Aged Riesling and the development of TDN

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Understanding and managing aged Riesling flavour has proven to be both complex and elusive. Some older Riesling wines have been described as having an aroma of 'kerosene', while most winemakers will describe the wines as displaying toasty, lime/marmalade flavours. This AWRI report provides winemakers with the most up-to-date information and advice on the management of the TDN compound in aged Riesling.

There are few aroma compounds in wine that are more distinctive or more polarising than TDN (1,1,6-trimethyl-1,2-dihydronaphthalene). It has been described as 'delicious', but 'undesirable' in excess, as it can give a kerosene-like aroma in some wines, depending on the age of the wine and individual preference. It is an important part of the bottle-aged bouquet of Riesling wines, with levels up to six times higher than in other varieties.

THE TIGHTROPE OF TDN

There is no doubt that TDN is potent. Research published in the *Journal of Agricultural and Food Chemistry* earlier this year (Sacks *et al.* 2012) revealed that 50% of the population should be able to perceive (but not necessarily recognise) TDN in most Riesling wines, and the detection threshold is much lower than previously thought. Until recently, the sensory detection threshold of TDN was believed to be 20µg/L, but that figure has now been dramatically revised. The new threshold is just 2µg/L, a concentration 10 times lower.

It remains difficult to predict, however, what concentration of TDN will make the aroma apparent, as other compounds can mask or strengthen TDN's flavour. Complex chemical interactions can mean that the compounds responsible for floral, fruity or citrus characters (monoterpenes) or other fruity characters (esters) in young wines may enhance or mask the effects of TDN, even when it is present at moderate levels. In the acidic environment of wine, these young aromas slowly break down and, coupled with an increase in TDN, they can make TDN a dominant factor. Accordingly, measuring TDN alone may not give an accurate picture of the likelihood of a wine to display or develop a strong 'aged' aroma.

Occasionally, particularly in warmer climates, younger wines can develop this aged character early, in which the heady aroma of TDN can overwhelm the highly attractive, delicate aromas of a young Riesling and disturb the balance of the wine. In fact, TDN can be used as a tool to distinguish whether a given Riesling wine has been made with grapes from warmer or cooler climates.

Early harvesting and managing sun exposure by shading berries are two management strategies that will be explored later in this article. First, the formation of TDN requires further explanation, particularly given the mystery concerning its chemical 'ancestry'.

THE FORMATION OF A FLAVOUR

Strangely, free TDN is generally not present in significant quantities in grapes and in juice. Its formation depends on the presence of non-volatile compounds called carotenoids, which occur in many plant species. In fact, these carotenoids give much of the colour to the autumn leaves of deciduous plants. At least a dozen carotenoids have been identified in grapes, falling into two categories: carotenes (which include beta-carotene) and xanthophylls. Both build up in the early stages of fruitset, then break down from veraison onwards (see Figure 1), forming smaller molecules called C13-norisoprenoids. The norisoprenoids, including compounds that give rise to TDN, become attached to sugar molecules. This provides a slow-release flavour reservoir – TDN can emerge during storage, although once formed, the compound is stable in wine.

It is known that higher carotenoid concentrations in Riesling grapes lead to higher TDN levels in the final wine. Wine scientists have discovered that carotenoids can be present in concentrations up to eight times higher in grape leaves and three times higher in grape skins when compared with berry pulp.

Still, the conditions that produce higher concentrations of TDN in Riesling have not yet been completely established. Investigations have targetted sun exposure, cluster temperature, grape maturity, water stress, soil nitrogen levels, ageing, storage temperature, wine pH, and yeast strains.

This report looks at some of those factors in more detail, so as to offer the most up-to-date advice regarding TDN management.

