PAPTAC Bleaching Committee

2012-2013 Bleaching Survey
SWD & O2-SWD
Updated Results & Analysis

(still a work in progress…)

Spring 2015 Meeting
Pointe-Claire, QC
May 4-6, 2015

Outline

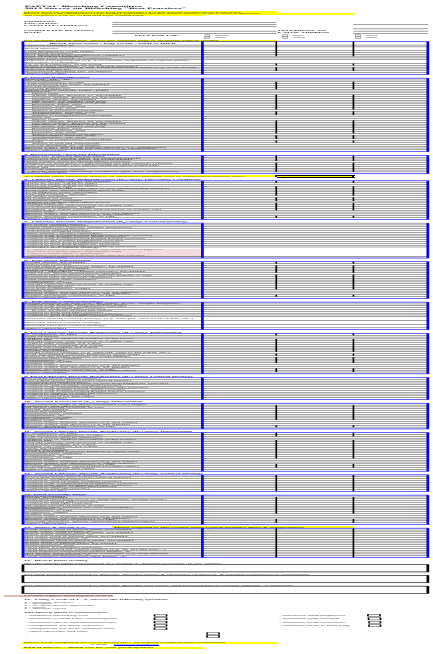
- Background
  - Survey response & methodology
- Results
  - SWD & O2-SWD
    - Comparison with 2003 results
    - Brownstock & Oxygen Delignification
    - Bleaching stages
    - Overall chemical use and bleaching cost
- Analysis
  - Differences between “Low” and “High” relative chemical consumption bleach plants
  - Trends since 2003
  - Identification of Bleaching “Best Practices”

Background

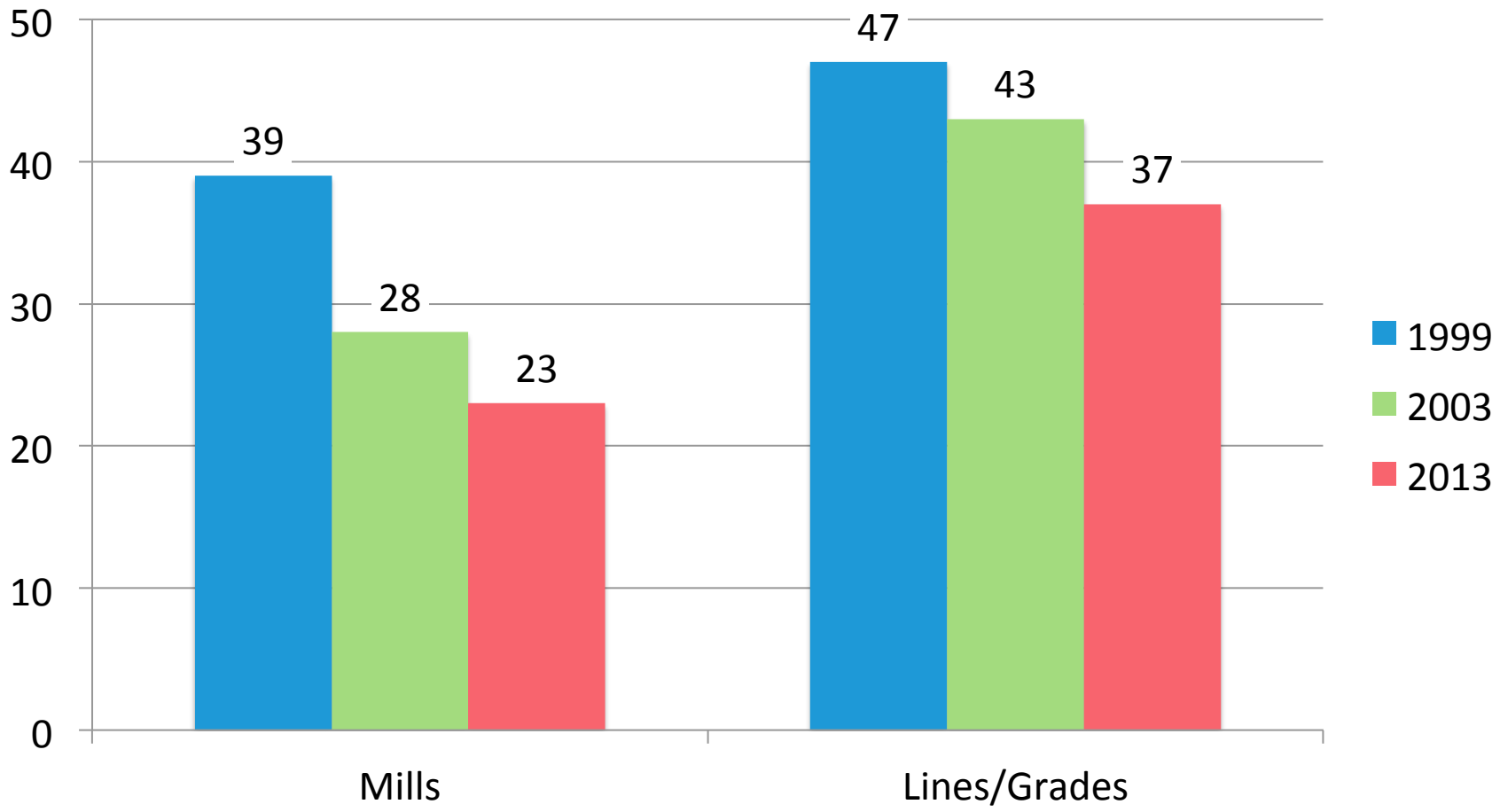
- Bleach Plant Surveys carried out in early 1990's, 1998-99, 2003-04
- Survey of Operational Parameters
  - Chemical use
  - Bleaching stage variables (time, temperature, pH)
  - Washers and showers
  - Energy use
  - Process control
- Last survey sent out January 2003, presented Spring 2004
  - 28 mills responded (~80% response)
  - 43 bleach lines or grades (72% response)

2012/13 Bleaching Survey

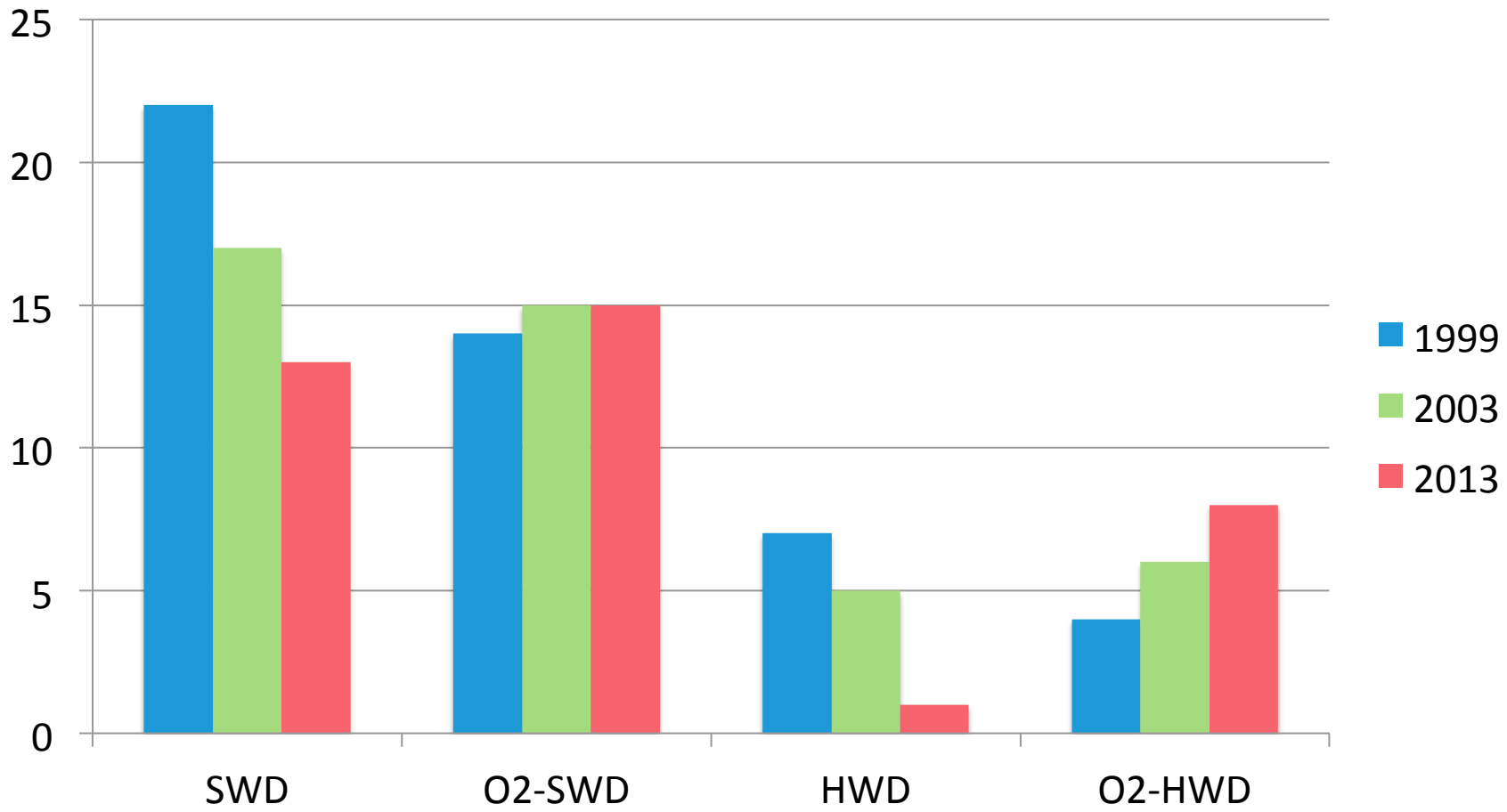
- ✓ Using previous survey as template (with modifications / additions)
  - spreadsheet, 300+ rows
- ✓ All dated is coded; no mill names
- Changes:
  - Includes Oxygen Delignification now
  - More details on steam & water use
  - Updated process control questions
- Project Team
  - Paul Earl, Dan Davies, Brian La Brash, Honey Nampak, Doug Reid, Murray Walters
- Survey initially sent out Sept. 7, 2012
  - First response Sept. 25, 2012
- 23 responses, representing 37 lines or grades



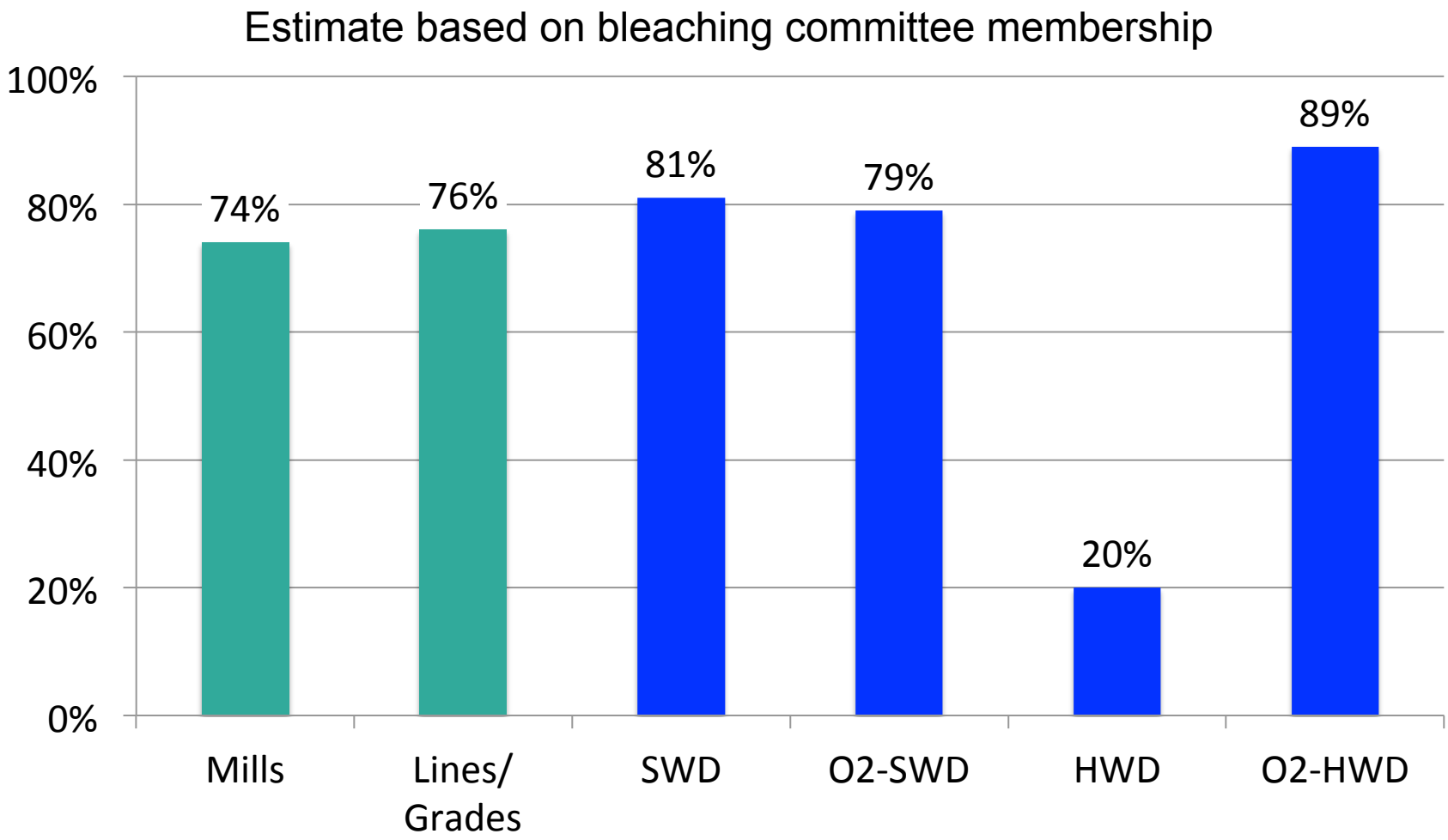
Survey Response



Response By Grade



Response Rate



Methodology

- Responses were coded
  - Wood furnish and ClO_2 generator removed
- Data converted to "standard" units:
  - *e.g.* chemicals as kg/ADMT, temperature in °C
- SWD & O2-SWD analysis = Fall 2014 / Spring 2015
- O2-HWD analysis = Fall 2015 ?
- Process Control and Water & Energy Use to be analyzed separately
- Results (coded spreadsheets & slides) posted after presentation on new members' website

Definitions

- "Kappa Factor" = $\frac{\%\ \text{Chemical on Bleached ADMT pulp (as eq. } Cl_2)}{\text{Kappa No. into bleach plant}}$
- Total ClO_2 Kappa Factor includes all ClO_2 used in bleach plant
- Sequence Kappa Factor includes all oxidizing chemicals in bleach plant (ClO_2 & H_2O_2 only)
    - Oxygen in Eop-stage is *not* included
- In each of the pulp grade categories, mills were sorted by Sequence Kappa Factor
  - Divided into two groups and averaged:
  - "Low Relative Chemical Consumption" are the mills below the median (*i.e.* the lower 50%)
  - "High Relative Chemical Consumption" are the mills above the median (*i.e.* the upper 50%)

Assumptions

- If ranges were provided instead of single data points, then the average was taken
  - *e.g.* "8-10 kg/t" = 9 kg/t
- Conversion of K# to Kappa No.
  - K# >14, Hatton SWD Eq'n
  - K# ≤14, Hatton HWD Eq'n
  - Eop K# x 1.35
- "*Bleaching Cost*" graphs assume all mills have same chemical costs:

  ClO_2 = \$1.30/kg H_2O_2 = \$0.65/kg

  O_2 = \$0.05/kg NaOH = \$0.60/kg
- Bleaching Cost does not include acid, $MgSO_4$, bleach plant steam, or the costs associated with oxygen delignification
- "Normalized Bleaching Cost" pro-rates the cost linearly to a constant bleach feed Kappa No.

