Stuck on you – Sulfur Spray Residues in the Vineyard and Winery

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12/16/2014
USDA-SCRI Northern Grapes Project

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Support: NY Farm Viability Initiative, Federal Formula Funds, USDA NE-SARE

The topics for today's talk

1) Review of literature: what problems do elemental S residues cause, and how much is too much?

2) New method: how do we quantifying S residues on grapes?

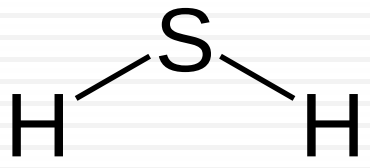
3) Results from field studies
   - What's a safe pre-harvest interval for elemental S?
   - What effects do pre-fermentation practices?

4) Ongoing work: can S-residues result in formation of H_2S and related off aromas in bottle?

Hydrogen Sulfide and "Reduction"

Aroma: rotten egg, flatulence

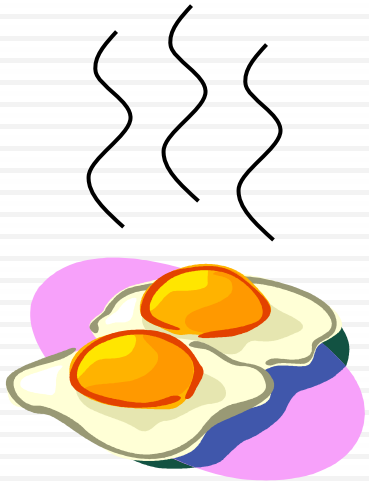
Detection threshold ~1 ng/mL



m.p. = -82°C
b.p. = -60°C

A contributor to **"reduced aromas"** or "sulfur-like off aromas" (SLOs) in wines

- 90% of wines with SLOs have supra-threshold H_2S (Siebert, et al 2010 JAFC)
- H_2S can react with other wine compounds to make even more potent odorants



H_2S: one contributor to "reduced" or sulfur like off-aromas (SLOs)

International Wine Challenge data	2006	2007	2008
Total faults, %	7.1	NA	5.9
Corked (% of total faults)	27.8	29.7	31.1
Brett	10.6	12.8	15.8
Oxidized	24.3	22.9	19.1
Reduced	29.2	26.5	28.9

Data from Chatonnet, The London International Wine Fair, 2009, adapted by John Thorngate

Major factors influencing H_2S production during fermentation

Nutritional deficiencies in must

1) Yeast assimilable nitrogen (YAN)
2) Other vitamins, e.g. pantothenic acid

Yeast strain dependence for all factors

Sulfur containing pesticides in must

1) Elemental sulfur
2) Other S-containing pesticides

H_2S

Other poorly understood factors,
e.g. cysteine (amino acid from grape) degradation

Elemental sulfur and powdery mildew

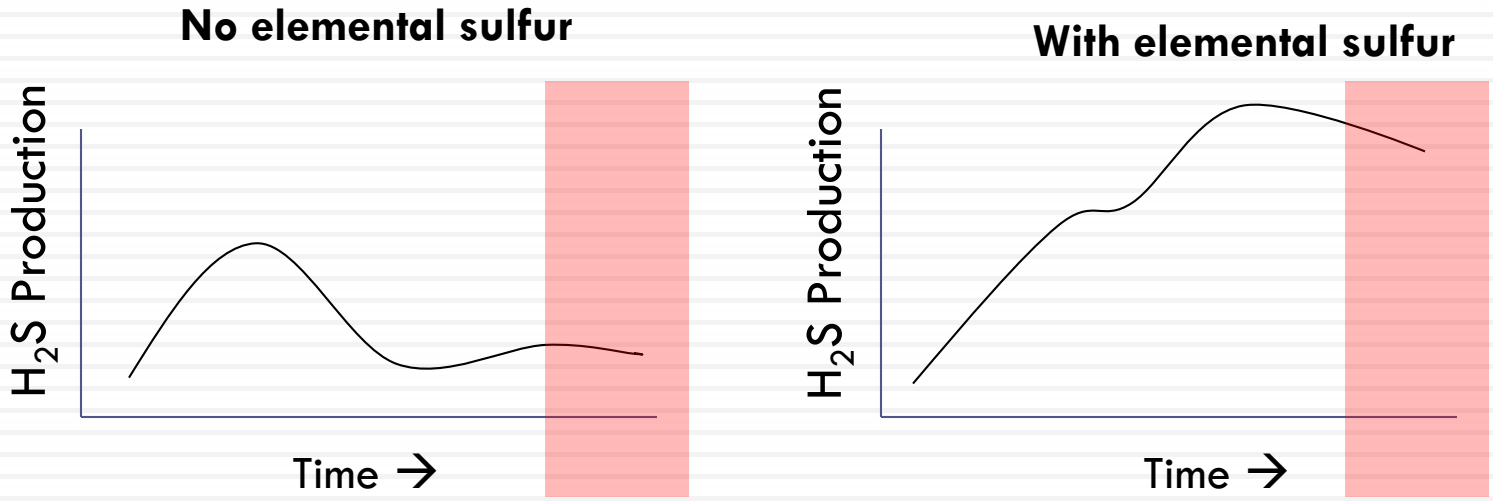
- Advantages of elemental sulfur over alternatives
  - Inexpensive, low toxicity
  - Low risk of resistance development
  - Appropriate for organic production