AT A GLANCE

The 'aged' character in Riesling is linked to the formation of TDN and its precursors, which increase in concentration when grapes are exposed to sunlight and warm temperatures.
High concentrations of TDN are also linked to bottle age, and higher temperatures when bottles are stored.
Closures also play a role, though winemakers seeking to 'fix' high levels of TDN should be wary of basing closure choice on this parameter alone, since the performance of the closure has a major impact on wine quality.
To reduce TDN levels, modifying canopy density early in the season can be effective; where possible, grapes should be harvested from cool locations; in warmer years, consider harvesting earlier.

SUN EXPOSURE – A KEY FACTOR

By far the most studied and accepted contributor to TDN is sun exposure. A number of scientific studies have shown that higher concentrations of TDN and its precursors are found in wines made from sun-exposed grapes.

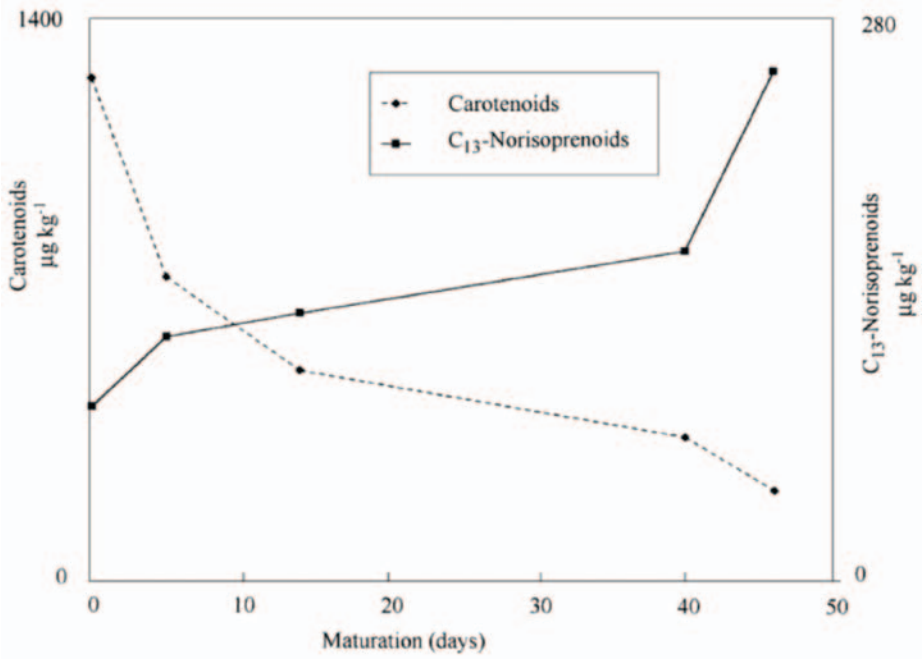

Figure 1. Carotenoid and norisoprenoid precursor concentration changes during maturation of Muscat berries. (From Baumes *et al.* 2002, reproduced with permission).

In one study (Gerdes *et al.* 2002), researchers measured TDN concentrations in Riesling at increasing levels of exposure. They found that anything higher than 20% of full sun exposure on the grape cluster from veraison onwards increases TDN levels.

Another, more recent investigation of Riesling produced in the US – in the Finger Lakes region of New York State – has pin-pointed a key period in the growing season when carotenoids develop due to sun exposure. In this study (Kwasniewski *et al.* 2010), researchers removed 75% of the leaves in the fruiting zone at three time points (two, 33 and 68 days post-berry set) to assess the effects of berry shading and increased sun exposure on the precursors that lead to TDN – the carotenoids.

The study measured levels of carotenoids in grapes, as well as wine made from grapes at each time point. They also measured the free and total TDN in each batch of finished wine. They discovered a spike in the levels of one carotenoid, known as zeaxanthin, mid-season at the 33-day mark. This correlated well with high TDN levels in the finished wine made from grapes harvested at that time.

Scientists were already aware that zeaxanthin forms in direct response to sun exposure; at lower temperatures its formation is strongly suppressed. A direct link between sun exposure, higher concentrations of carotenoids and TDN production does not tell the whole story, however. Researchers have found that concentrations of other carotenoids remain stable – despite increased exposure to sunlight – and do not multiply in the same way. This finding is in keeping with one line of thought that increased sun exposure leads to relative amounts of carotenoids being altered, rather than a rise in overall carotenoid concentration.

