



## Myth busting "Dry ice creates an protective layer"

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- Typical operational practices
- Theory the issues at stake
- Experimental observations
- Operational implications





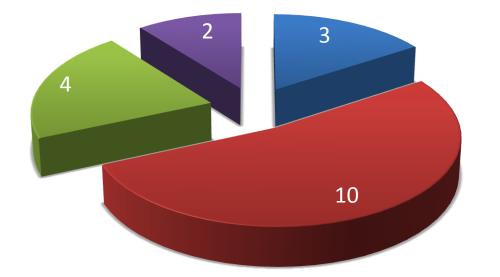
## "Dry ice forms a protective layer"

- Ullage management and oxygen exclusion is multifaceted
  - Tank evacuation
  - Tank blanketing
  - Wine sparging



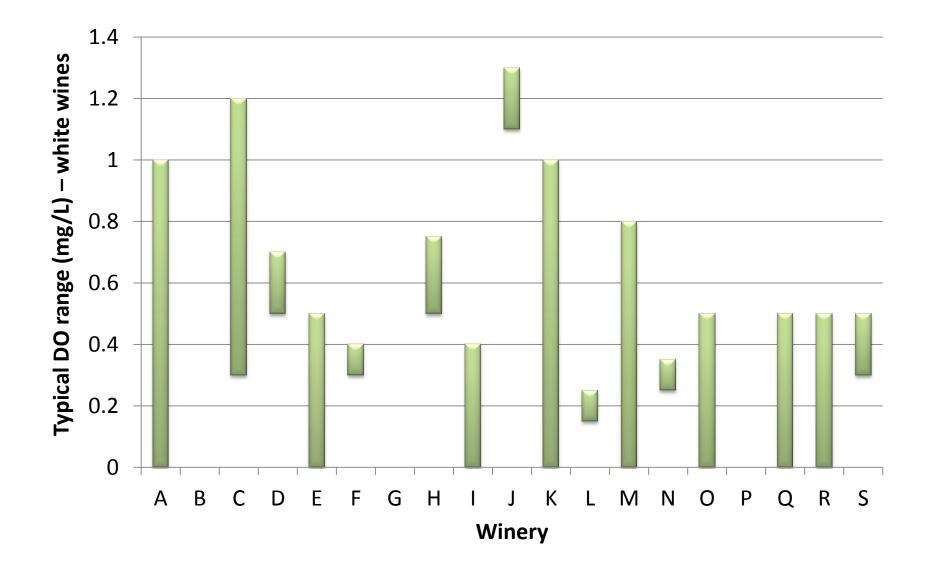
### Method of venting on storage tanks





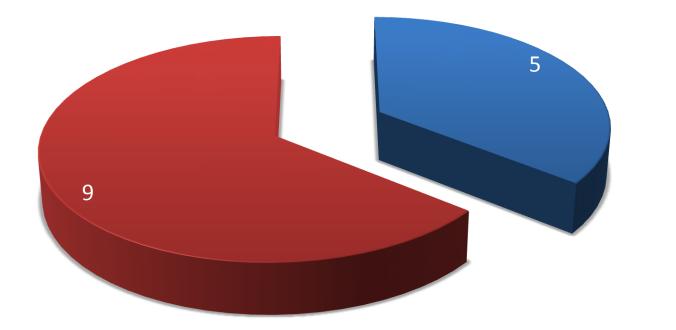
manual
 water trap
 left unfastened
 water trap/breather valve

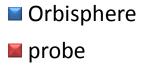
### **Typical levels of DO in white wines**