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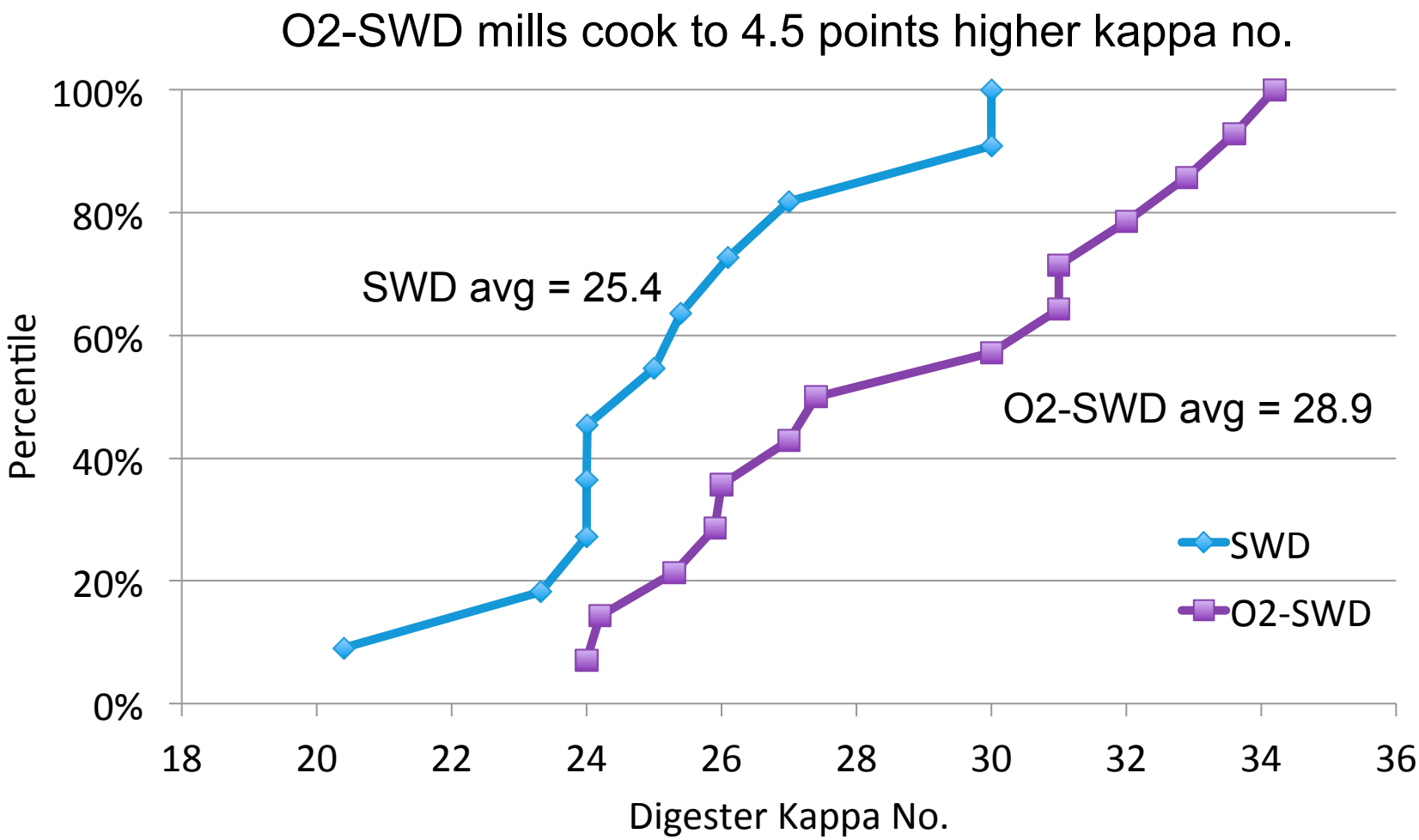
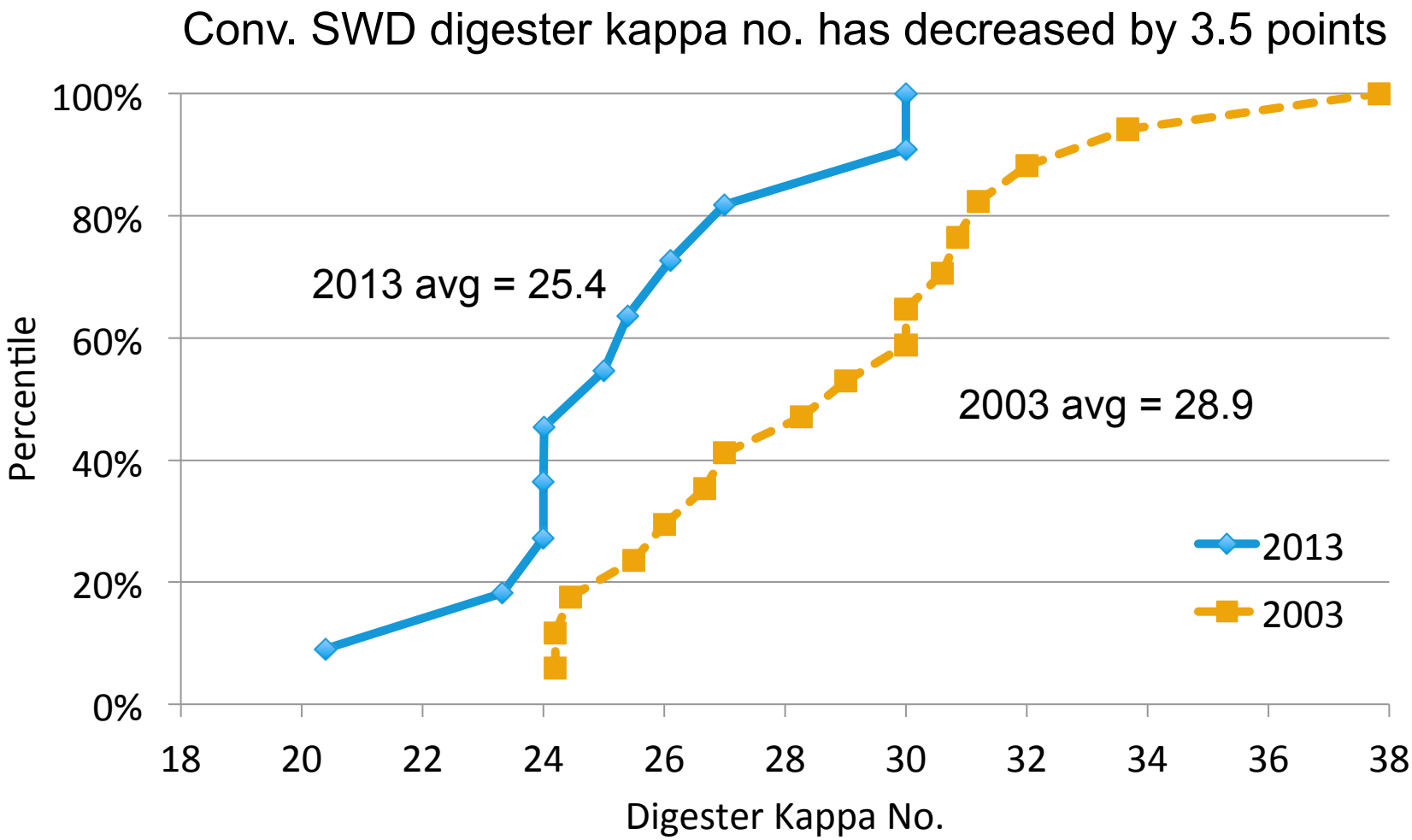
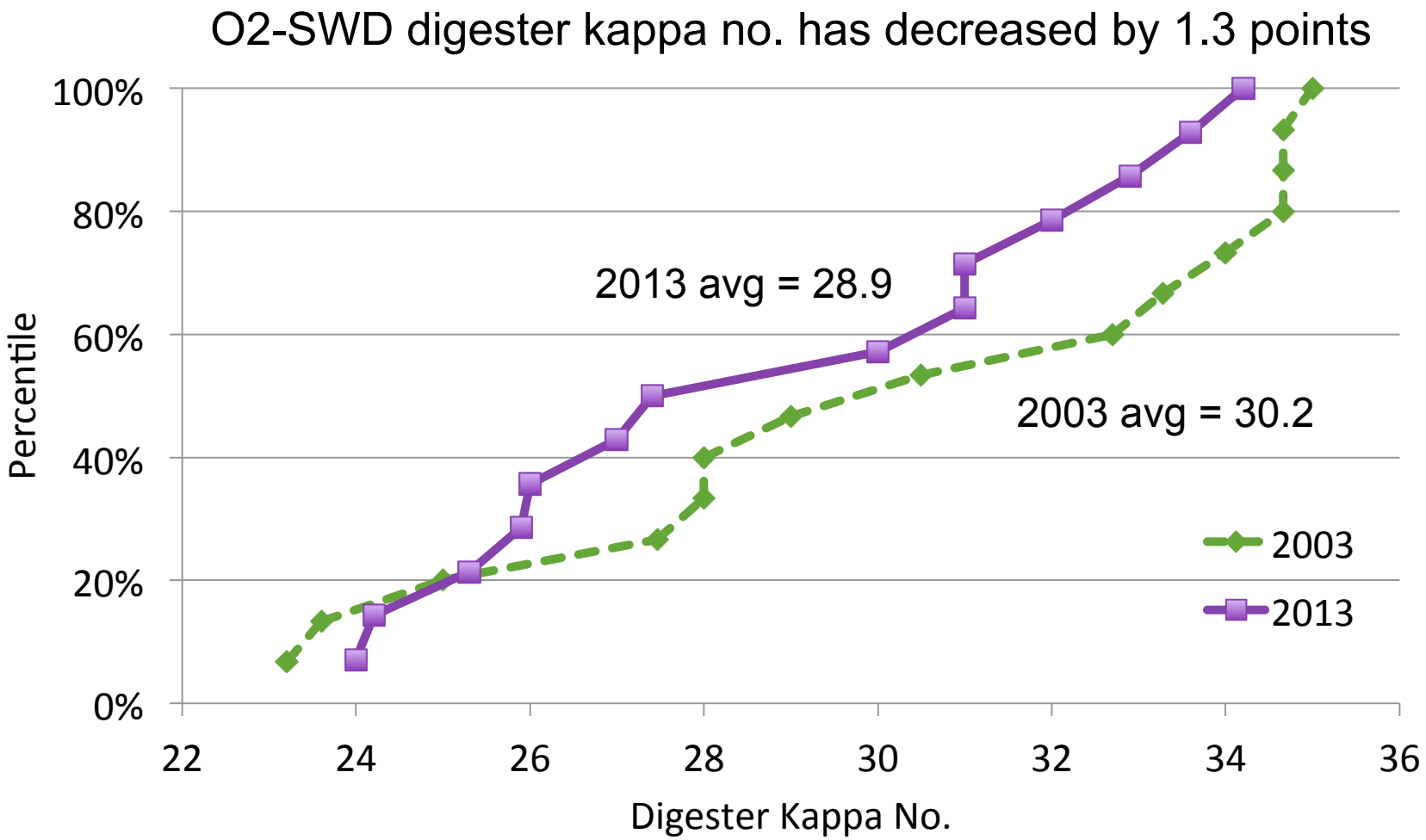
Digester Kappa No.



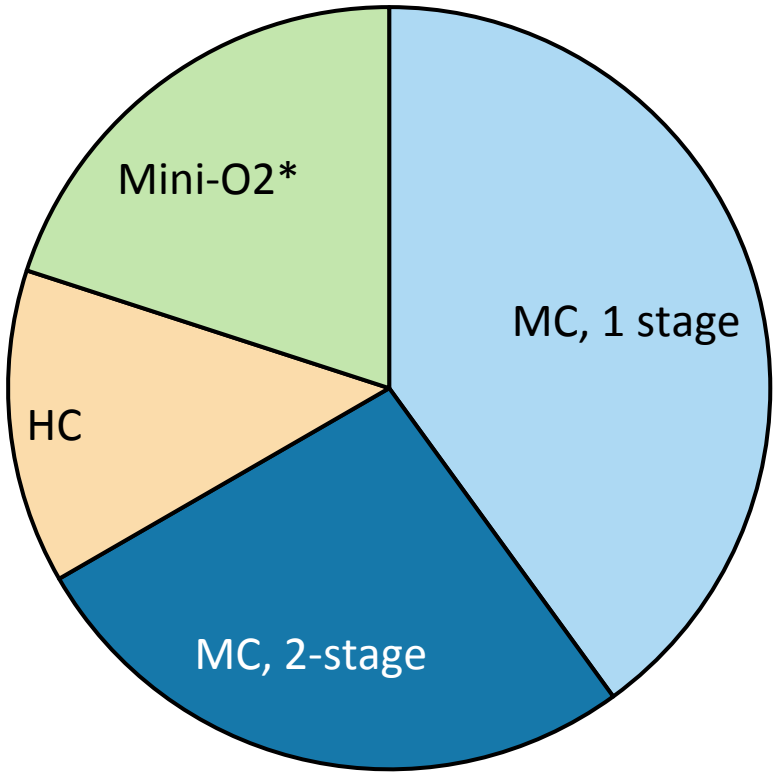
SWD Digester Kappa No.



O2-SWD Digester Kappa No.

