc composts from both the Yarra Valley and Goulburn Valley do not pose any environmental concerns. The levels present in grape marc composts were significantly lower than those found in the two commercial composts, which are sold for use in the horticultural industry.

3.6 Germination and Toxicity Tests

The germination and toxicity test were carried out by the Victorian Department of Primary Industry Laboratory (Werribee) according to AS4454 - 1999. This test was undertaken as a single procedure. Seeds of the radish cultivar, *Long Scarlet*, were germinated in the compost sample and the growth of roots was compared with the root growth of a reference medium that was known to be non-toxic. The germination index is the percentage of seedlings that germinated in the test samples compared with the reference. The seedlings were then permitted to continue growing and the toxicity of the growing medium was investigated by determining how the seedlings survived into plants.

The toxicity index compares the length of these germinated seedlings to the specific reference medium. (toxicity index equation is in appendix e of AS4454)

In this study, all compost samples were able to bring about germination of the seeds, however, only the Coles supermarket compost, and the Mitchell City Council compost were able to sustain these seedlings into plants. The majority of the seeds grown in the grape marc samples showed a small amount of root growth, but the root tips subsequently blackened and dried. The two non grape marc composts supported healthy growth of the seedlings.

Table 13. Germination & Toxicity Index (see also photos in Appendix 3)

Sample	% Germination	Toxicity Index (%)
COMPOSITE DE BORTOLI GRAPE MARC	95	5
DE BORTOLI 'WORM DEVOID' GRAPE MARC	90	5
DE BORTOLI 'WORM RICH' GRAPE MARC	90	3
HENKELL GRAPE MARC	95	3
MITCHELTON 1 YR OLD COMP GRAPE MARC	100	4
MITCHELTON FRESH 3 MTH OLD GRAPE MARC	95	3
YARRA RIDGE (RACECOURSE) GRAPE MARC	95	4
GREENWASTE COMP EX MITCHELL CITY COUNCIL	95	96
COLES SUPERMARKET COMPOST EX COLLEX	100	96

The results of the germination and toxicity tests should not be interpreted to mean that grape marc composts will cause problems. The pure grape marc composts used in this study, have nutrient imbalances and would not be expected to function as a medium that sustains healthy plant growth, particularly in the artificial conditions of the test itself. The Mitchelton 3 month-old and Composite De Bortoli grape marc samples in particular, showed evidence of incomplete maturity and continuing composting biological activity. These would not be appropriate conditions for supporting healthy plant growth. A number of scientific studies (e.g. Baran et al., 2001, Mandelbaum et al., 1988) have confirmed that composts containing large proportions of mature grape marc are able to support healthy plant growth and even assist in suppressing soil pathogens.

3.7 Organic Residues

The organic residues shown in the Tables listed in Appendix 1 are predominately chlorinated hydrocarbons. Most of these compounds or compound classes were used as herbicides and pesticides in the past, but are no longer used today. Many were subsequently found to have deleterious effects on ecosystems and particular organisms and plants. (e.g DDT). These compounds were also notorious for their persistence in the environment particularly in the soil (e.g dieldrin can persistence for several decades). Some of these may also be taken up by plants and can be translocated into animal tissues (Brady and Weil, 2003).

Any residues in plant material may be concentrated during composting, although some compounds may also be broken down by the composting process itself.

All the grape marc composts tested were found to have negligible or insignificant levels of organic residues in the compound classes tested.

4 Conclusions

Grape marc composts obtained from the Mitchelton Winery (Nagambie district, Goulburn Valley) and several wineries in the Yarra Valley (De Bortoli, Henkell and Yarra Ridge) of Victoria were chemically analysed in detail. It was found that:

- All the grape marc composts contained significant levels of free potassium, at levels (2-3% w/w) that require the compost to be considered as a significant potassium source.

- Other plant macronutrients (e.g. Ca, S, Mg) were present at low levels (< 1 %w/w).

- The phosphorus (0.1-0.3% w/w) and nitrogen (1-2 %w/w) levels in the grape marc composts were not very high and most of these elements were in "plant unavailable" form, however, release is likely, depending on the prevailing conditions where the compost might be used. The Mitchelton composts samples showed a high potential for "nitrogen drawdown".

- The levels of micronutrients (Cu, Zn, B, Mn, Mo, Fe) present are not excessive and would serve to partially, if not completely, replace micronutrients removed from the soil.

- Undesirable organic residues (e.g. chlorinated hydrocarbons) and heavy metals were not present at any significant levels.

- Levels of soluble salts were elevated in all the grape marc composts. The salt levels, though not excessive, could cause a problem in soils that are prone to salinity and where drainage is poor. Nevertheless, salt levels should be carefully monitored in both the grape marc composts and vineyard soils before reapplying into the vineyard.

- The organic carbon in the grape marc composts was mainly in carbohydrate and lignin type forms. There was evidence of humification from the spectral studies, although not high levels in the humic/fulvic acid fraction.

- It was noted that all the grape marc composts varied considerably with respect to their extent of maturation even within the paddock for material produced in the same year. A systematic approach to the composting procedure, where optimum conditions are maintained, wherever possible, would produce a more homogeneous, well composted, end product. The inability to support plant growth in a seedling test on all the grape marc composts, regardless of compost age, reflected this lack of proper maturation, rather than any inherent toxicity problem with the compost itself. The establishment of optimum conditions for grape marc composting needs further research.