But, concerns about sulfur residues at harvest result in restrictions on use

Specifically, S → H_2S during fermentation

Elemental sulfur: rather toxic to yeast, will be converted to H_2S during fermentation

Elemental sulfur → *Fermentation* → H_2S



Adapted from Acree, et.al. AJEV 1972

Previous Sulfur Residue Research – Sensory and Viticultural

- Maximum desirable S-residue in **must** before excess H_2S is produced: **1-10 mg/L,** depending on report

- How late can one spray and have 1-10 mg/L? Depends who you believe . . .
  - Germany: 6 weeks (Wenzel, 1980)
  - California: 8 weeks (Thomas, 1993)
  - California: 2 weeks, based on sensory of wines (Sawyer-Ostrom, 1995)

  - *Hmm. Somewhere between 2 and 8 weeks. Not at all helpful.*

“So, how late can I spray?”

Riesling with elemental sulfur spray residues, in a Finger Lakes vineyard less than 2 weeks before harvest in 2009

Large variation in persistence expected based on: Formulation; Rate; Weather; Sprayer; and other factors

Previous methods for elemental S analyses required expensive equipment, resulting in limited number of studies, sites, and replicates

Need an easy, inexpensive test for sulfur residues!

Analytical method developed by our group for S-residues: appropriate for small operations

- Limited specialized equipment
- Inexpensive (<$5/run)
- Quick (20-30 minutes, can do multiple tests at once)
- Simple (at, least we think it's simple)

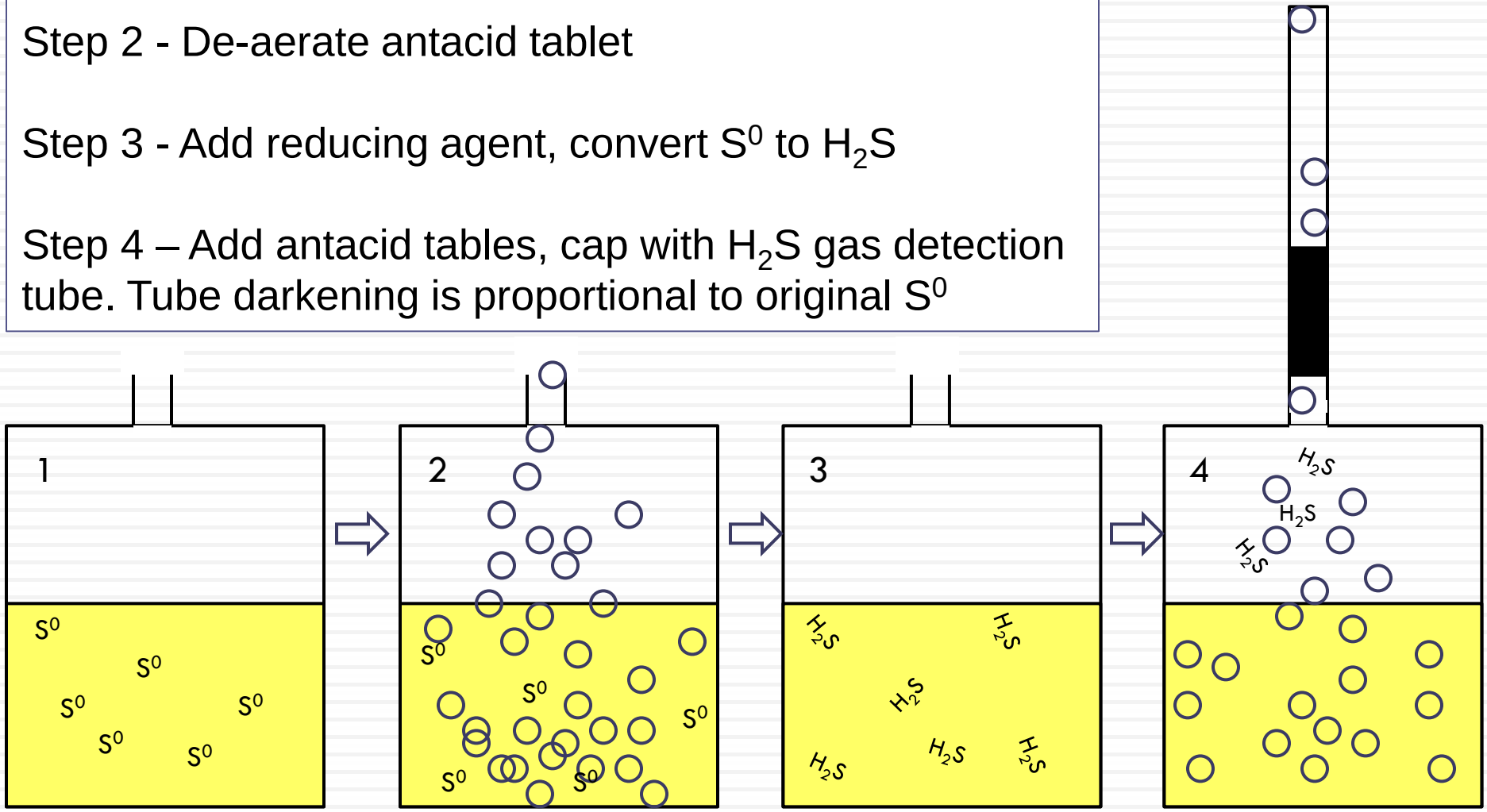
Overview of the Method

Step 1- Grape macerate or juice + buffer

Step 2 - De-aerate antacid tablet

Step 3 - Add reducing agent, convert S^0 to H_2S

Step 4 – Add antacid tables, cap with H_2S gas detection tube. Tube darkening is proportional to original S^0