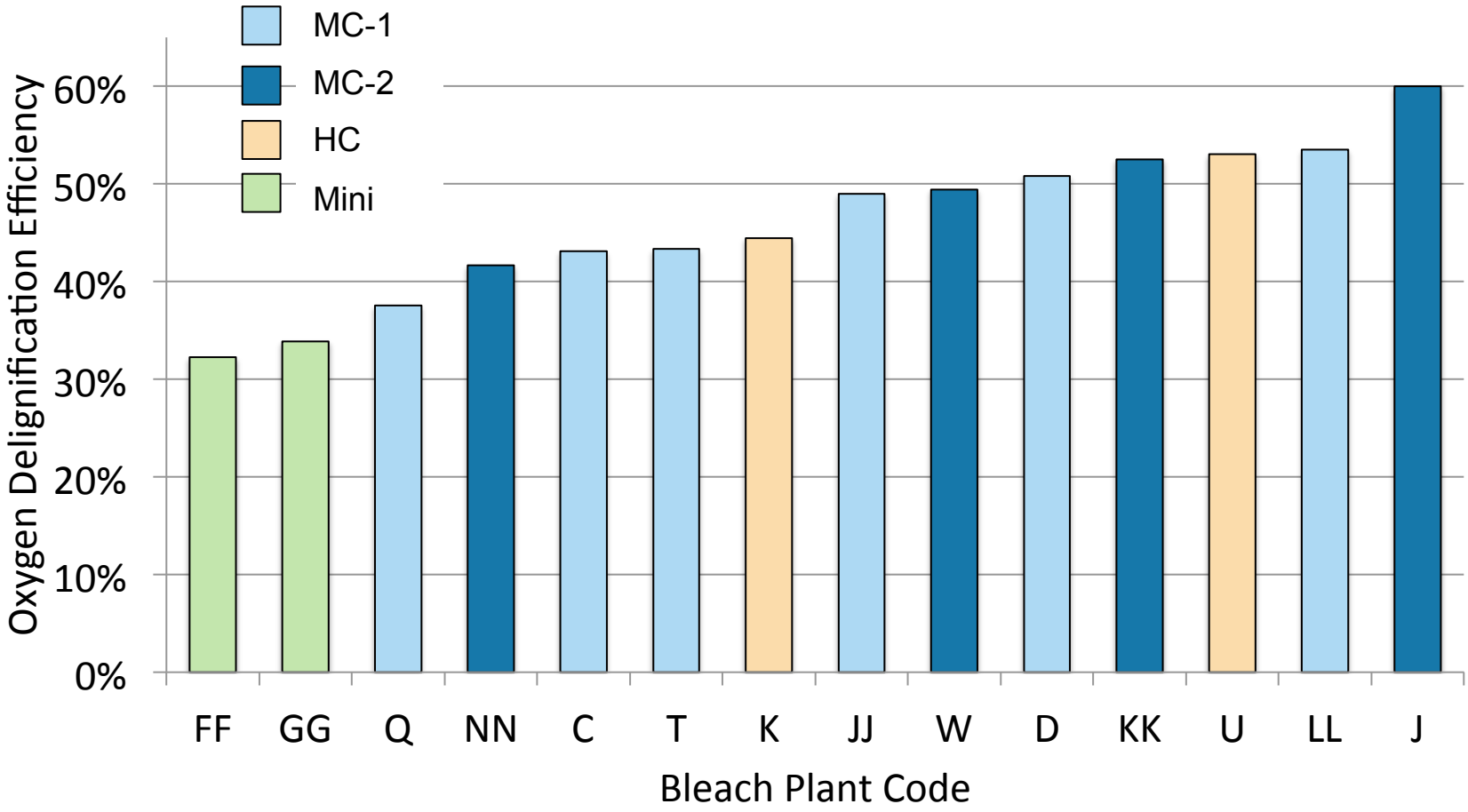


O2 Delignification Systems

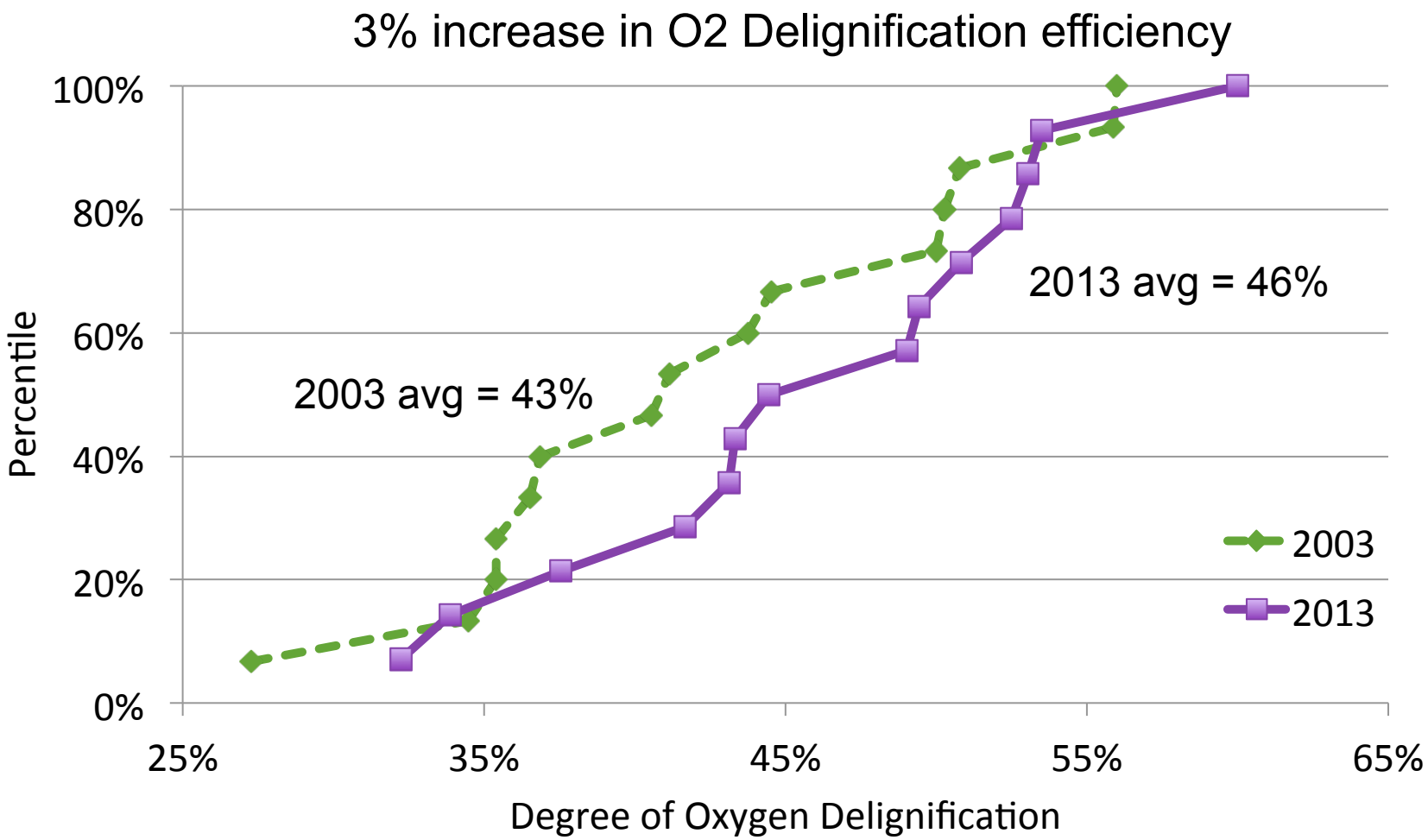


* One mini-O2 bleach plant removed from analysis due to very low delignification efficiency

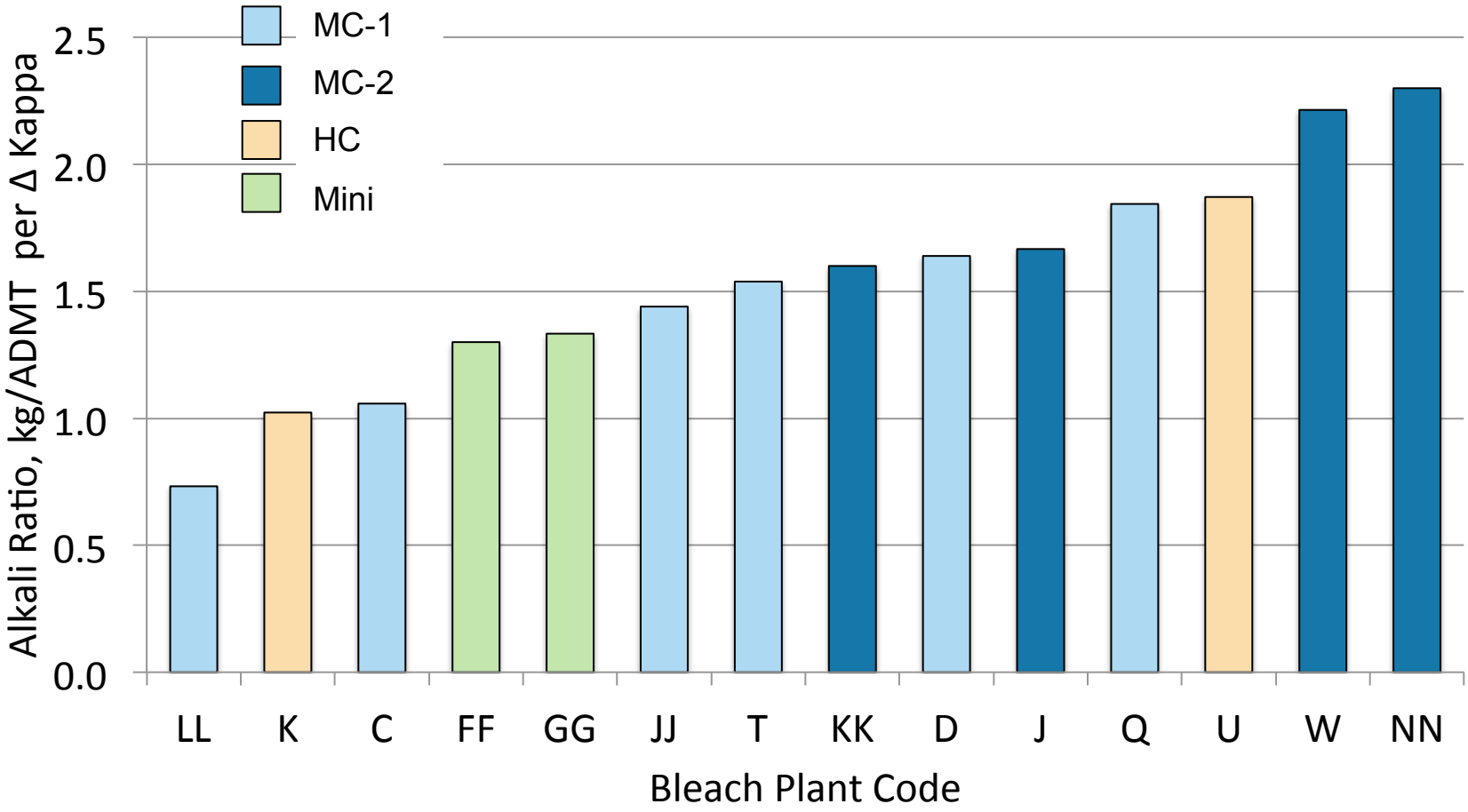
Oxygen Delignification



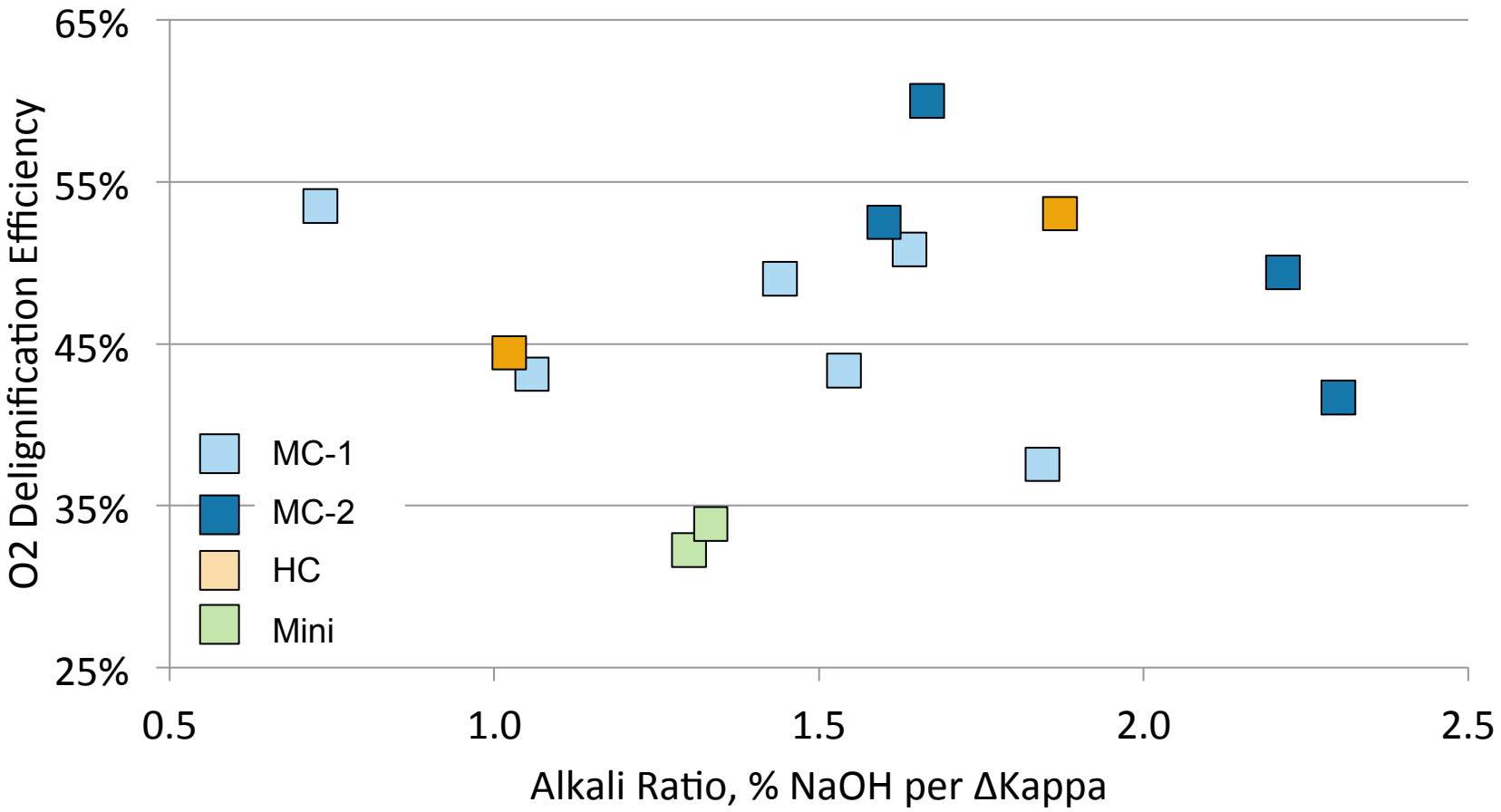
Oxygen Delignification



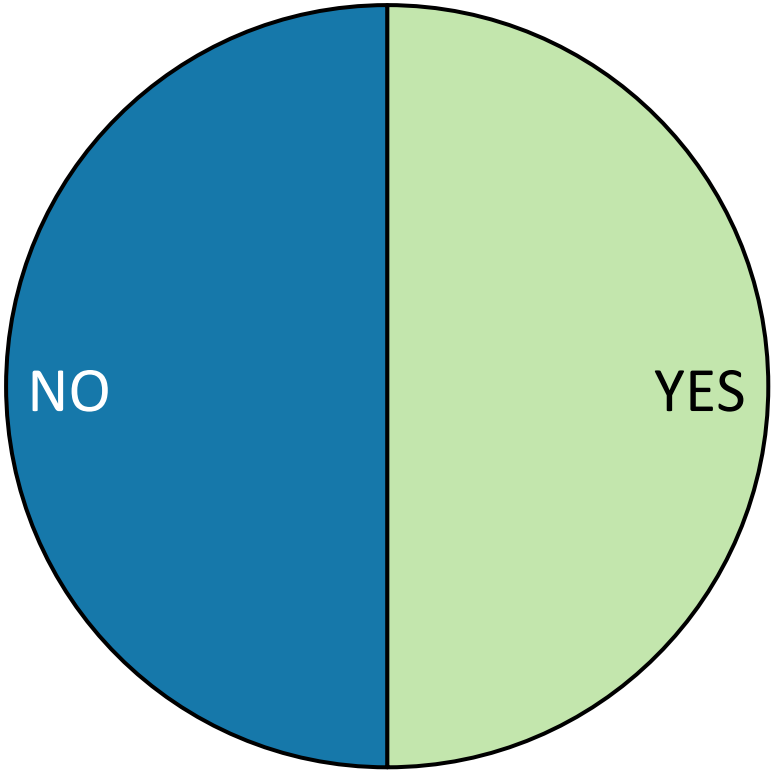
O2D Alkali Ratio



O2D Alkali Ratio

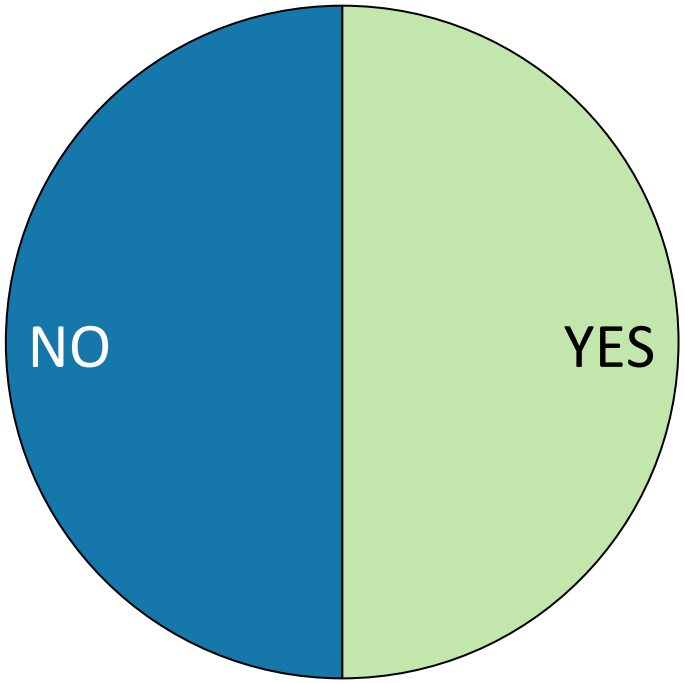


O2-SWD: Magnesium Sulfate?