- Nutrient analysis of locally produced grape marc compost in conjunction with soil analysis should be conducted at least on an annual basis, when returning the compost to the vineyard, especially if high levels of application are used.

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Appendix 1 - Organic Residues

Sample	PCB Residues (mg/kg)	α-BHC (mg/kg)	β-BHC (mg/kg)	δ-BHC (mg/kg)	Hexachlorobenzene (mg/kg)
COMPOSITE DE BORTOLI GRAPE MARC	<0.1	<0.05	<0.05	<0.05	<0.05
DE BORTOLI 'WORM DEVOID' GRAPE MARC	<0.1	<0.05	<0.05	<0.05	<0.05
DE BORTOLI 'WORM RICH' GRAPE MARC	<0.1	<0.05	<0.05	<0.05	<0.05
HENKELL GRAPE MARC	<0.1	<0.05	<0.05	<0.05	<0.05
MITCHELTON 1 YR OLD COMP GRAPE MARC	<0.1	<0.05	<0.05	<0.05	<0.05
MITCHELTON FRESH 3 MTH OLD GRAPE MARC	<0.1	<0.05	<0.05	<0.05	<0.05
YARRA RIDGE (RACECOURSE) GRAPE MARC	<0.1	<0.05	<0.05	<0.05	<0.05
GREENWASTE COMP EX MITCHELL CITY COUNCIL	<0.1	<0.05	<0.05	<0.05	<0.05
COLES SUPERMARKET COMPOST EX COLLEX	<0.1	<0.05	<0.05	<0.05	<0.05

Sample	Aldrin (mg/kg)	Lindane (mg/kg)	Heptachlor (mg/kg)	Heptachlor Epoxide (mg/kg)	Dieldrin (mg/kg)
COMPOSITE DE BORTOLI GRAPE MARC	<0.05	<0.05	<0.05	<0.05	<0.05
DE BORTOLI 'WORM DEVOID' GRAPE MARC	<0.05	<0.05	<0.05	<0.05	<0.05
DE BORTOLI 'WORM RICH' GRAPE MARC	<0.05	<0.05	<0.05	<0.05	<0.05
HENKELL GRAPE MARC	<0.05	<0.05	<0.05	<0.05	<0.05
MITCHELTON 1 YR OLD COMP GRAPE MARC	<0.05	<0.05	<0.05	<0.05	<0.05
MITCHELTON FRESH 3 MTH OLD GRAPE MARC	<0.05	<0.05	<0.05	<0.05	<0.05
YARRA RIDGE (RACECOURSE) GRAPE MARC	<0.05	<0.05	<0.05	<0.05	<0.05
GREENWASTE COMP EX MITCHELL CITY COUNCIL	<0.05	<0.05	<0.05	<0.05	<0.05
COLES SUPERMARKET COMPOST EX COLLEX	<0.05	<0.05	<0.05	<0.05	<0.05

Sample	DDE (mg/kg)	DDD (mg/kg)	o,p-DDT (mg/kg)	p,p-DDT (mg/kg)	α-Endosulfan (mg/kg)
COMPOSITE DE BORTOLI GRAPE MARC	<0.05	<0.05	<0.05	<0.05	<0.05
DE BORTOLI 'WORM DEVOID' GRAPE MARC	<0.05	<0.05	<0.05	<0.05	<0.05
DE BORTOLI 'WORM RICH' GRAPE MARC	<0.05	<0.05	<0.05	<0.05	<0.05
HENKELL GRAPE MARC	<0.05	<0.05	<0.05	<0.05	<0.05
MITCHELTON 1 YR OLD COMP GRAPE MARC	<0.05	<0.05	<0.05	<0.05	<0.05
MITCHELTON FRESH 3 MTH OLD GRAPE MARC	<0.05	<0.05	<0.05	<0.05	<0.05
YARRA RIDGE (RACECOURSE) GRAPE MARC	<0.05	<0.05	<0.05	<0.05	<0.05
GREENWASTE COMP EX MITCHELL CITY COUNCIL	<0.05	<0.05	<0.05	<0.05	<0.05
COLES SUPERMARKET COMPOST EX COLLEX	<0.05	<0.05	<0.05	<0.05	<0.05

Sample	β-Endosulfan (mg/kg)	Endosulfan sulphate (mg/kg)	Endrin (mg/kg)	Oxychlordane (mg/kg)	cis-Chlordane (mg/kg)	Trans-Chlordane (mg/kg)
COMPOSITE DE BORTOLI GRAPE MARC	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
DE BORTOLI 'WORM DEVOID' GRAPE MARC	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
DE BORTOLI 'WORM RICH' GRAPE MARC	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
HENKELL GRAPE MARC	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
MITCHELTON 1 YR OLD COMP GRAPE MARC	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
MITCHELTON FRESH 3 MTH OLD GRAPE MARC	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
YARRA RIDGE (RACECOURSE) GRAPE MARC	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
GREENWASTE COMP EX MITCHELL CITY COUNCIL	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
COLES SUPERMARKET COMPOST EX COLLEX	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05

Appendix 2

Germination and Toxicity Test Photographs