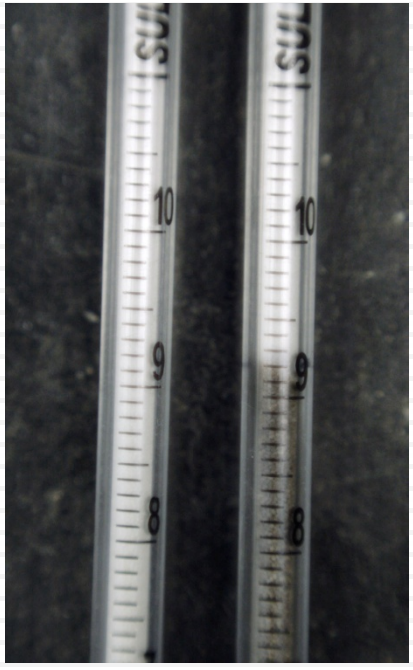


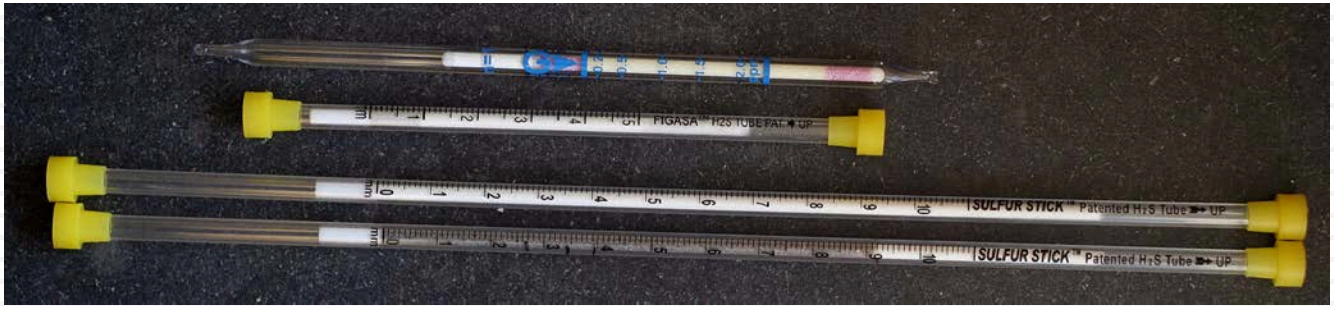
H_2S Detection Tubes – reactive immobilized metal salt

Hydrogen Sulfide + Lead Acetate (White) → Lead Sulfide (Black)

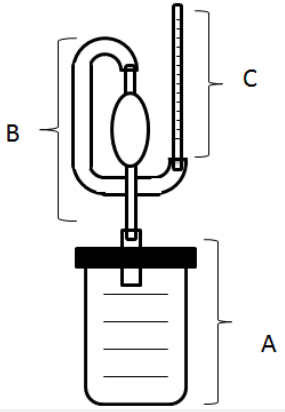
Options

- "The Sulfur Stick" – Wine focused tube produced by Figara Technologies
- Mining Industry detection tubes (Gastec and others)





Elemental Sulfur Method



http://www.lib.fit.edu

"plop plop fizz fizz let's see how much sulfur there is"

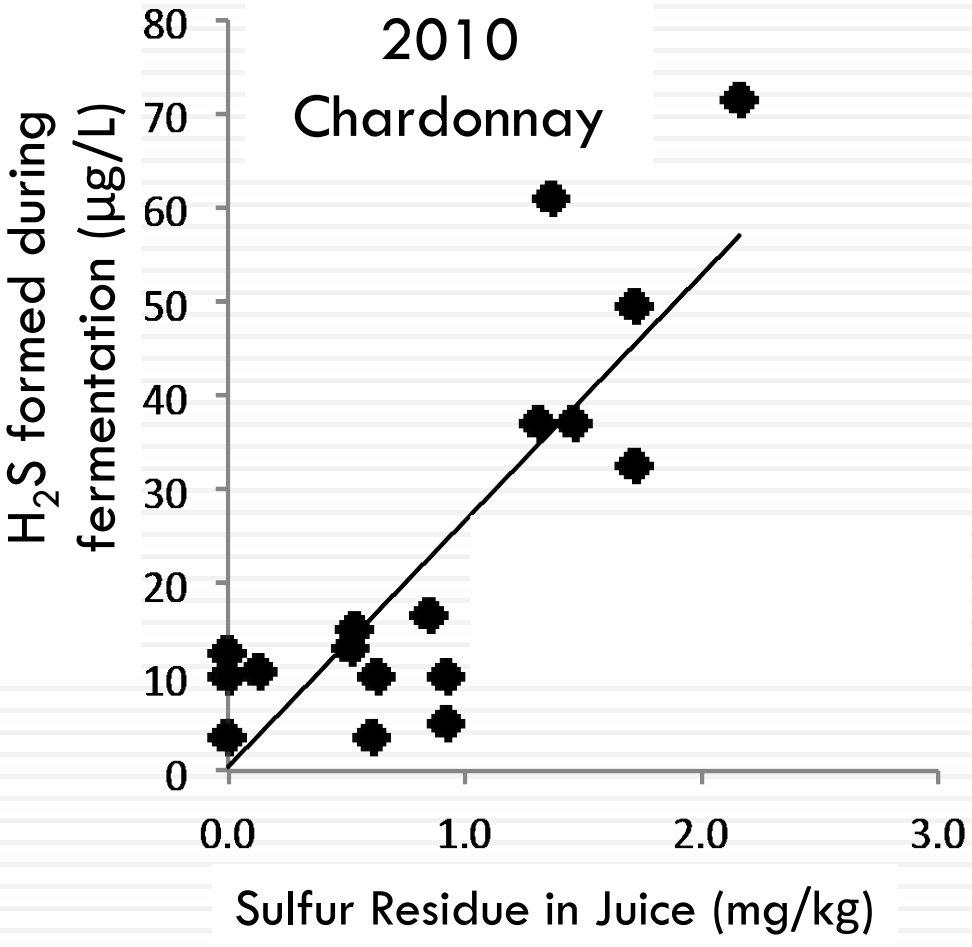
Want full info on method?