#### Method of DO measurement

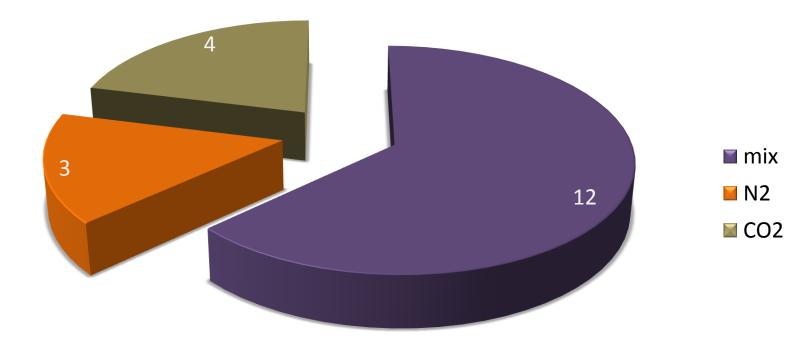






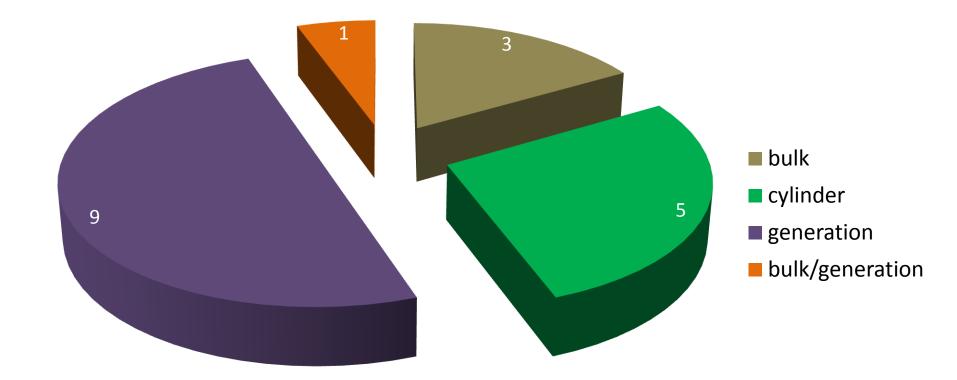
#### Gas types used





## Source of nitrogen used on site

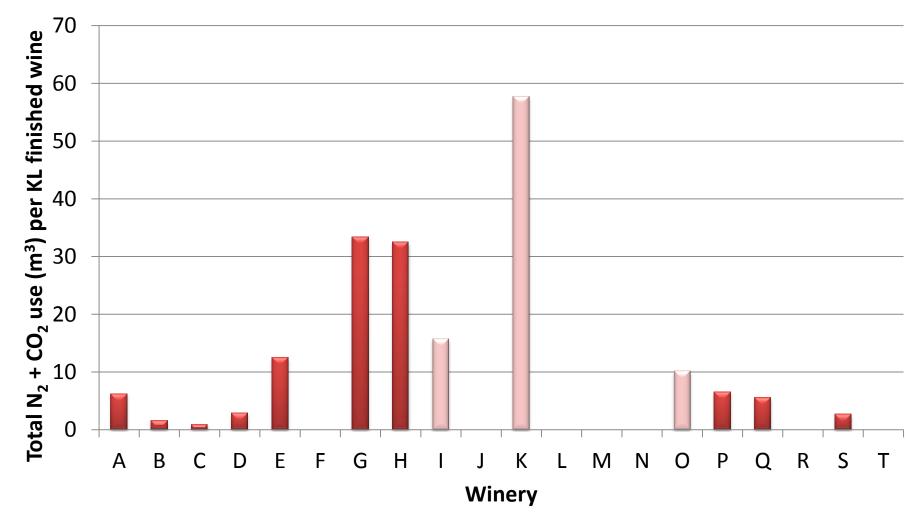




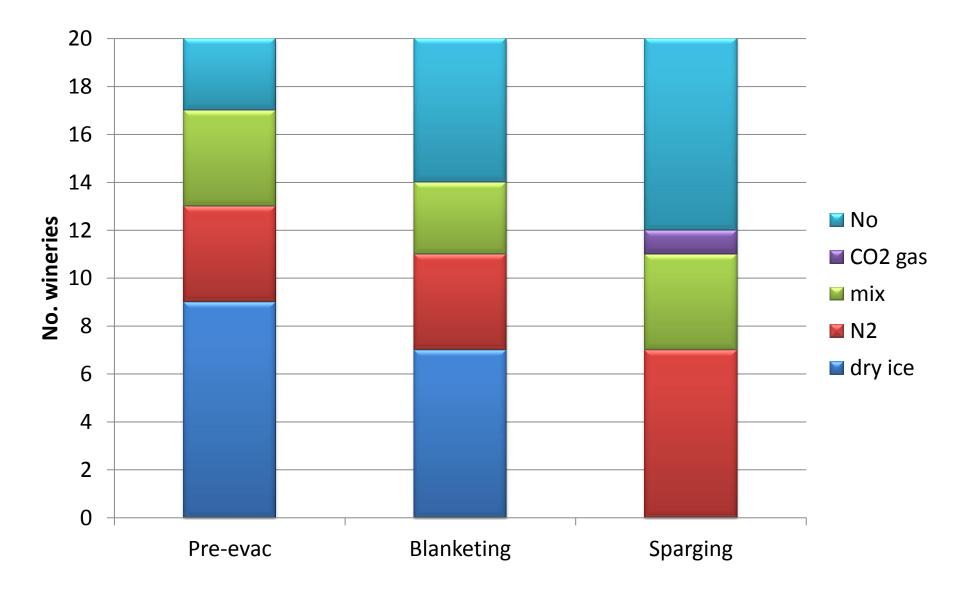
## **Overall gas usage**



#### Total gas use (normalised)

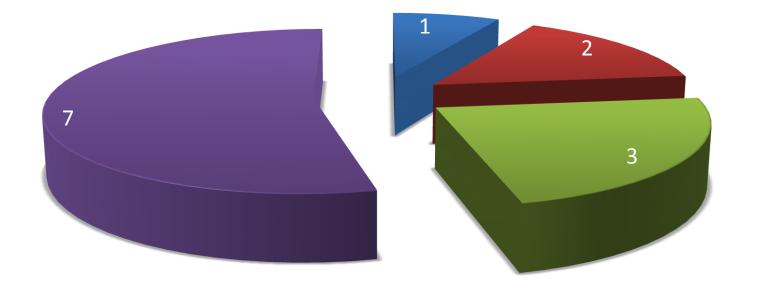


## Type of gas application used during tank filling



## Frequency of dry ice application for stored wines – no. per week







## **Operational practices**

- Minimise ullages
  - Not always possible
    - Infrastructure
    - Operational requirement
  - Thermal expansion
    - Refrigeration cycles
    - Seasonal fluctuation
- Manage ullages
  - Dry ice addition
  - Gas cover







- Dry ice addition
  - Typically ½ 1 bucket (2- 8kg)
  - Maybe 3 times per week
  - Largely independent of ullage volume (and tank sealing mechanisms)
  - Time consuming
  - Expensive
  - Potentially ineffective





- Continual gas cover
  - 24/7 gas application
  - Typical flowrate around 10 L/min
  - Applied using diffuser
  - Creating positive pressure to prevent ingress of oxygen
  - Gas selection important to maintaining dissolved CO<sub>2</sub> levels





- Periodic gas flushing
  - Typically a manual system enabled during racking or filling
  - Periodic application during storage