The mid-season spike at 33 days remains significant, however. More than twice as much TDN was detected in the wine produced from the 33-day grapes, compared with the other two time points and the control sample. The minimal effect of sun exposure on carotenoid/TDN levels at the other time points (two and 68 days) suggests that the strategic exposure of grape clusters to sunlight can still be used at other time points to optimise grape quality.

Grape and wine producers may consider shading berries or harvesting early to reduce the amount of TDN in a finished wine, for example.

ADDITIONAL FACTORS

Sunlight and temperature alone do not account for all increases in TDN – other factors also play a part (Lee *et al.* 2007). As grape berries ripen, TDN precursors will naturally increase in concentration. Sun-exposed grapes will show a more rapid accumulation than shaded grapes, but concentrations of TDN can also be enhanced, or reduced, by other factors during the winemaking process. ▸

Bottle age and temperature

It is now well accepted that TDN concentrations increase with bottle age. Cellar or storage temperature is also a factor. In one study, wine samples stored at 30°C showed considerably higher increases in TDN than was found in those stored at 15°C.

Oxidation

Oxidation can also play a part – in some cases, it has been shown to contribute to an increase in TDN; in other cases, high levels of oxidation in fortified wines have been found to severely decrease levels of the compound.

Water stress and soil nitrogen

Although water stress is not directly responsible, partial drying of the rootzone has been found to have an indirect affect on the production of TDN: it reduces canopy size and, therefore, increases sunlight penetration. Nitrogen deficiency in soil has also been examined as a possible cause for high TDN levels. Some researchers have hypothesised that fertilisation has an effect by encouraging more leaf cover and berry shading.

Yeast activity

The activity of different yeast strains has been shown to have little effect on TDN levels in Rheingau Riesling, according to one study (Sponholz and Hühn 1997).

Closures

Closure choice is also a significant factor. When AWRI researchers investigated the ability of five different closure types to absorb different aroma/flavour compounds, they discovered that TDN was affected the most. The study showed that cork and synthetic closures absorbed more than 50% of the TDN present in a wine over two years in bottle. Wines under screwcap were found not to 'lose' any TDN.

Wine acidity

Finally, pH can play a part: more acidic wines have been shown to develop TDN more quickly than others.

UNDERSTANDING TDN AND TEMPERATURE

To understand the impact of Australia's climate on Riesling's aged character, AWRI researchers, working with the Adelaide Hills Wine Region and , carried out a survey of Riesling wines from a number of vintages and regions, also collecting mean January temperatures (MJT). A comparison of Adelaide Hills and Eden Valley was particularly important since, anecdotally, TDN levels are said to develop earlier in Eden Valley Riesling than the Adelaide Hills. The study followed similar work overseas: a comparison of South African and European Riesling found that lower rainfall, higher sunshine hours and higher average temperatures in South Africa coincided with higher TDN.

For the AWRI study, 116 Riesling wines were collected from regions including Adelaide Hills (40), Eden Valley (36), Clare Valley (14), Tasmania (12), and Victoria (7), with smaller numbers from Canberra (1), France (1), Germany (3), New Zealand (1) and Slovakia (1). The wines spanned a range of vintages and included nine vertical series (defined here as three or more wines of different vintages from the same winery). The largest number of wines were drawn from the 2010 vintage (26 wines) in order to investigate TDN levels in younger wines. A majority (89) of the wines were sealed under screwcap, while 26 had cork stoppers and one was under a glass seal.