www.extension.org/pages/69748/analyzing-elemental-sulfur-residues-on-grapes for written protocol

http://www.youtube.com/watch?v=yH83vDX8ORQ for video demo

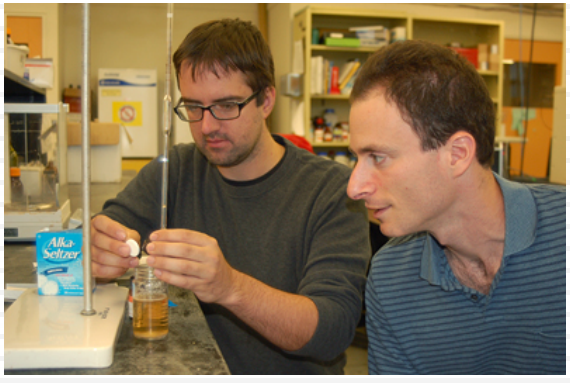
http://www.sciencedirect.com/science/article/pii/S0003267011009512 for link to original Kwasniewski, Allison, Wilcox, and Sacks article.

Similar to previous reports: H_2S problems with >1 mg/kg residues



Always background H_2S due to yeast metabolism

. . . but we see increased H_2S production starting at 1 mg/kg S-residues (left)



"So, what results in 1 mg/kg S at harvest?" Sulfur Residue Field Trials, 2009-2011

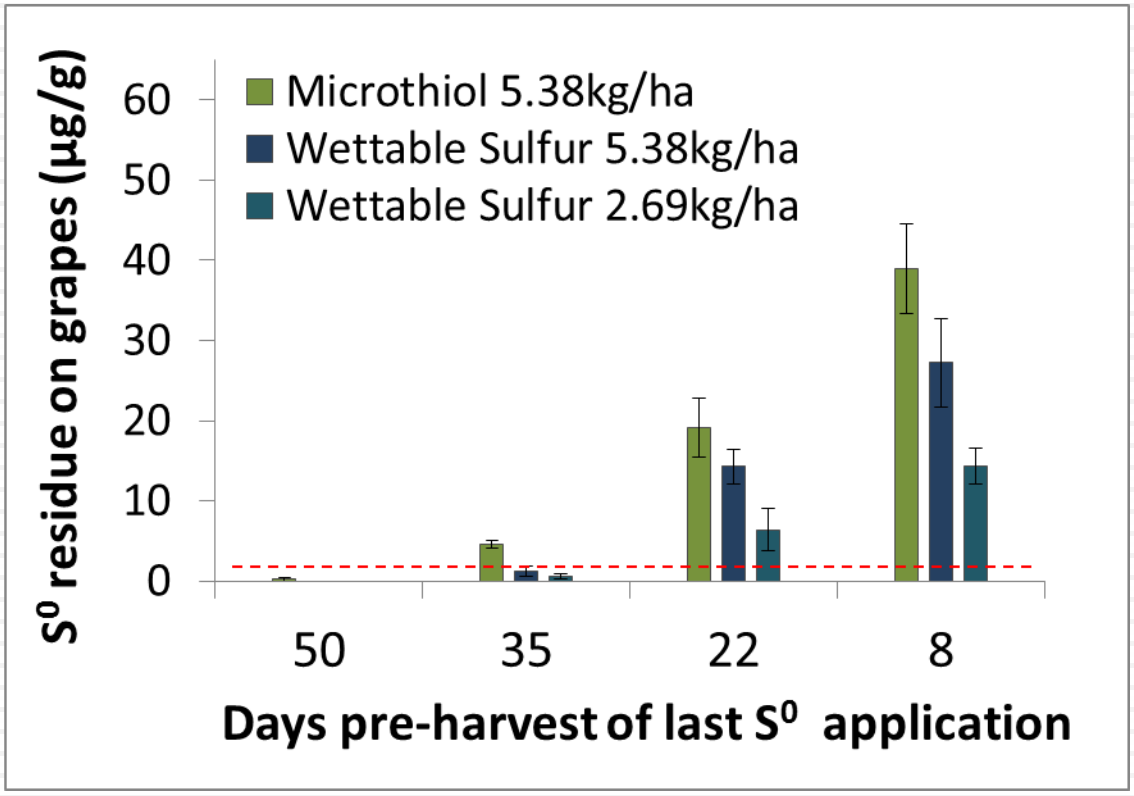
- Collaboration with Wayne Wilcox (Cornell, Plant Pathology)
- Finger Lakes region (Geneva, NY).
- S^0 containing fungicides applied by over-the-row hooded sprayer
- Treatments varied:
  - Application rates
  - Formulation
  - Pre-harvest spray interval
- Samples taken at roughly 1-2 week intervals
- 4 replicate panels per treatment, 5 clusters per panel per time point