  - Potentially automated to ensure sufficient protection from oxygen without excessive gas utilisation





- Primary Goal
  - Protect wine from oxygen penetration
- Secondary Goals
  - Manage dissolved gases
    - Particularly CO<sub>2</sub> and O<sub>2</sub>
- Do some gases for a LAYER?



## **Gas Species – Some Details**



	Nitrogen	Carbon dioxide	Argon
Mol. Weight	28	44	40
Boiling Point	-196	-78	-186
Specific Volume (m3 per kg at 15°)	0.84	0.53	0.59
Specific Gravity (rel. air)	0.97	1.53	1.38
Solubility (v/v)	0.017	1.01	0.038





### Diffusion is the spread of particles through random motion from an area of high concentration to an area of low concentration







# $J = -D. \frac{d\emptyset}{dx}$

- J = rate of gas exchange
- *D* = *diffusion coefficient*
- $\emptyset$  = concentration
- X = position (length of interface)



#### Fick's Law - What's really important

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- Forces faster/greater than diffusion
- Physical constraints distance, layering, space filling, gas density
- Generation of new gases gases super saturated in solution
- Diffusivity of the gas species (CO $_2$  in air 0.13 v N $_2$  in air 0.17)



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In a typical storage tank, diffusion will occur:

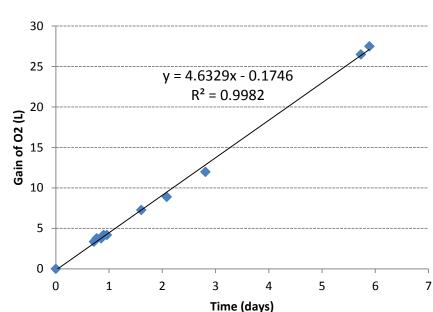
- through tank seal / entry point
- through headspace
- solution into wine
- through wine until reaction.