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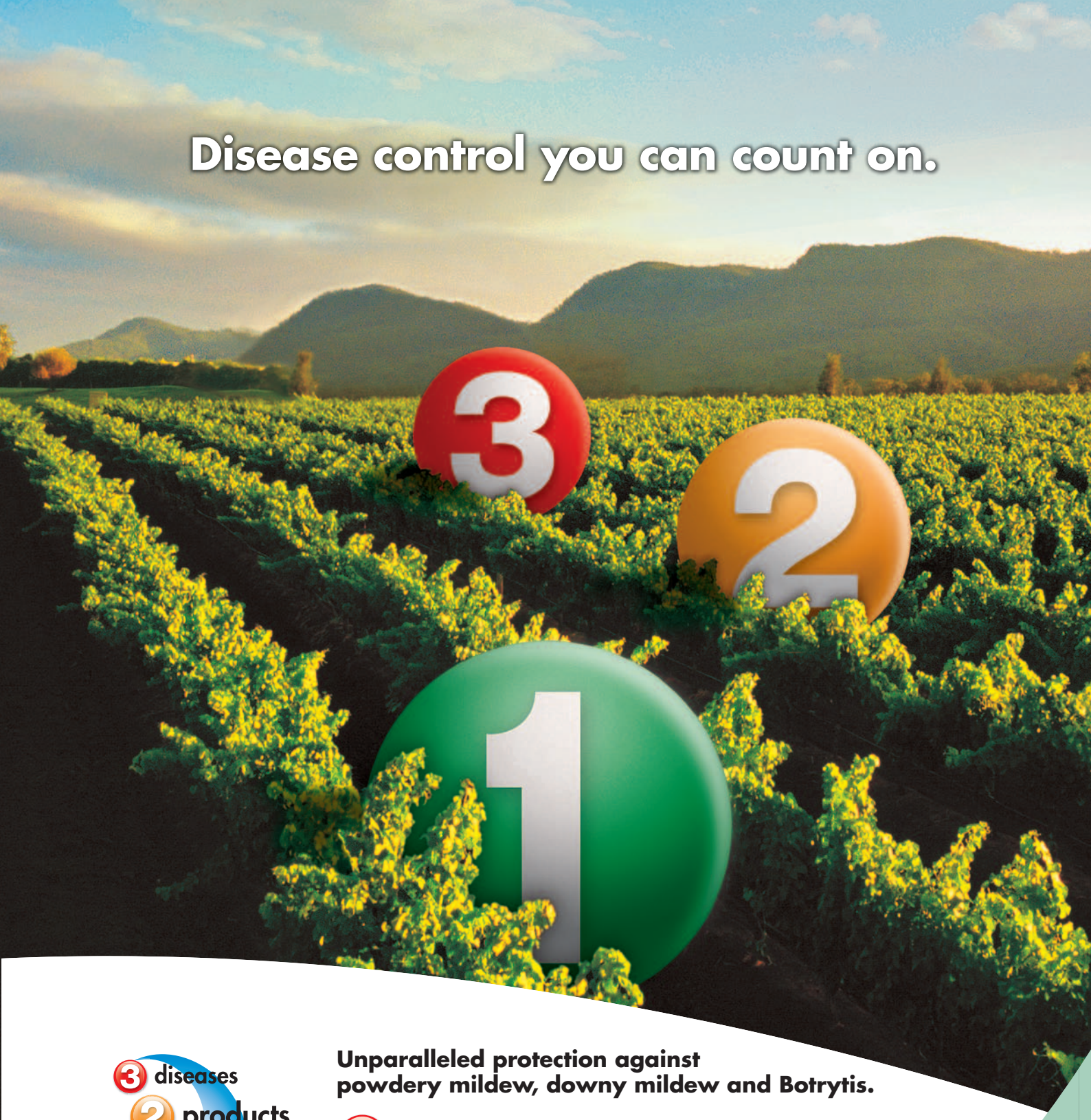

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The wines underwent an informal sensory evaluation with 12 panellists, including winemakers and members of the AWRI's Technical Quality sensory panel. The wines were scored on a nine-point scale for 'TDN', 'floral', 'fruity' and 'oxidation' characteristics, and were then given an overall quality score out of 20. It should be noted that due to issues with sample volumes available, the tasting was not replicated and the data are indicative only.