Example data:
2010 Treatments- Chardonnay

- Treatments began at veraison, additional sprays applied at approximately 2-wk intervals
- Spray cessation
  - 50, 35, 22, or 8 days before harvest
- Formulations
  - Microthiol Disperss (5.38 kg/ha application rate)
  - Kumulus (2.69 or 5.38 kg/ha)

**50 day preH stopping point only included Microthiol at 5.38kg/ha*

2010 Field Trials – Results - Harvest



Above: the control treatment
No S-residues detectable

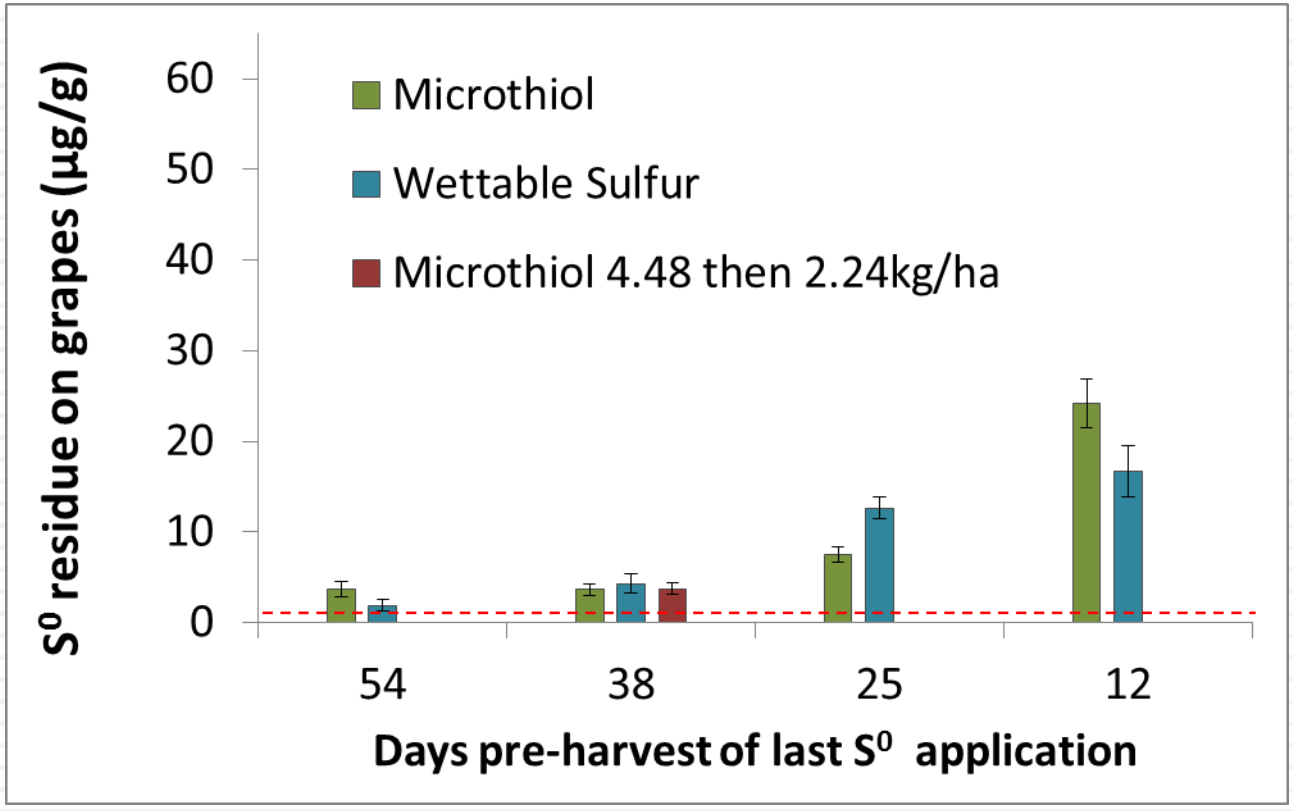
Summary of results for 2009 and 2010: pre-harvest interval of **>5 weeks** results in S-residues < 1 mg/kg at harvest

Kwasniewski, Sacks, and Wilcox; *AJEV* **2014**

2011 Treatments - Riesling

- Treatments began on July 13, 2011, with additional sprays applied at approximately 2-weeks intervals
- Pre-harvest interval: 12, 25, 38 or 54 days before harvest
- Formulations
  - Microthiol Disperss; 4.48kg/ha*
  - Kumulus , 4.48kg/ha
  - *Microthiol at 4.48kg/ha then 2.24kg/ha for final two treatments ending 38 days pre-harvest*