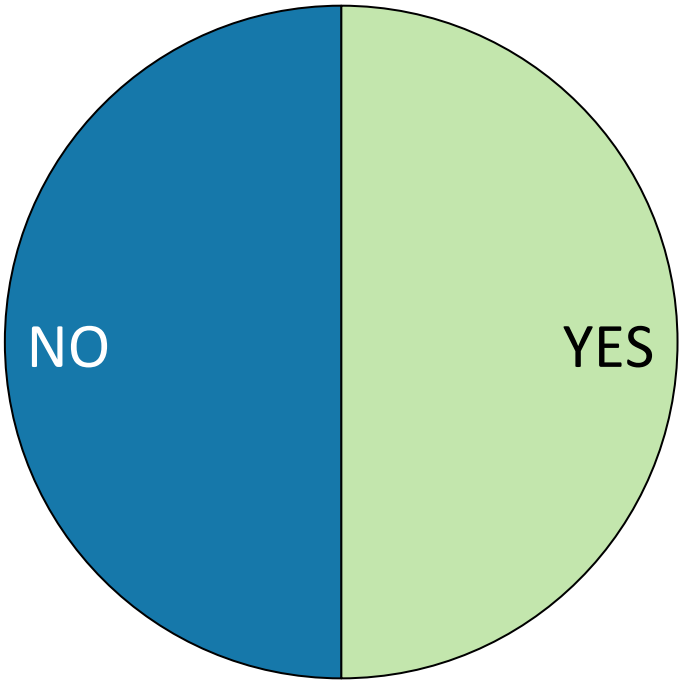


Open Washer Ahead of Bleach Plant?

Half of all bleach plants have open pre-bleach washers



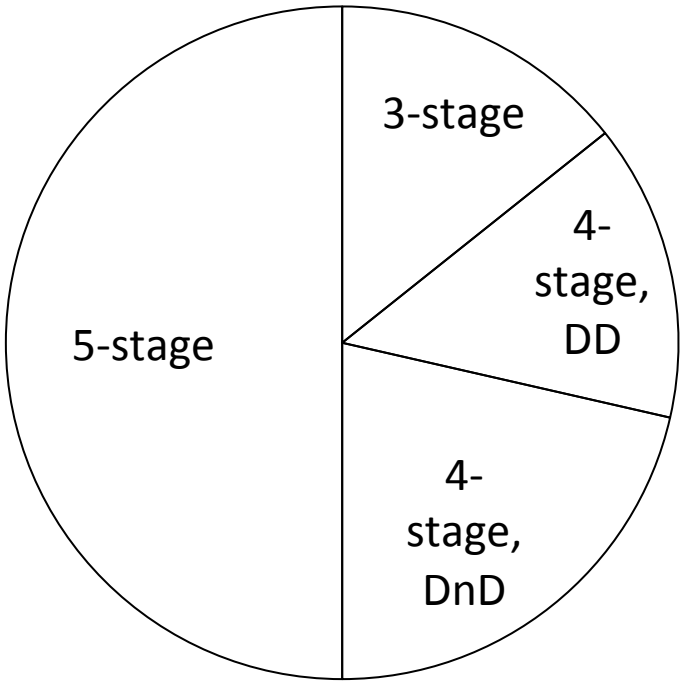
O2-SWD



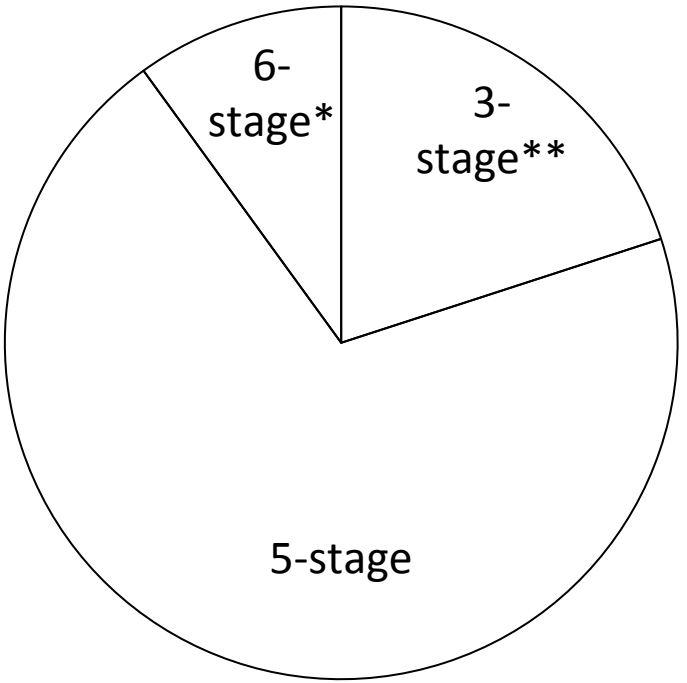
SWD

SWD Bleach Plants

O2-SWD

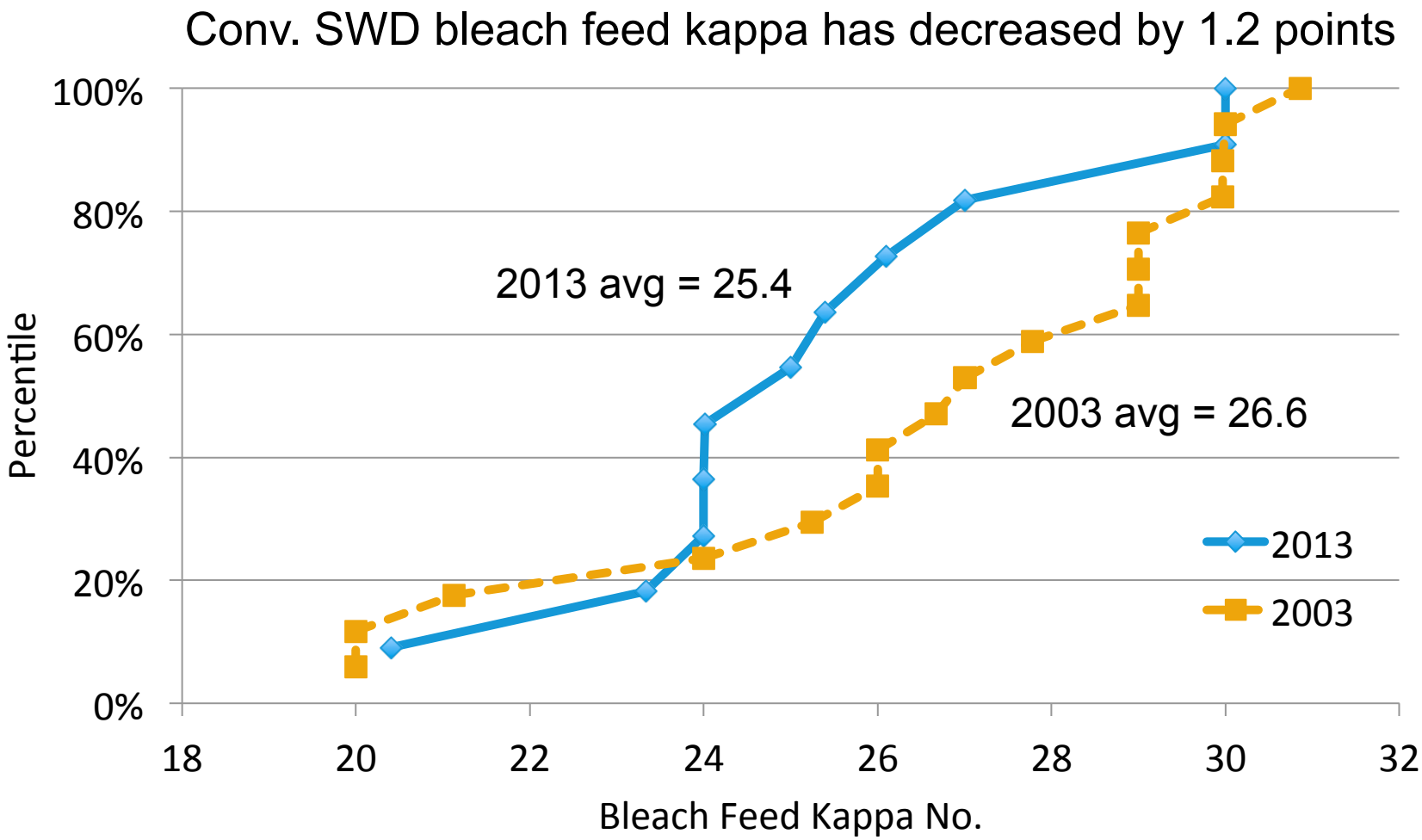


SWD



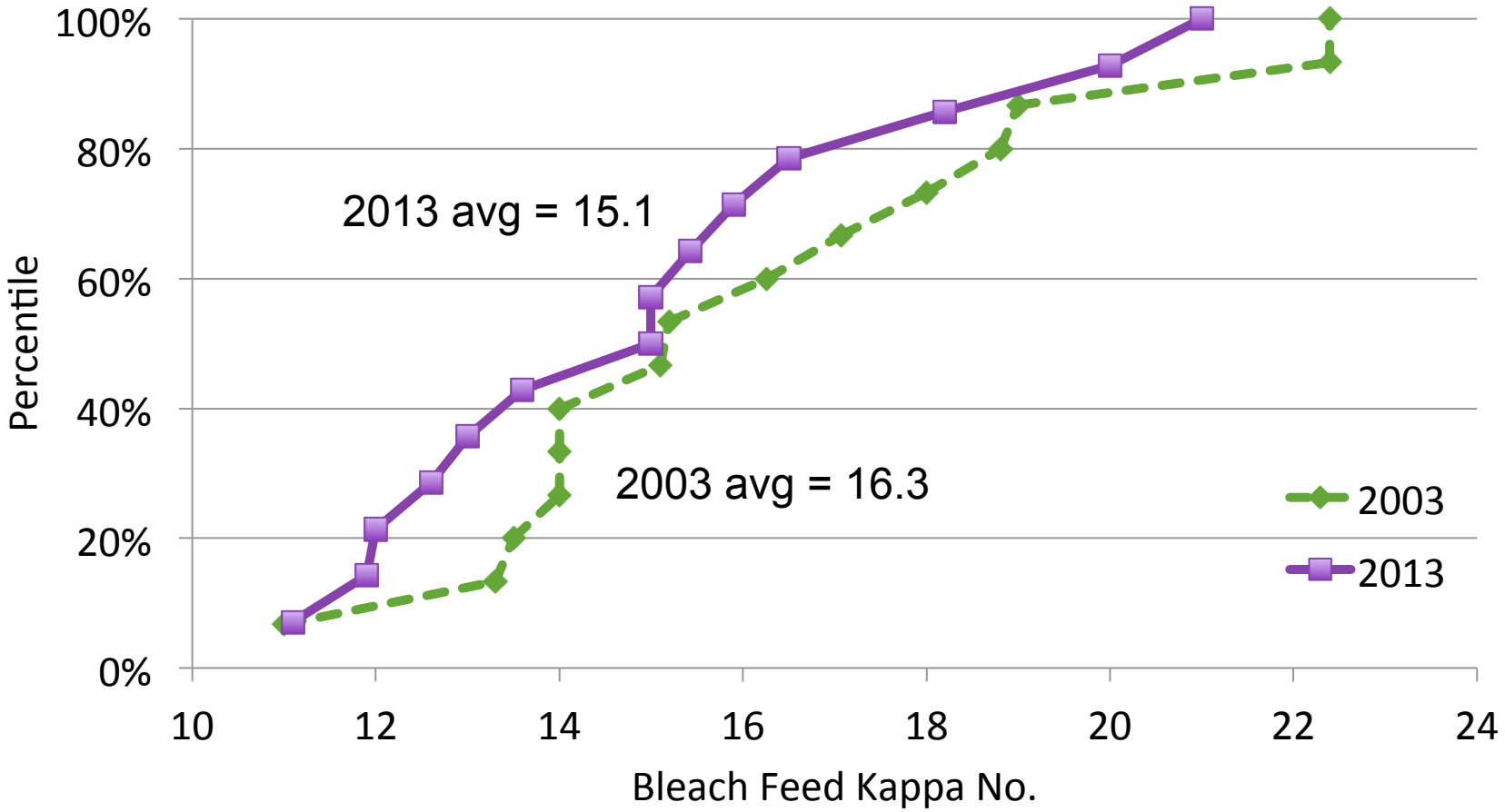
* 6 stages includes Papricycle
** Both using DEopWpD sequences

SWD Bleach Feed Kappa No.