Immediately after sensory evaluation, concentrations of TDN and a selection of other flavour compounds (monoterpenes) were determined by gas-chromatography mass-spectrometry. The minimum, median and maximum TDN levels found in each region are displayed in Table 1. This analysis found all of the wines to be at or above the recently reported sensory detection threshold (2µg/L) for TDN. However, the tasting panel found far fewer wines to have a 'an undesirable character' aroma. In the younger wines, there were also higher concentrations of flavour compounds (monoterpenes) that may have masked TDN .

Wine colour was also assessed to indicate the extent of oxidation. Varying degrees of oxidation were detected by the sensory panel in older wines (>7 years), irrespective of closure. Oxidation was considerably more variable under cork, however. In general, higher oxidation scores were given for those wines. When oxidised wines were excluded from the data set, the panel's ratings of TDN related much better to the measured concentrations. There was no significant relationship between quality score and perceived TDN, with a number of wines containing high TDN levels (including the second-highest TDN concentration of 246µg/L found in a 1998 Eden Valley Riesling) having high quality scores. This indicates that even very high levels of TDN do not mean that the wine concerned will be considered objectionable. In fact, consumer testing at the AWRI in a previous Riesling study showed that kerosene aroma alone was not important to consumers, as long as there were other bottle-age flavours present, such as honey, toast and lime. The wines with oxidised flavour, however, were not liked by consumers.

Careful investigation of the data showed that there was a link between TDN concentrations and the age of a wine, the closure used and MJT in the region concerned.

The TDN levels for each vintage are shown in Figure 2. As expected, age was

Table 1. Minimum, median and maximum TDN levels found for Riesling wines in the survey.*

Region	N	Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)
Adelaide Hills	40	2	36	172
Clare Valley	14	12	74	115
Eden Valley	36	5	88	255
Tasmania	12	10	63	103
Victoria	7	25	47	210
Non-domestic	6	2	14	33