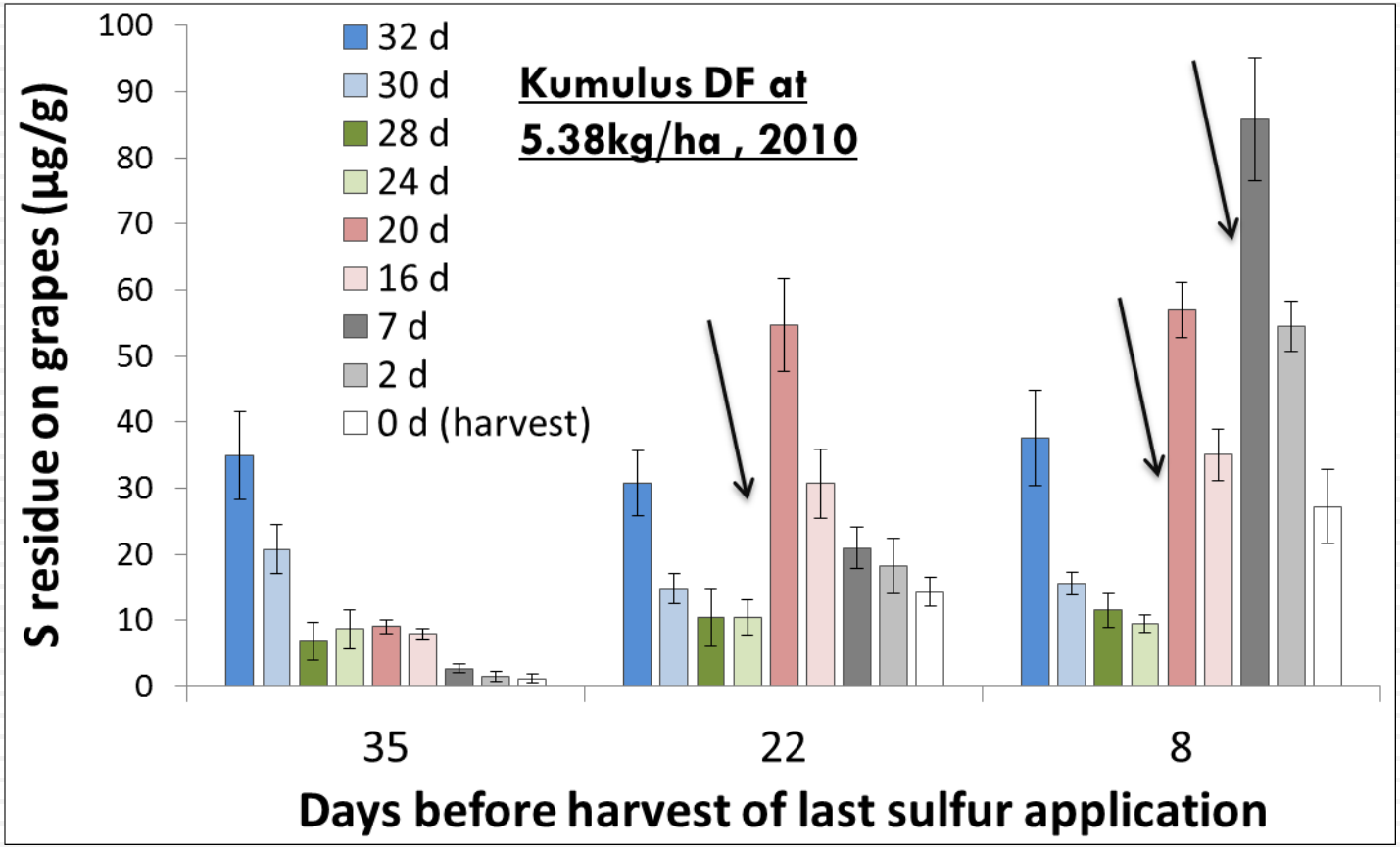
2011 Field Trials – Results - Harvest



Kwasniewski, Sacks, and Wilcox; *AJEV* **2014**

Summary of results: 54 day pre-harvest interval can still yield potentially problematic spray residues (> 1 mg/kg) !

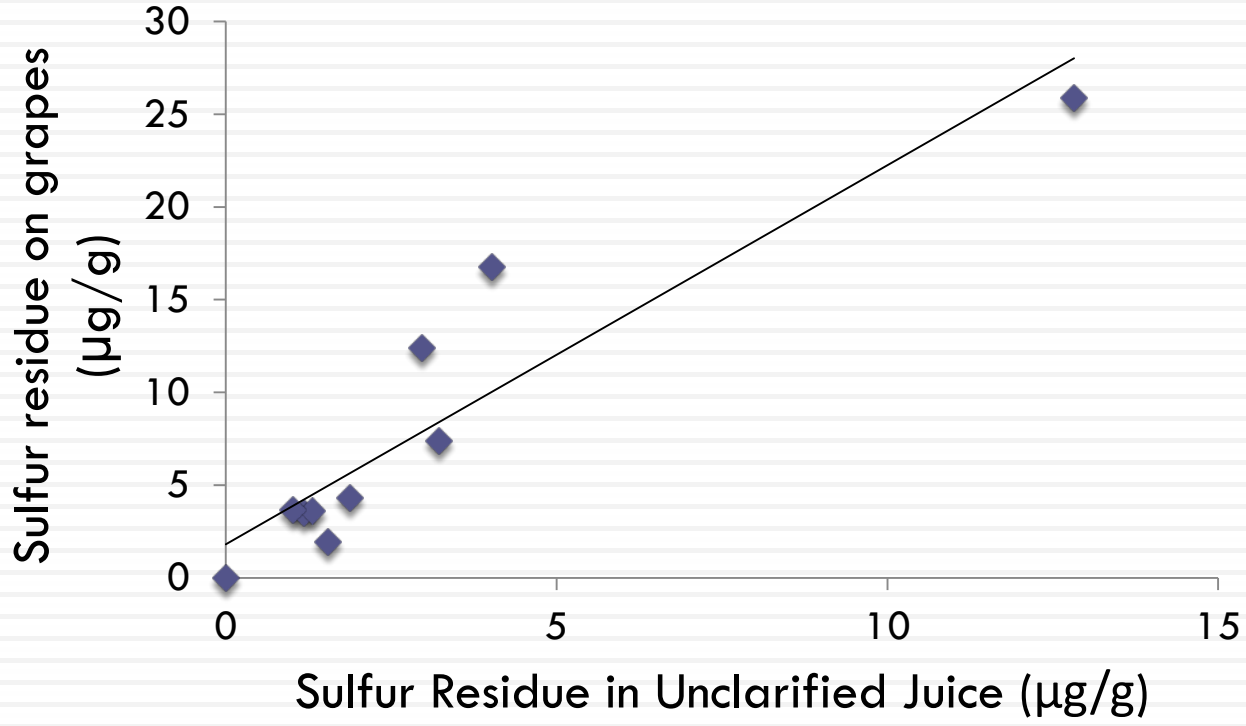
Ongoing work: Understanding the rate at which S-residues are lost