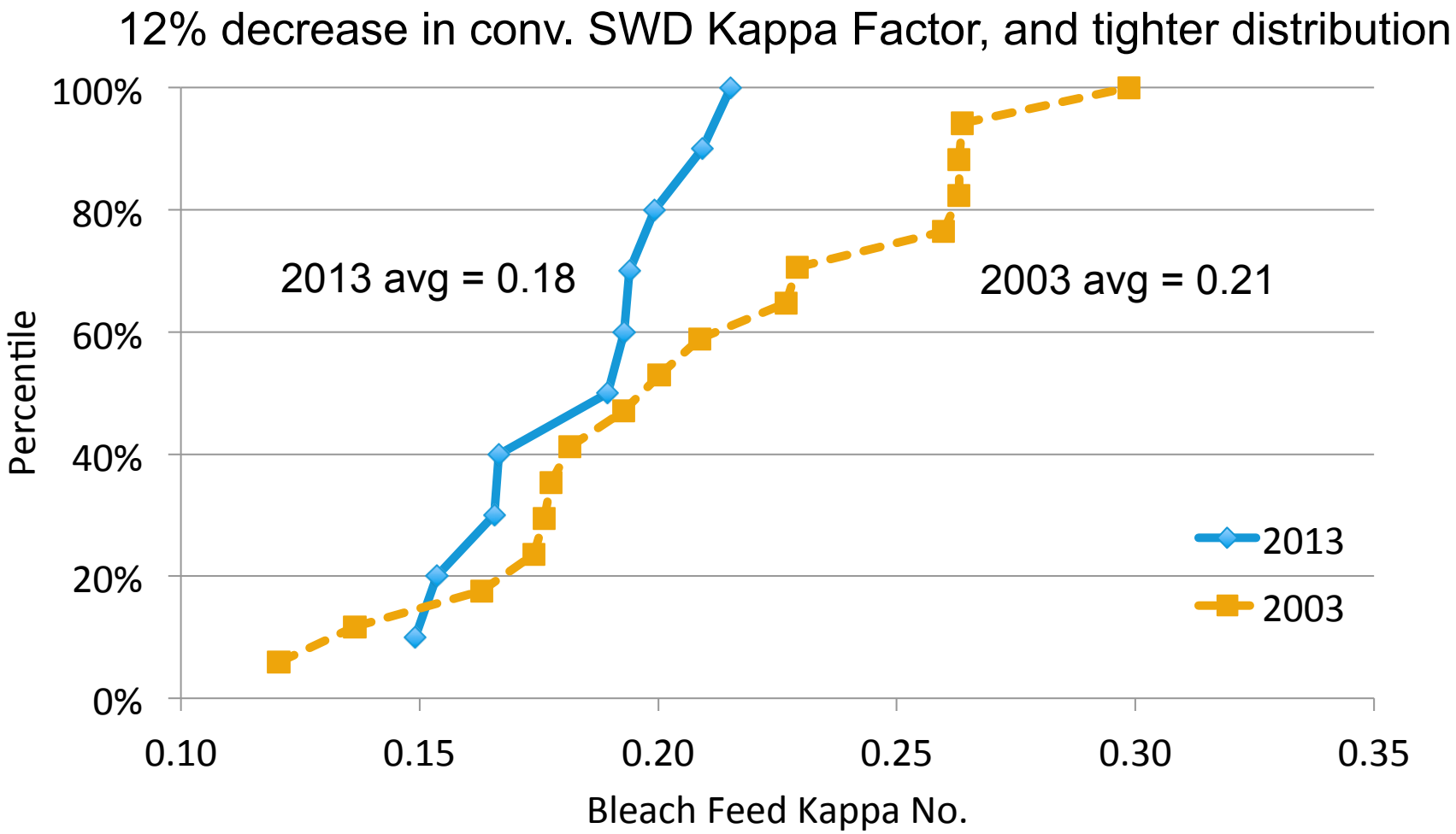


O2-SWD Bleach Feed Kappa No.

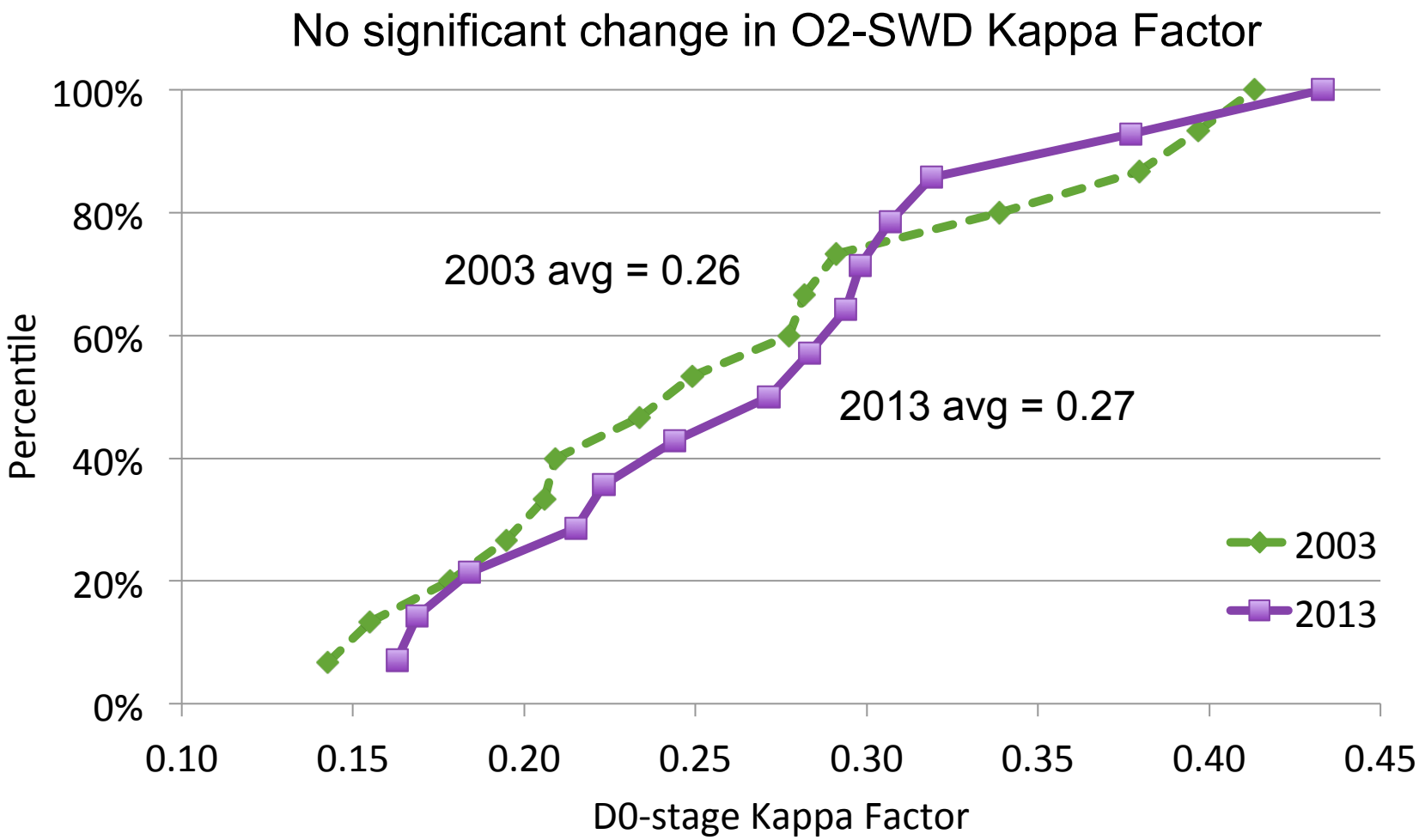
Average O2-SWD bleach feed kappa no. has decreased by 1.2 points



SWD D_0 Kappa Factor



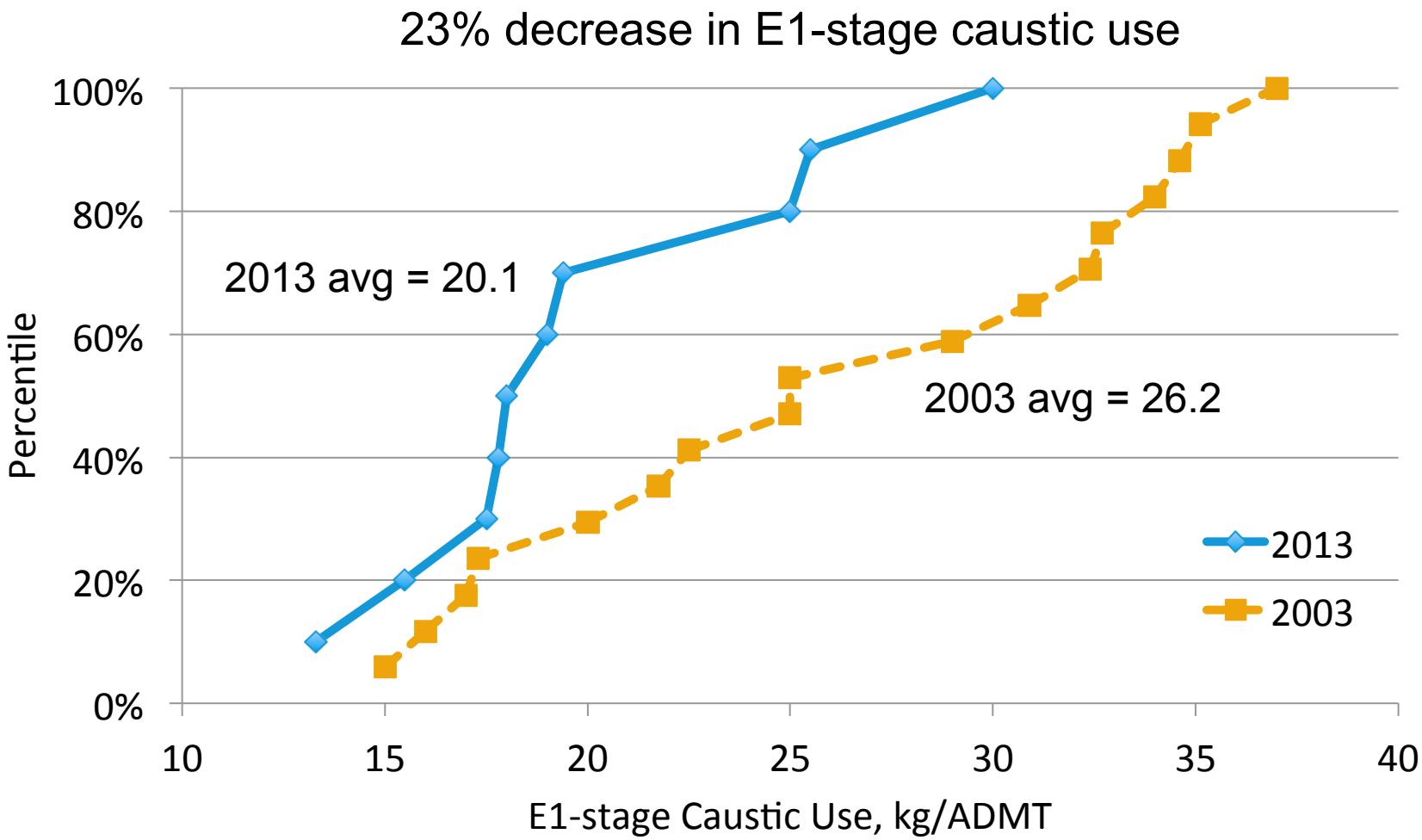
O2-SWD D_0 Kappa Factor



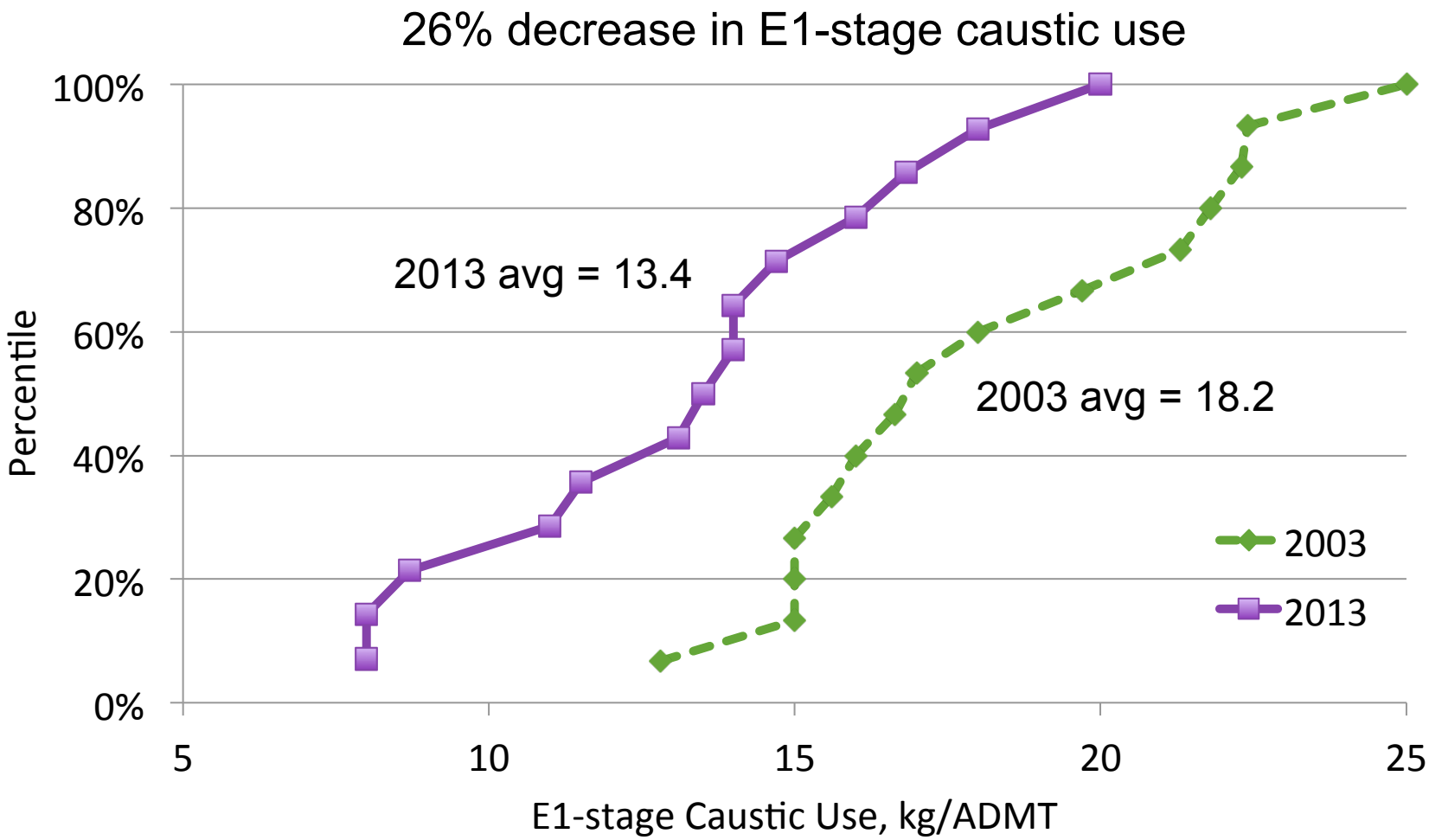
D0-stage Operating Conditions

	Softwood	O2-SWD
Bleach Feed Kappa No.	**24.9** (20 – 30)	**15.1** (11 – 21)
Chlorine Dioxide, kg/ADMT	**17.2** (15 – 19)	**15.1** (10 – 26)
D0 Kappa Factor	**0.183** (0.15 – 0.22)	**0.270** (0.17 – 0.43)
Retention Time	**33 min** (25 – 75)	**56 min** (22 – 145)
Temperature	50 – 60 °C	50 – 64 °C
Terminal pH	1.5 – 3.0; many do not test	1.8 – 3.0
Terminal Residual	Zero; many do not test. One report of 0.33 g/L	0 – 0.02 g/L
Terminal Brightness	33 – 65% many do not test	45 – 50% most do not test