#### How much oxygen enters a tank?

**Tank OTR** 

- AWRI measurement on 760 L tank, with standard lid and breather valve.
- Tank inerted with dry ice to <  $0.2 \% O_2$
- 1
  - Over 4 L of oxygen ingress per day!!







## **Tank OTR**



- 4 L ~ 5g = 5000 mg  $O_2$ 
  - On a 1000 L tank, theoretical exposure equals
    5 mg/L/day
  - On a 10kL tank, theoretical exposure equals
    0.5 mg/L/day
  - On a 200kL tank, theoretical exposure equals
    0.025 mg/L/day
- Whilst theoretical exposure is unlikely to be realised, tank OTR is significant!



## **Thermal expansion**



- Typical expansion coefficient for wine is ~ 0.2 ml/L/Deg C
- Given a refrigeration deadband of 3 degrees, each refrigeration cycle has the potential to draw in this equivalent volume of air.
- This corresponds to approximately 0.15 mg/L oxygen
- This can occur daily with refrigeration events





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What oxygen level is acceptable?

 Generally accepted to be < 0.5 % to prevent growth of aerobic bacteria

Wine quality impact evidence is largely anecdotal – but real

Oxidation damage must be decoupling volatile loss and natural ageing



#### Gas cover



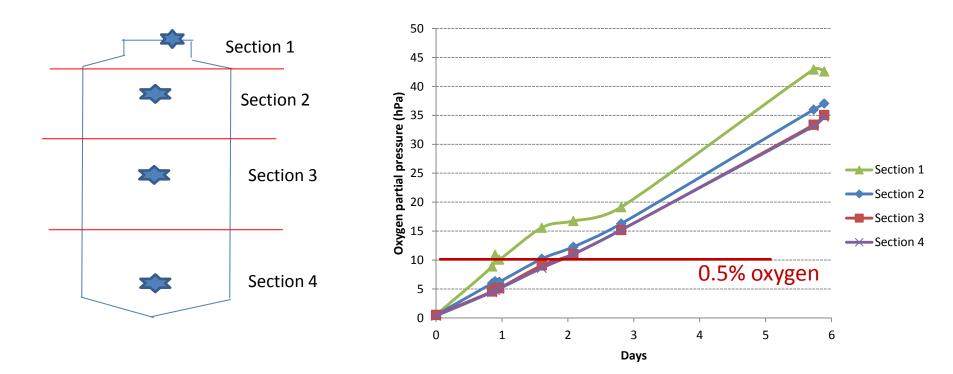
- Carbon dioxide
  - CO<sub>2</sub> offers superior evacuation performance due to higher density through displacement of oxygen
  - Gaseous application through diffuser is best
  - Solubility in wine is high
  - Dissolution into wine can create a vacuum
  - Protection is short lived. CO<sub>2</sub> cover is not impermeable to oxygen.
  - Continuous application/ replenishment is required
  - Operation costs of manual dry ice application are high







#### Diffusion of O<sub>2</sub> through CO<sub>2</sub>









- Nitrogen
  - Cost advantage over CO<sub>2</sub>
  - Comparable density to O<sub>2</sub>, therefore diffuses with oxygen.
  - Large volumetric usage required to therefore displace oxygen.
  - Previous studies report a 3 5 volume to volume ratio is required.
  - Significantly shorter protection times than CO<sub>2</sub>







- Mixed gas
  - Benefit of CO<sub>2</sub> whilst partially offsetting the higher costs
  - Reduced operation expenses associated with adjusting DCO<sub>2</sub> levels.
  - $N_2/CO_2$  ratios of 60/40 up to 80/20 sufficient to maintain desired  $DCO_2$  levels.
- Automation has the potential to optimise the efficiency and the gas cost of the system



## Improving Ullage Management



- Minimising wine movements
  - Software systems (optimisation)
  - Evaluate the cost/benefit of packaging run scheduling
  - Implications on other aspects of wine production
- Tank design and tank sealing/breather systems
  - Maintain water traps and lid seals
  - Opportunities exist for further development of tank sealing mechanisms
- Design and evaluation of best mechanism to introduce mixed gas to tanks
  - Floating distribution systems