Arrows indicate timing of S application

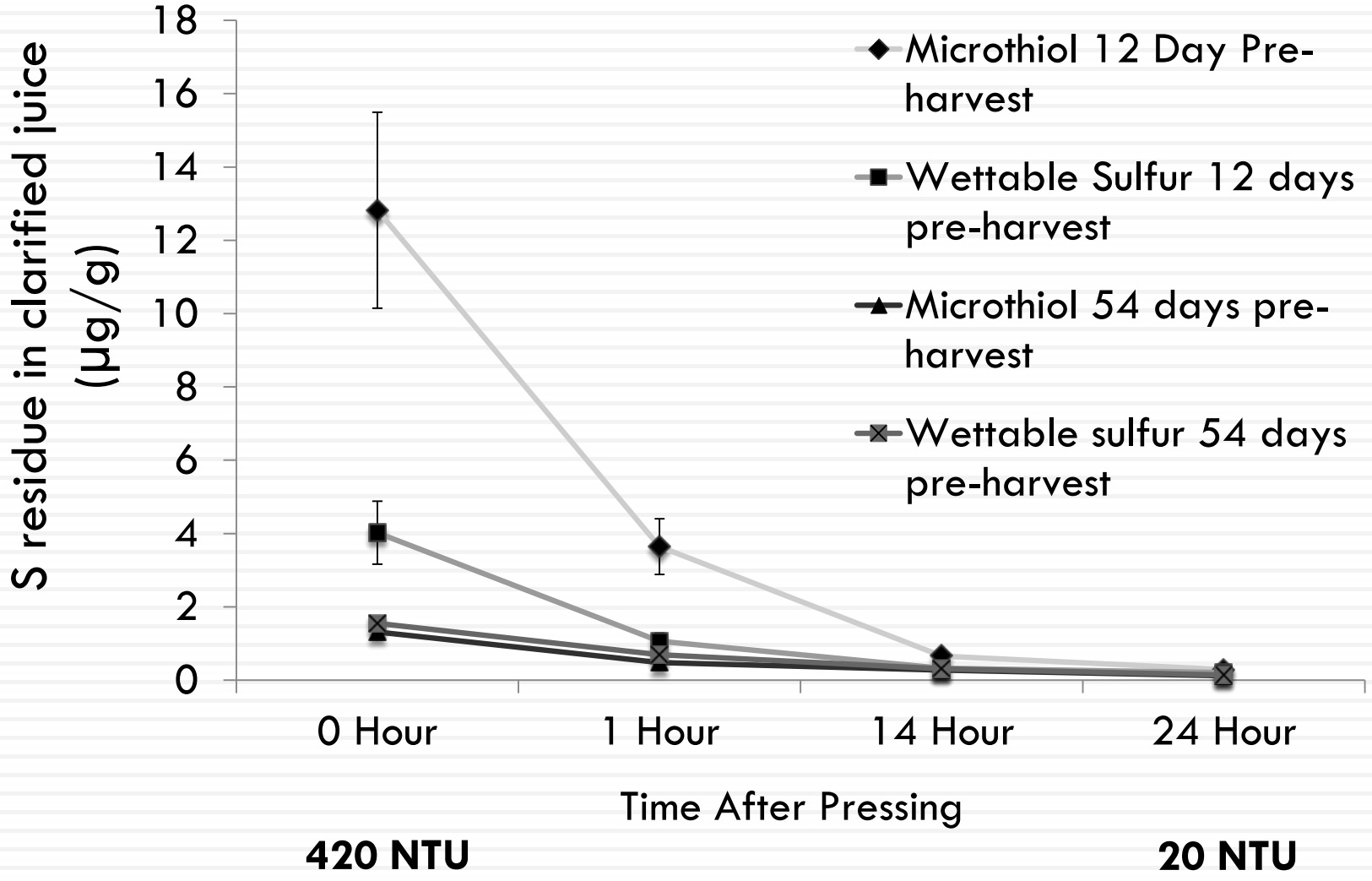
Can we correlate differences in rate of S loss to environmental differences (e.g. temperature, sun, rainfall, etc)?