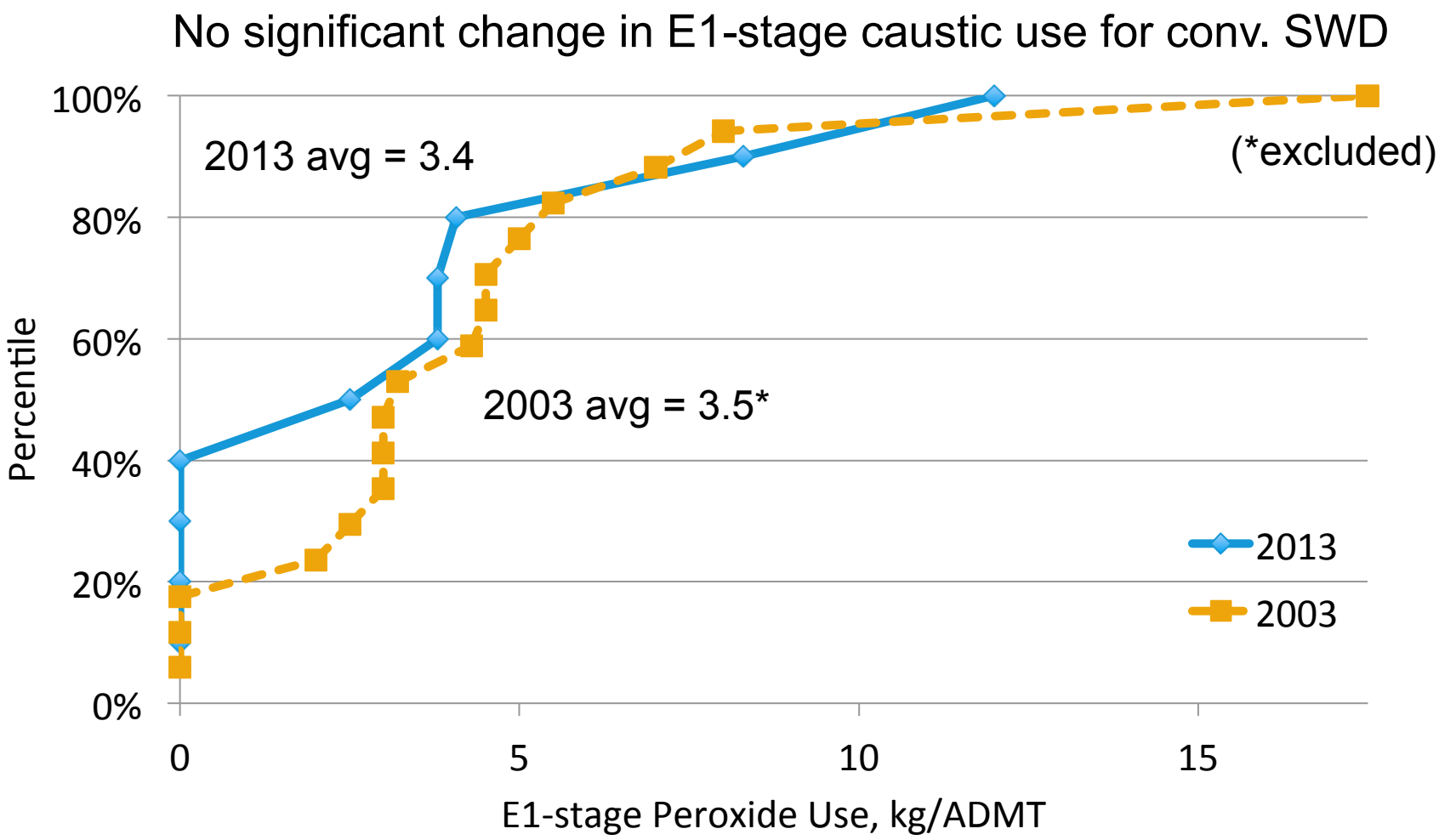
SWD E1-stage Caustic Use



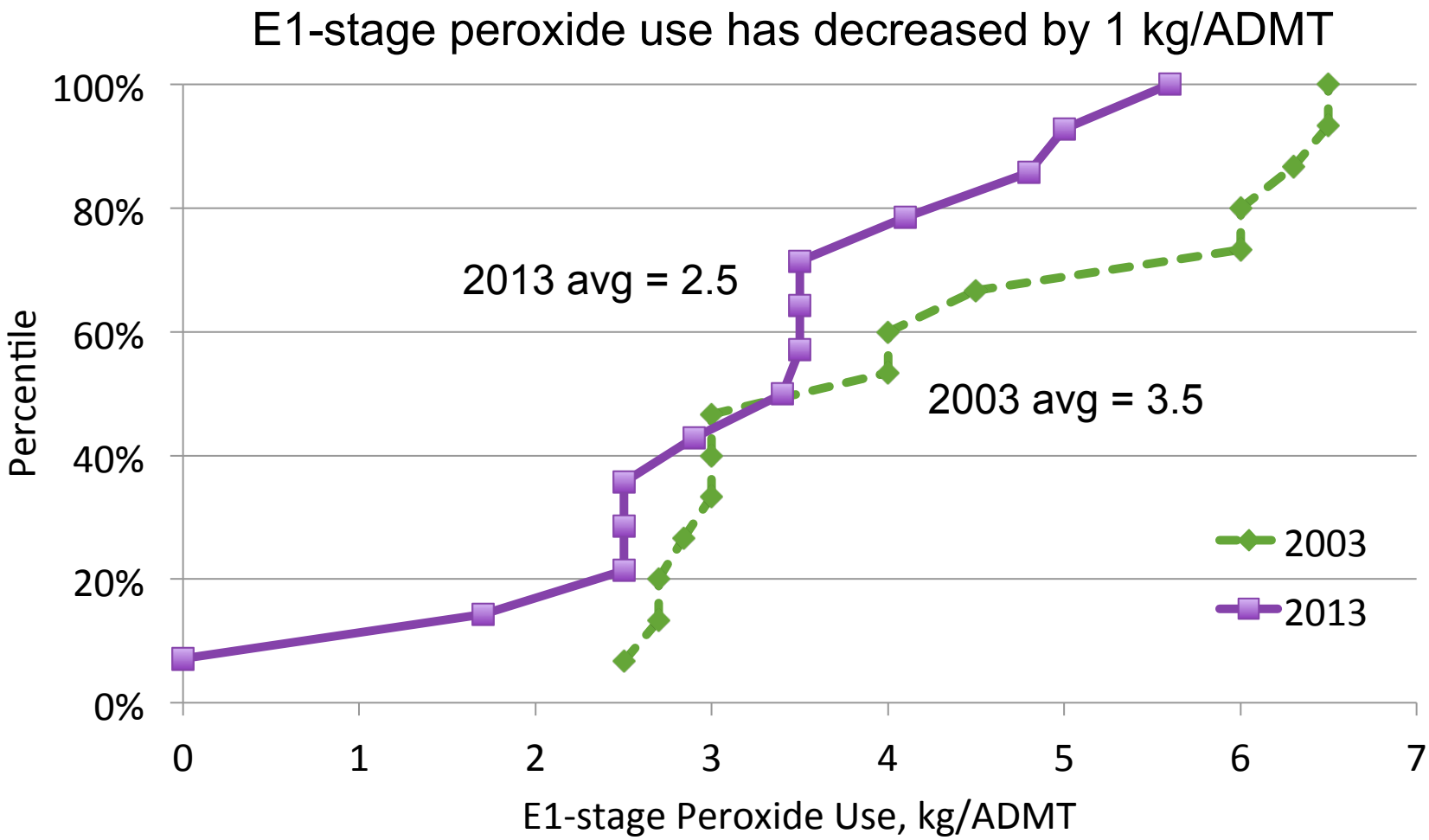
O2-SWD E1-stage Caustic Use



SWD E1-stage Peroxide Use



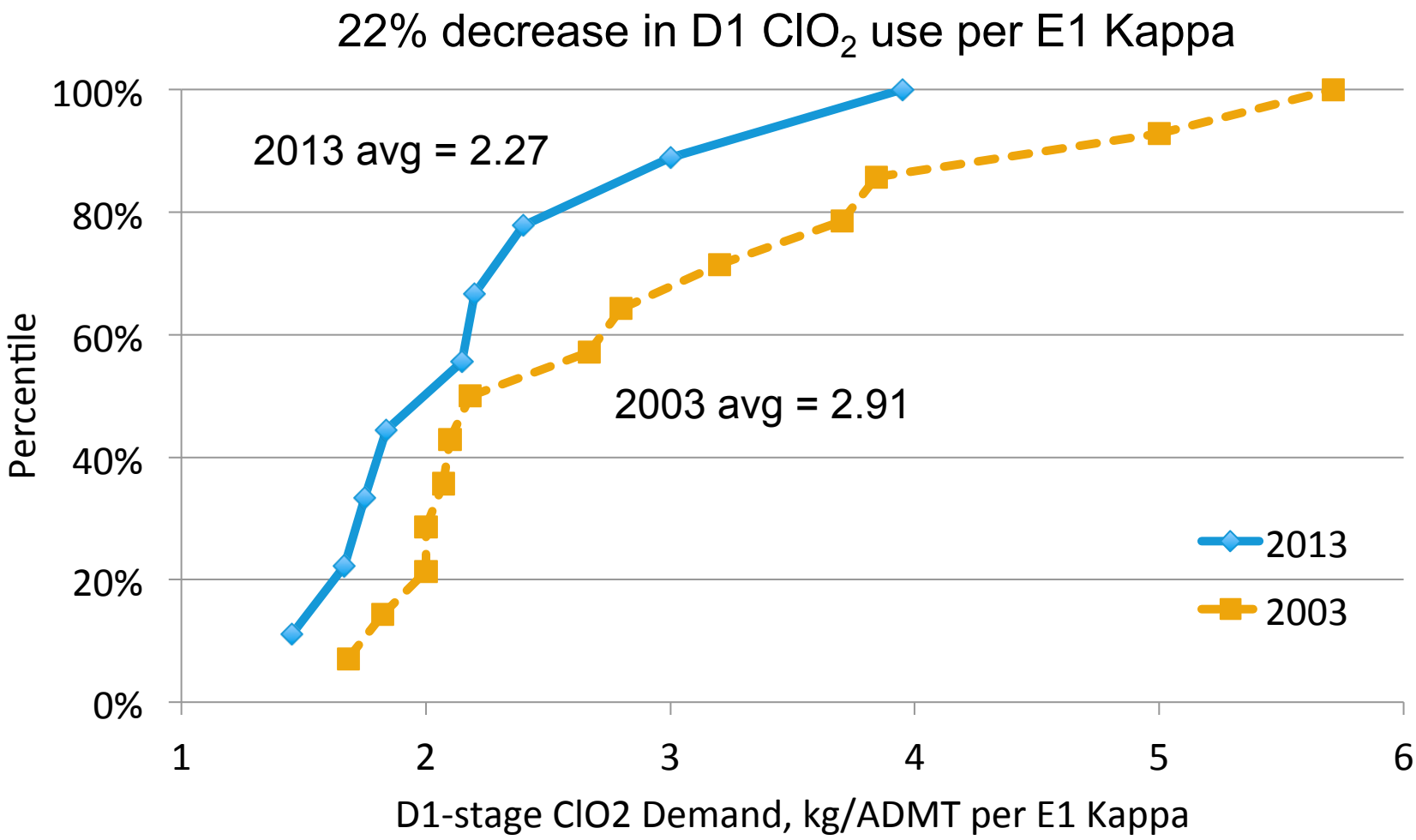
O2-SWD E1-stage Peroxide Use



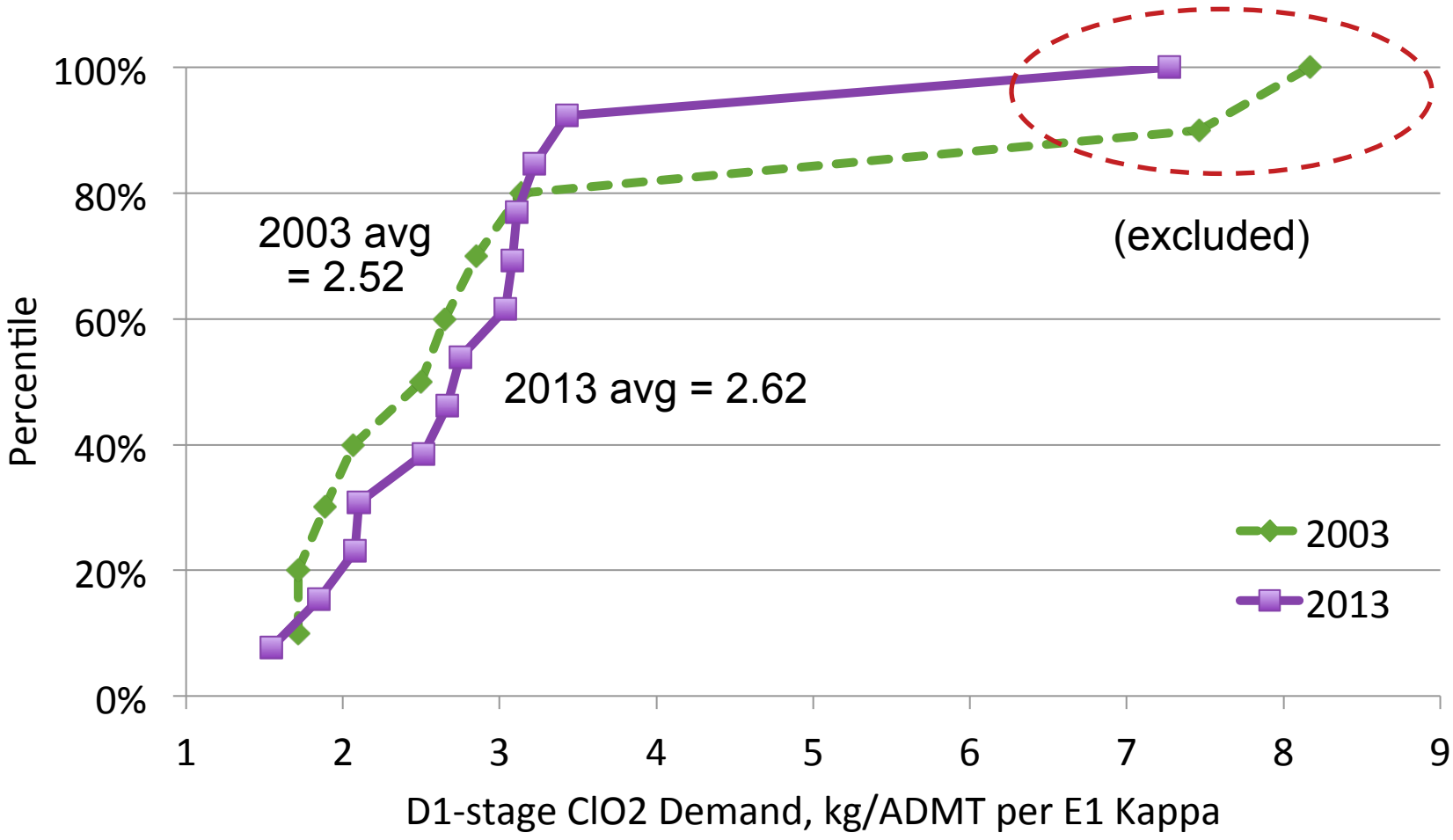
Eop-stage Operating Conditions

	Softwood	O2-SWD
NaOH, kg/ADMT	**20.1** (16 – 30)	**13.4** (8 – 20)
Peroxide, kg/ADMT	**3.4** (0 -12)	**2.5** (0 – 5.6)
Oxygen, kg/ADMT	**7.0** (5 – 12)	**3.7** (0 – 6.0)
Temperature	75 – 95 °C	70 – 89 °C
Total Retention Time	**80 minutes** (37 – 110)	**65 minutes** (20 – 90)
Pressure	40% pressurized; Up to 50 psig at top	Up to 40 psig at top
Time under pressure	**32 minutes** (10 – 60)	**15 minutes** (0 – 25)
Terminal pH	9.3 – 10.6	9.7 – 10.8
Post-Eop Kappa No.	**5.3** (4.2 – 6.5)	**3.2** (1.0 – 4.6)
Post-Eop Brightness	48 – 68%; most do not test	52 – 83%; half do not test