*** Canberra not shown – only one sample with 21µg/L.**

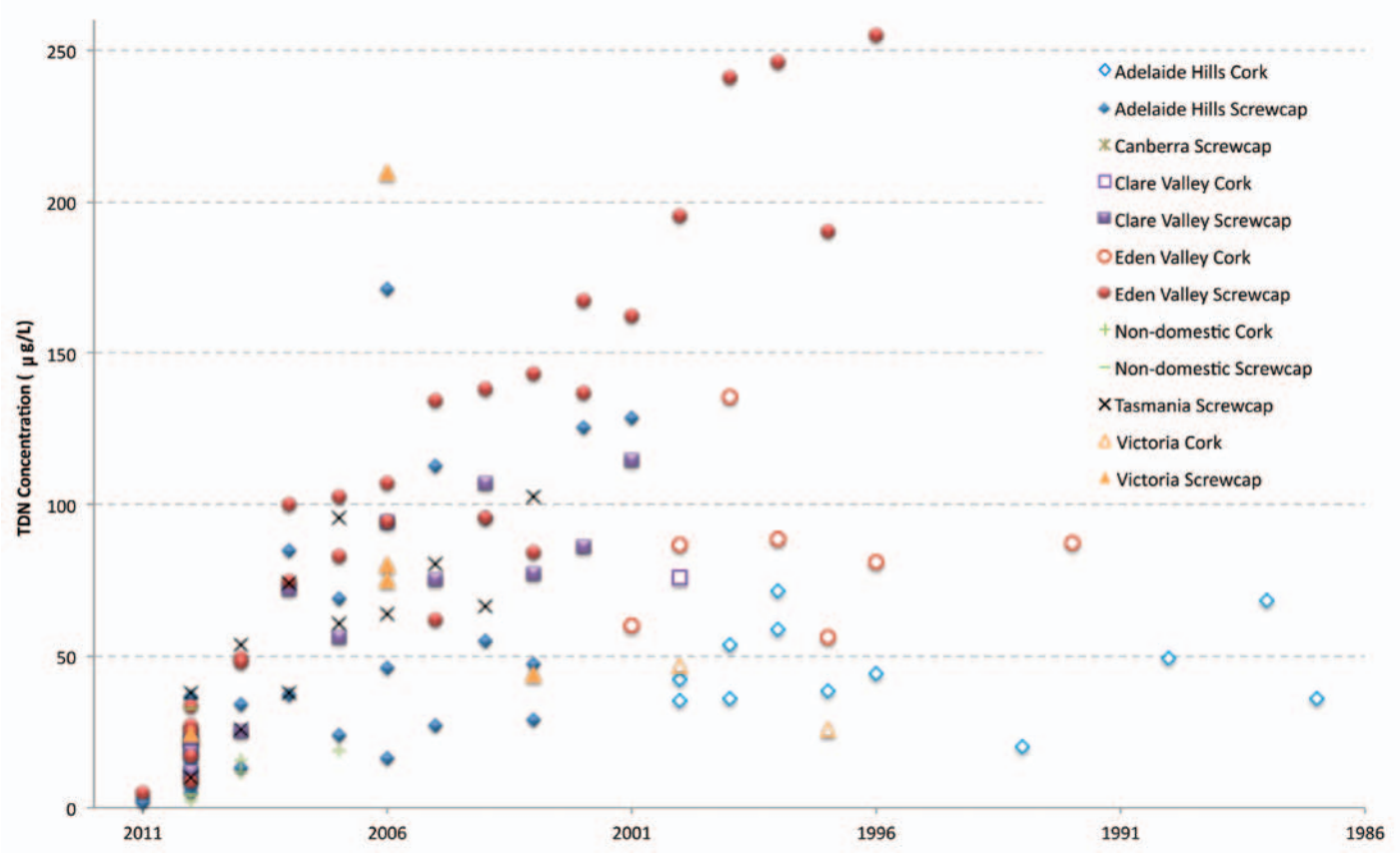

Figure 2. TDN concentration (µg/L) by vintage, highlighting region and closure.

the most important factor, with older vintages displaying significantly higher levels of TDN.

Closure type was the next most important, with wines under cork generally having much lower TDN concentrations compared with those under screwcap of the same vintage. Flavour 'scalping' of TDN by cork is a likely explanation, although high levels of oxidation cannot be ruled out entirely as another factor.

Finally, although not as significant, there was some connection between MJT and TDN levels. Despite the data being relatively scattered, higher TDN concentrations were generally found in wines after a higher MJT. This finding supports other research that shows the 33 day post-berry set time-point to be a crucial stage in the development of TDN precursors.

The study also found that wines from the Adelaide Hills (with one exception) had TDN levels below the average found for Eden Valley (23µg/L) in 2010. The results were not clear-cut, however, in that two of the six Eden Valley wines from the 2010 vintage had comparable levels of TDN to those found in the Adelaide Hills. The Clare Valley wines had a narrower range of concentrations, but were generally higher than the Adelaide Hills wines.

KEEPING CHARACTER IN CHECK

There is little doubt that TDN, with its low detection threshold and distinctive flavour, makes an important contribution to Riesling character. Identifying the precursors to TDN in wine has been a long, complicated process spanning three decades, but flavour scientists are now closer to specifying which carotenoid precursors are the most important, and which conditions will bring about higher concentrations in the resultant Riesling wine.

A number of interactions involving sun exposure and temperature, as well as indirect factors, make it difficult to accurately predict final TDN concentrations.

What is known is that cool locations should be selected wherever possible if low levels of TDN are desired. Warm seasons may require an early harvest and/or attention to berry shading to reduce the build-up of precursors that could lead to undesirable elevated levels of this compound.

Table 2. TDN concentrations for wines from the 2010 vintage from three regions.

Region	N	Minimum (µg/L)	Median (µg/L)	Maximum (µg/L)
Adelaide Hills	9	5	12	37
Clare Valley	4	12	20	22
Eden Valley	6	9	25	33

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