That's fine for skin-fermented grapes
What if I'm making a white wine?



- About 50% of grapes S-residues are transferred to must
- But, clarification/must settling has a major impact! (see next slide)

Effects of settling on S residues



For white wines, most S-residue will be in tank bottoms

Original fruit with > 40 mg/kg sulfur residue

Fraction	Sulfur residue (mg/kg)	St Dev
Crushed, free run	1.2	0.29
Turbid must, pressed	6.8	1.23
Sediment (after settling)	46.6	5.20
Clarified, settled must	0.1	0.03

Good clarification
=
Less stinky times

Do you measure your solids/turbidity during clarification?

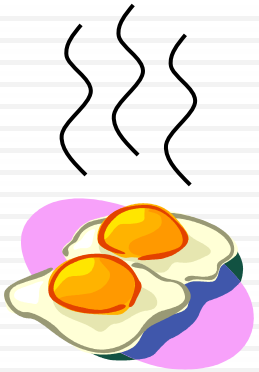
What to do if residues are too high?

- Delay harvest: weathering will remove elemental S
- Wash grapes? Probably unrealistic
- Not efficiently extracted into juice, so if using white grapes . . .
  - Hand harvest: reduce skin contact
  - Whole-cluster press (if possible)
  - Good must clarification (can remove >90%)

- Just as importantly, can confirm when sulfur is not the cause of H_2S during fermentation

A final issue: what's the right metric for limits on 'maximum recommended S-residues"?

- Forming more H_2S during or right after fermentation?



- Having off-aromas present soon after fermentation?

- Having off-aromas or H_2S appear during tank or bottle storage?

Evidence that H_2S or SLOs *can* reappear during reductive storage

Sauvignon blanc wine with undetectable H_2S before bottling, stored for 2 years

	Sealed ampoule	**Saran-Tin Screwcap**	**Natural cork**	**Nomacorc synthetic**
H_2S after 2 years (ng/mL)	29.6	21.1	15.5	3.5

Adapted from Lopes, et.al. **2009,** *JAFC*

Other supporting data

Ugliano, et al **2011,** *JAFC;* Ugliano, et al **2012,** *JAFC;* Viviers, et al **2013,** *JAFC*

Research focus to date on SLO appearance in bottle – Closures and oxygen ingress

Closure trials:

- AWRI
- Bordeaux
- Geisenheim
- Oregon State
- Constellation Brands
- and others?

What has not been well studied: **the wine!**

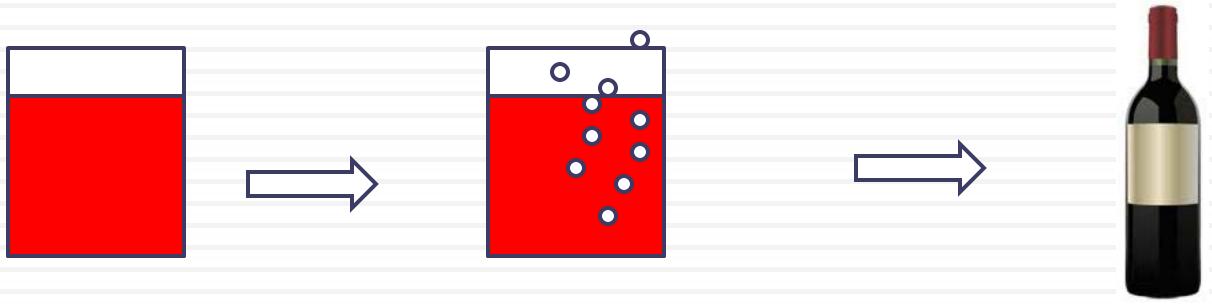
SLO occurrence is wine-dependent as well as packaging dependent.

How are these wines making H_2S and related compounds?

Hypotheses for sources of "latent" H_2S during anaerobic storage of wine

- Degradation of cysteine, a sulfur containing amino acid
  - (Ugliano, J. Ag Food Chem, 2011)
- Reduction of copper sulfide (CuS) complexes
  - (Ferreira, J. Ag Food Chem, 2014)
- Reduction of bisulfite or sulfur dioxide to H_2S (?)
  - (Lopes, J. Ag Food Chem, 2009)
- Degradation of S-pesticide residues in bottle (uh-oh)
  - Rauhut (Der Deutchse Weinbau, 1986)

Our own work: can wines made from grapes with sulfur residues evolve H_2S during storage?



Wine from different spray treatments

Sparge to remove H_2S

Bottle, store, check for new H_2S after *n* months

Elemental sulfur residues: another potential source of latent H_2S?

Elemental sulfur in fermentation (mg/L)	Free H_2S at bottling (ppb)	Free H_2S at 3 months (ppb)
0	nd	nd
20	nd	2.4
100	nd	10.0

Jastrzembski and Sacks
Unpublished work

Ongoing mysteries . . .

- How important is this phenomenon?
- What are the intermediates in wine?

Summary

1) New, inexpensive method for quantifying S residues on grapes and in must

2) Results from field studies of S-sprays

   - 5 weeks pre-harvest okay for 2 out of 3 years, but borderline for one year. **Variation is expected**

   - Juice clarification greatly reduces S residues (>98%)

3) Future directions:

   Is reappearance of H_2S in bottle occasionally related to S-residues?

   Do we need to think about limits based on storage effects?