SWD D1-stage ClO_2 Demand



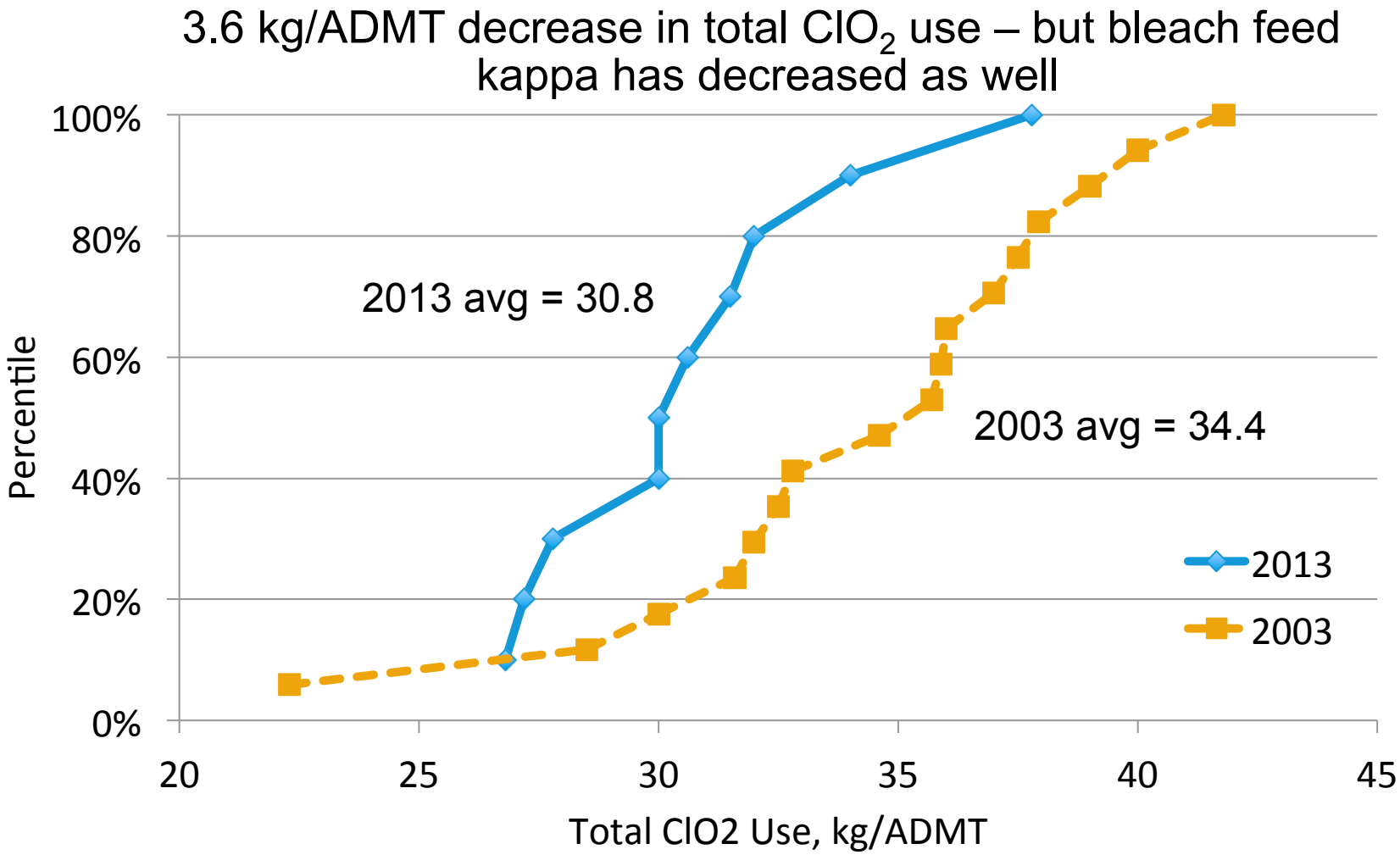
O2-SWD D1-stage ClO_2 Demand



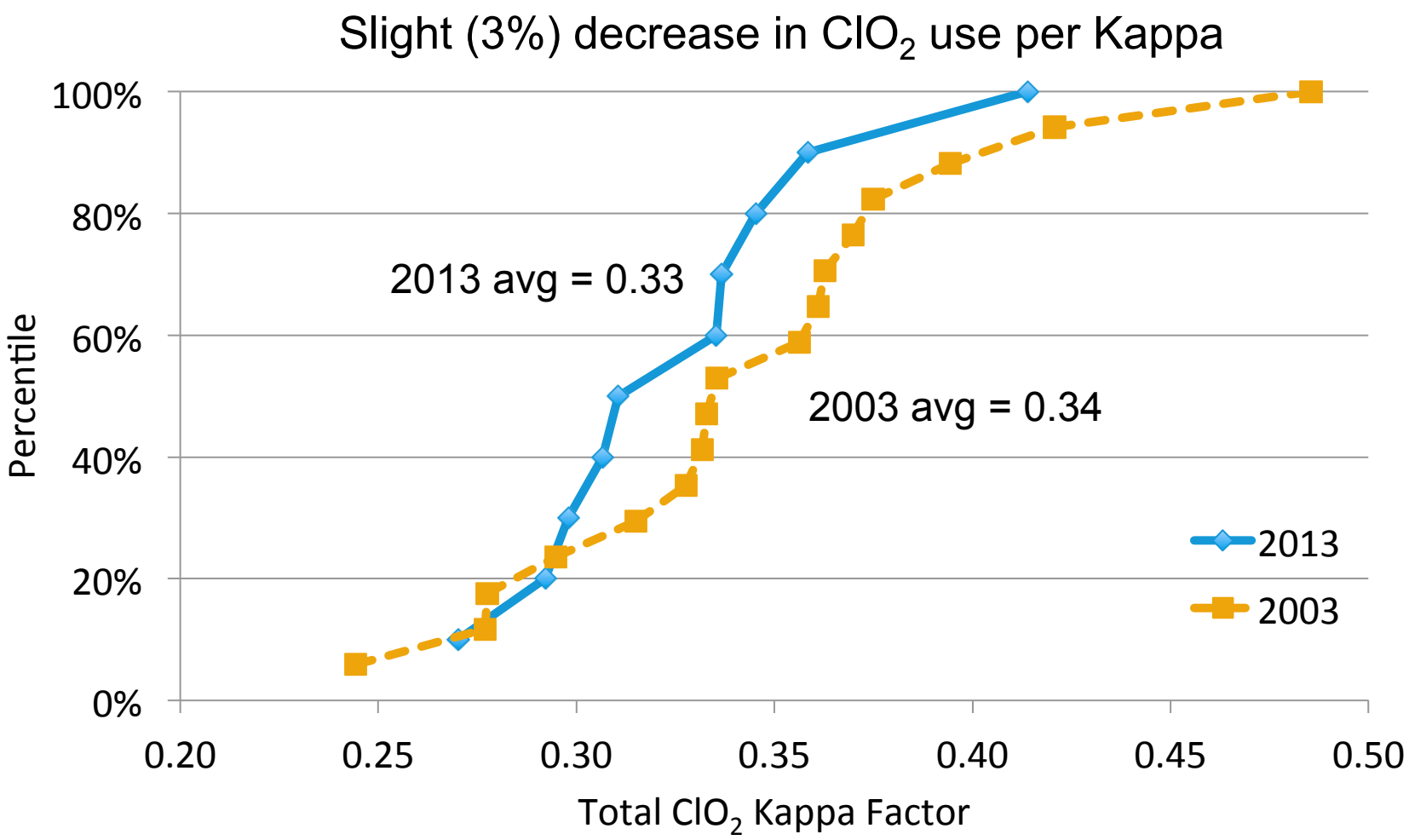
D1-stage Operating Conditions

	Softwood	O2-SWD
Post-Eop Kappa No.	**5.3** (4.2 – 6.5)	**3.2** (1.0 – 4.6)
Chlorine Dioxide, kg/ADMT	**11.6** (8.0 – 16.7)	**8.9** (2.8 – 14.5)
Retention Time	**151 minutes** (108 – 240)	**158 minutes** (80 – 300)
Temperature	60 – 84 °C	68 – 87 °C
Upflow/inlet pH	**3.9** (3.7 – 4.0); most do not measure	**4.4** (2.5 – 6.3)
Terminal pH	2.5 – 4.0	2.3 – 4.9
Terminal Residual	**0.030 g/L**; many do not measure	0 – 0.040 g/L
Terminal Brightness	**81.4%** (73 – 89)	**84.4%** (79 – 90)

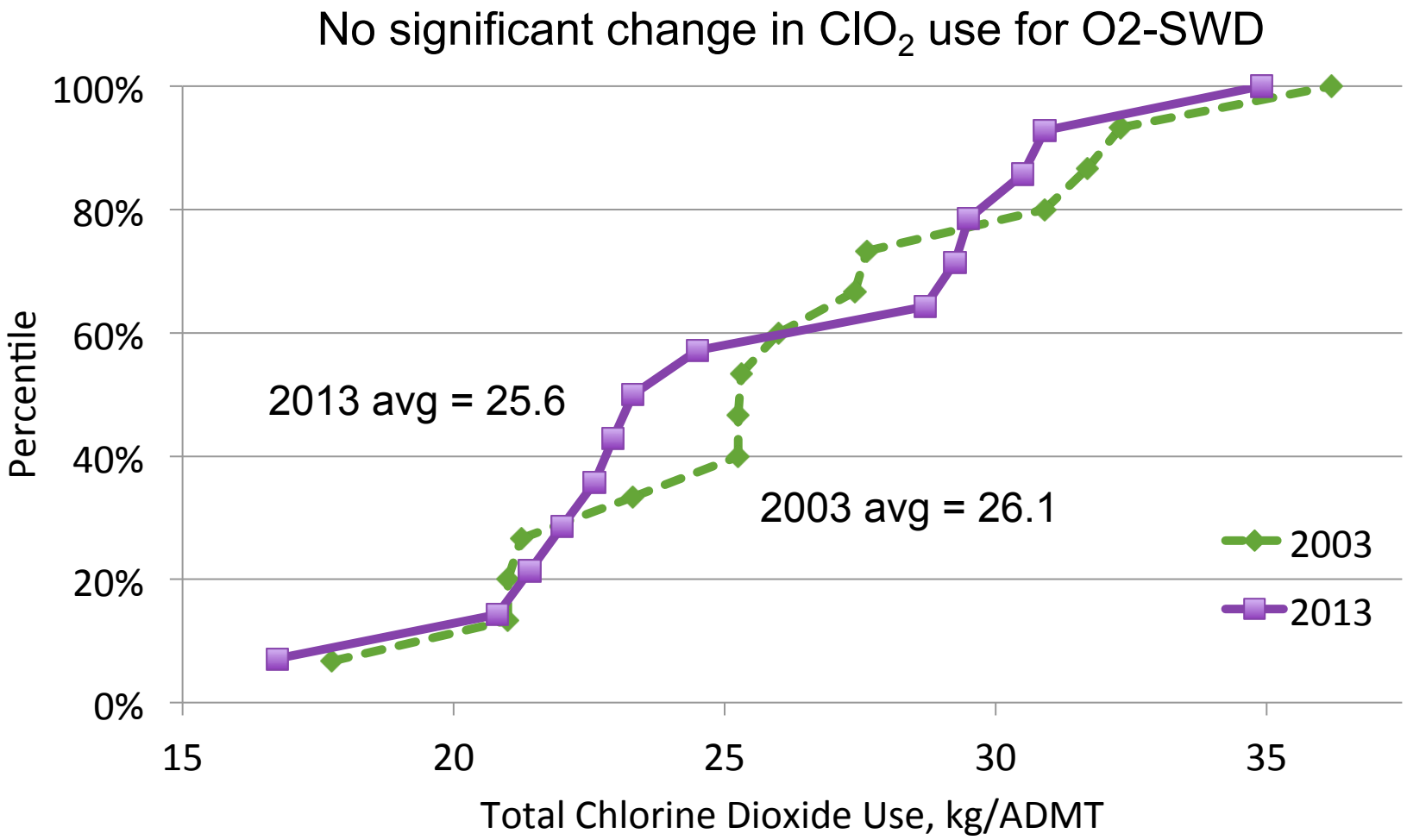
SWD Total ClO_2 Use



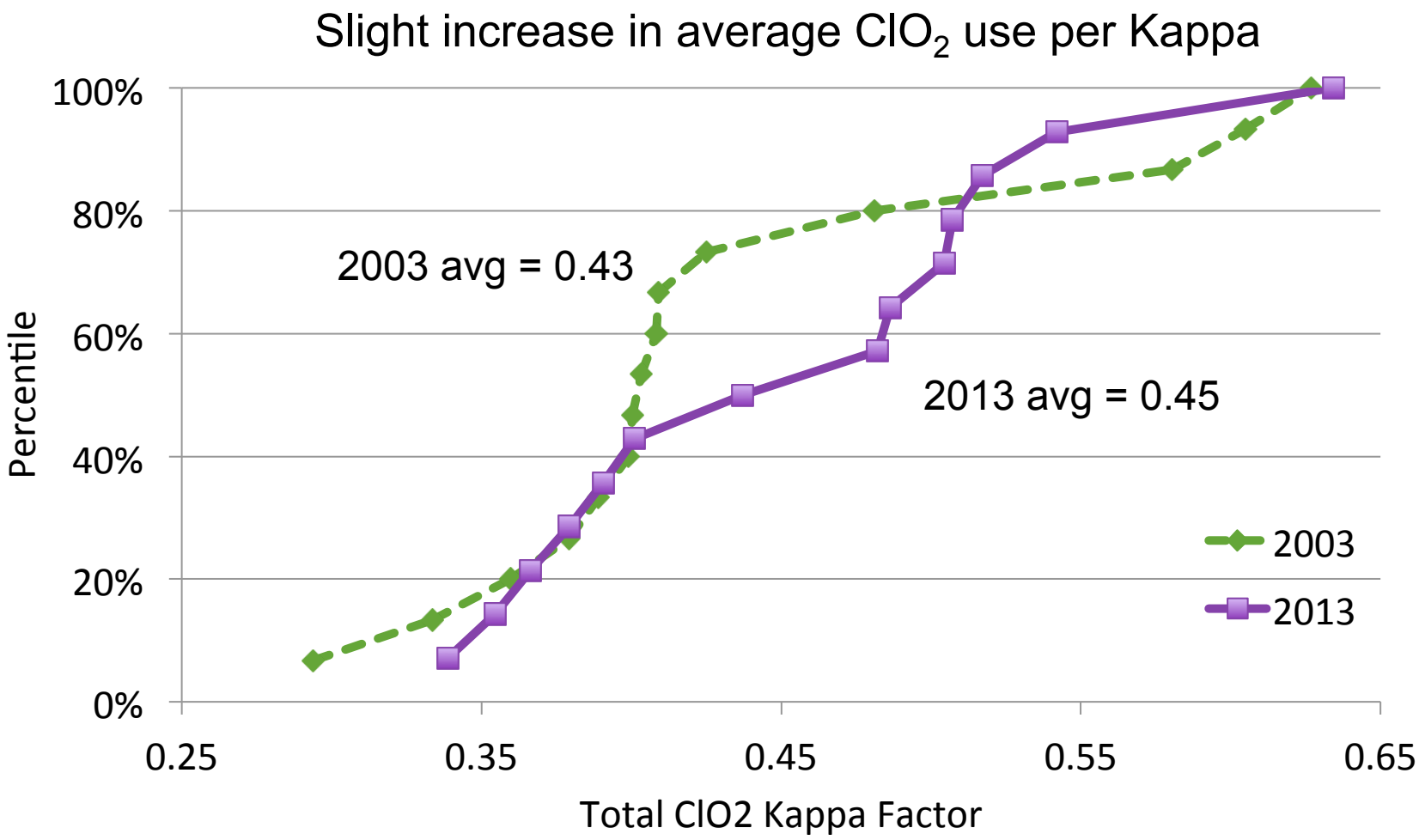
SWD Total ClO_2 Kappa Factor



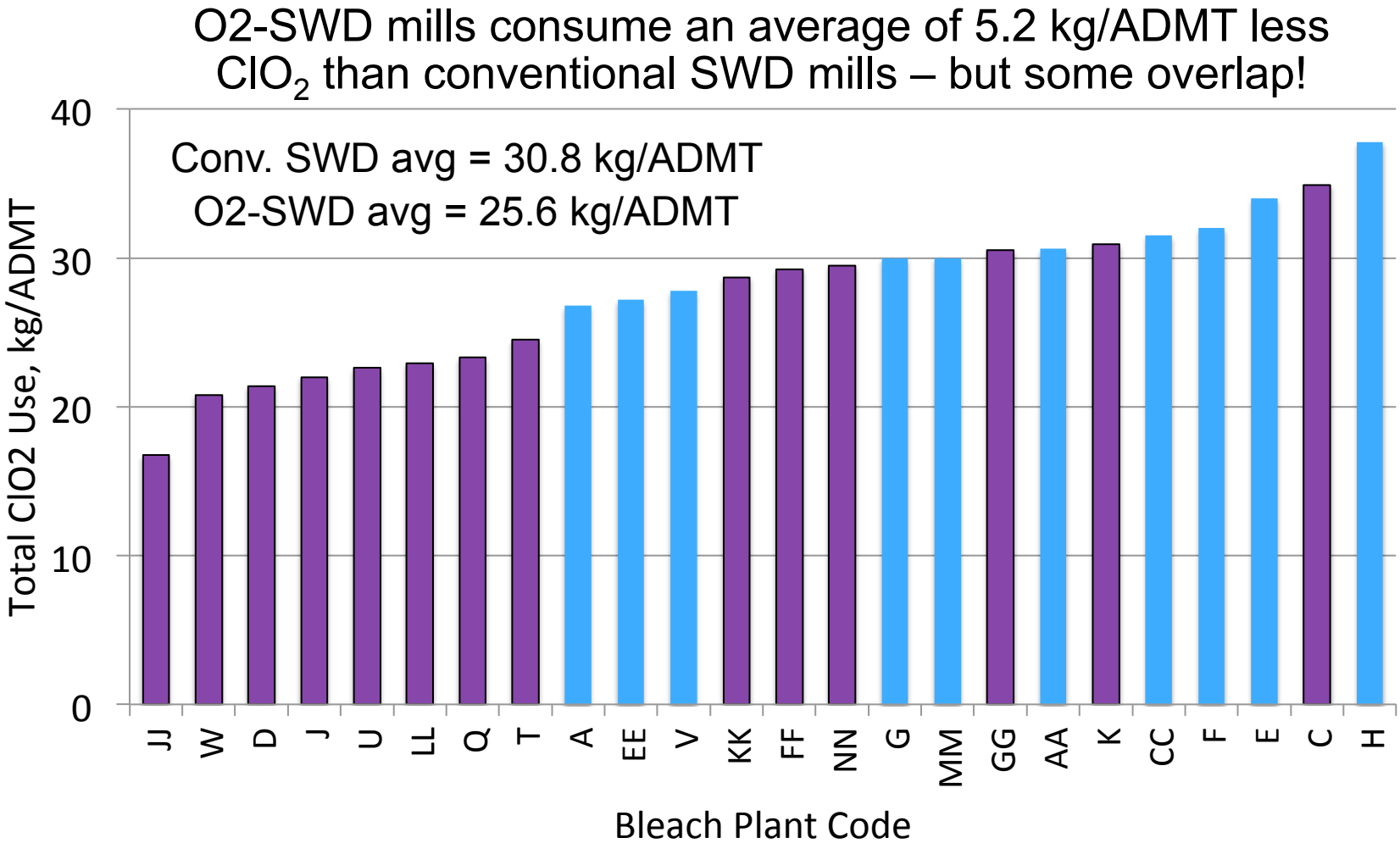
O2-SWD Total ClO_2 Use



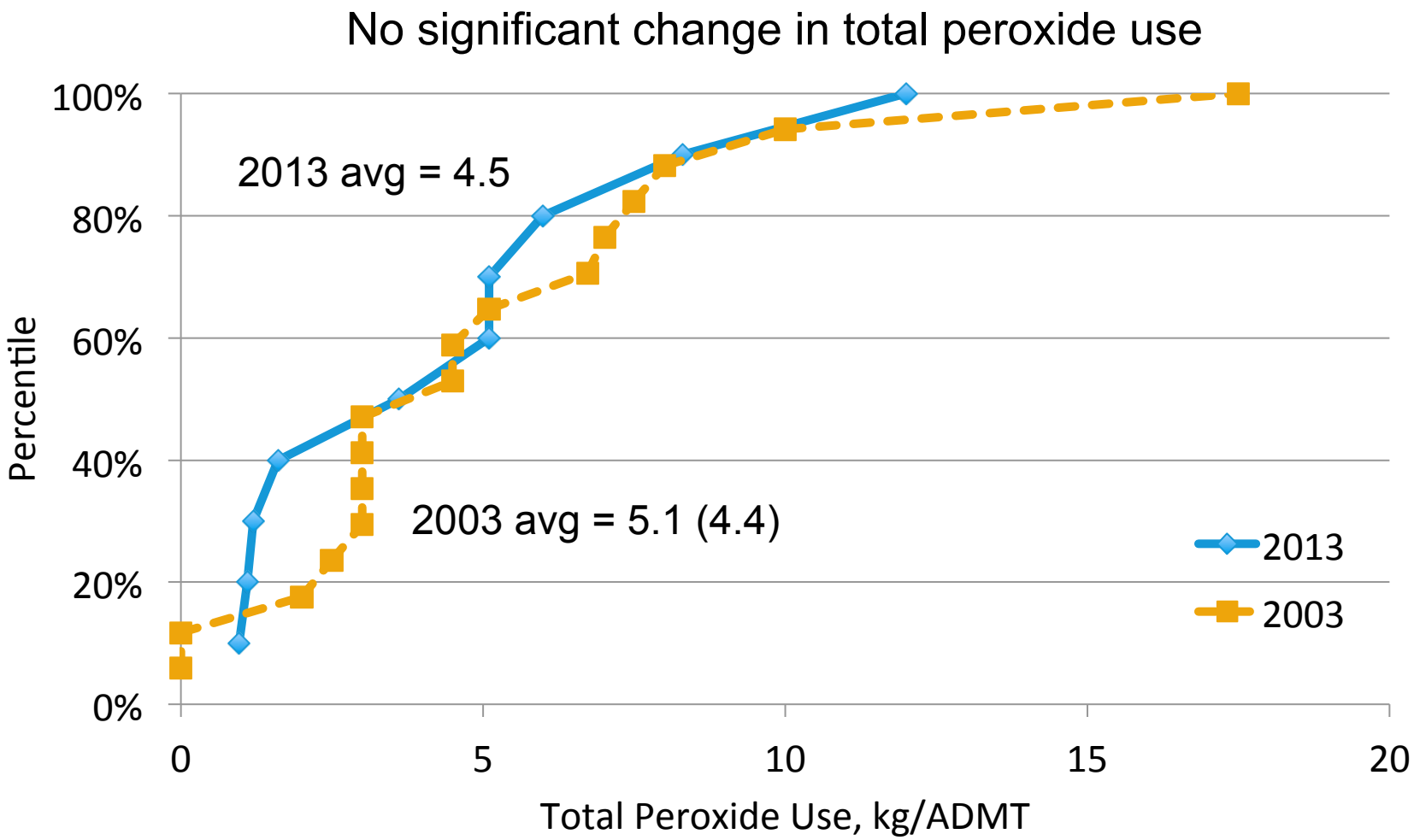
O2-SWD Total ClO_2 Kappa Factor



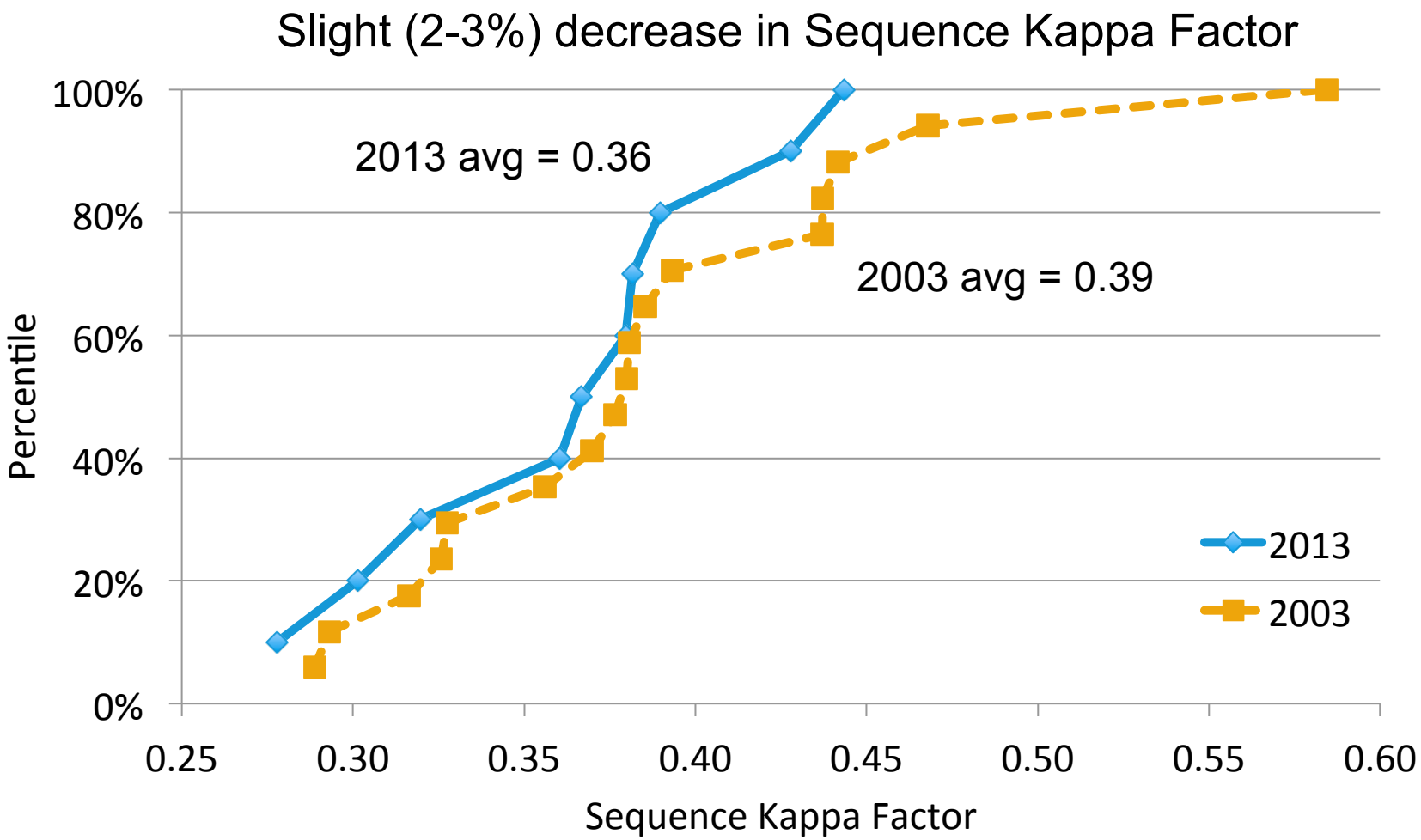
Total Chlorine Dioxide Use



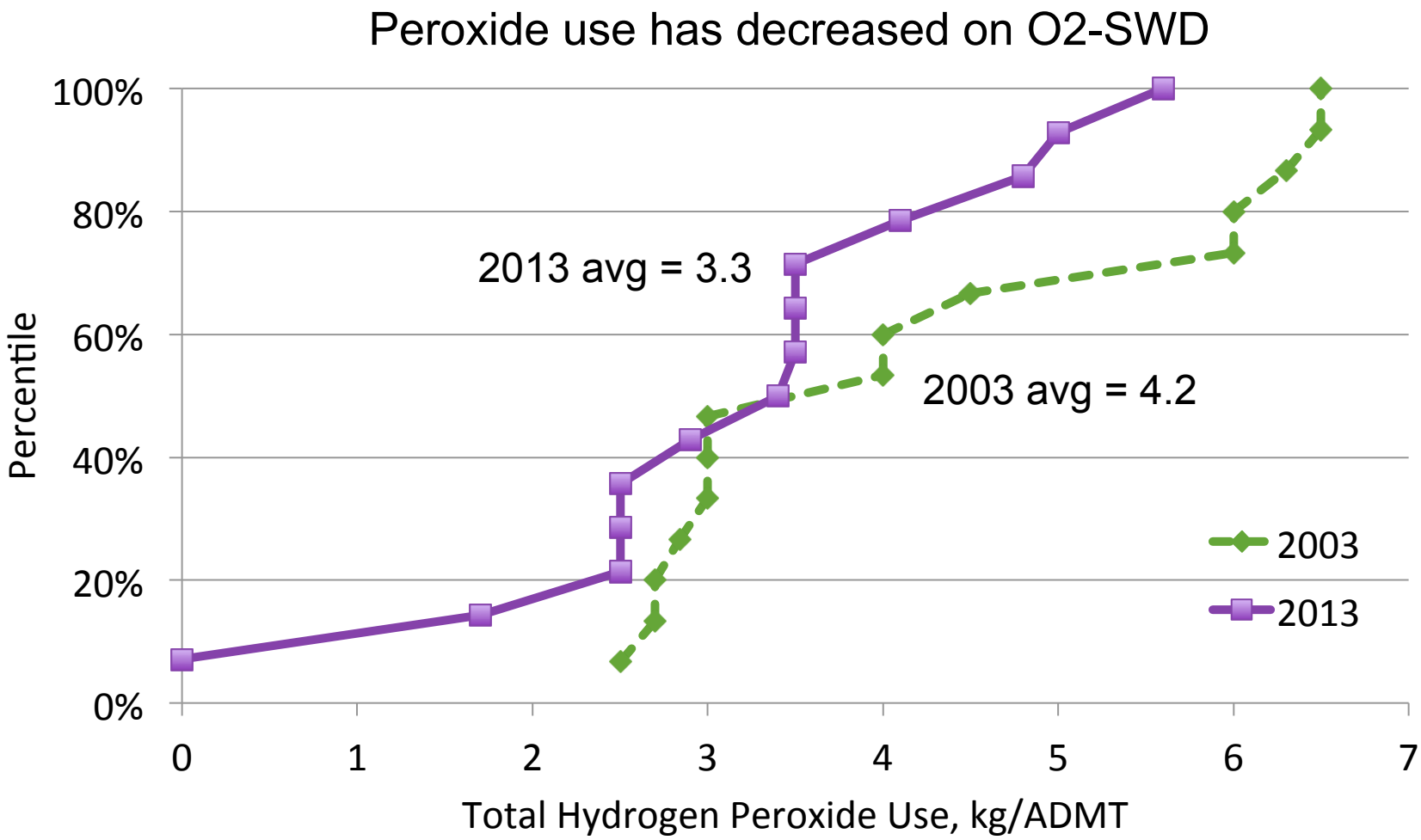
SWD Total H_2O_2 Use



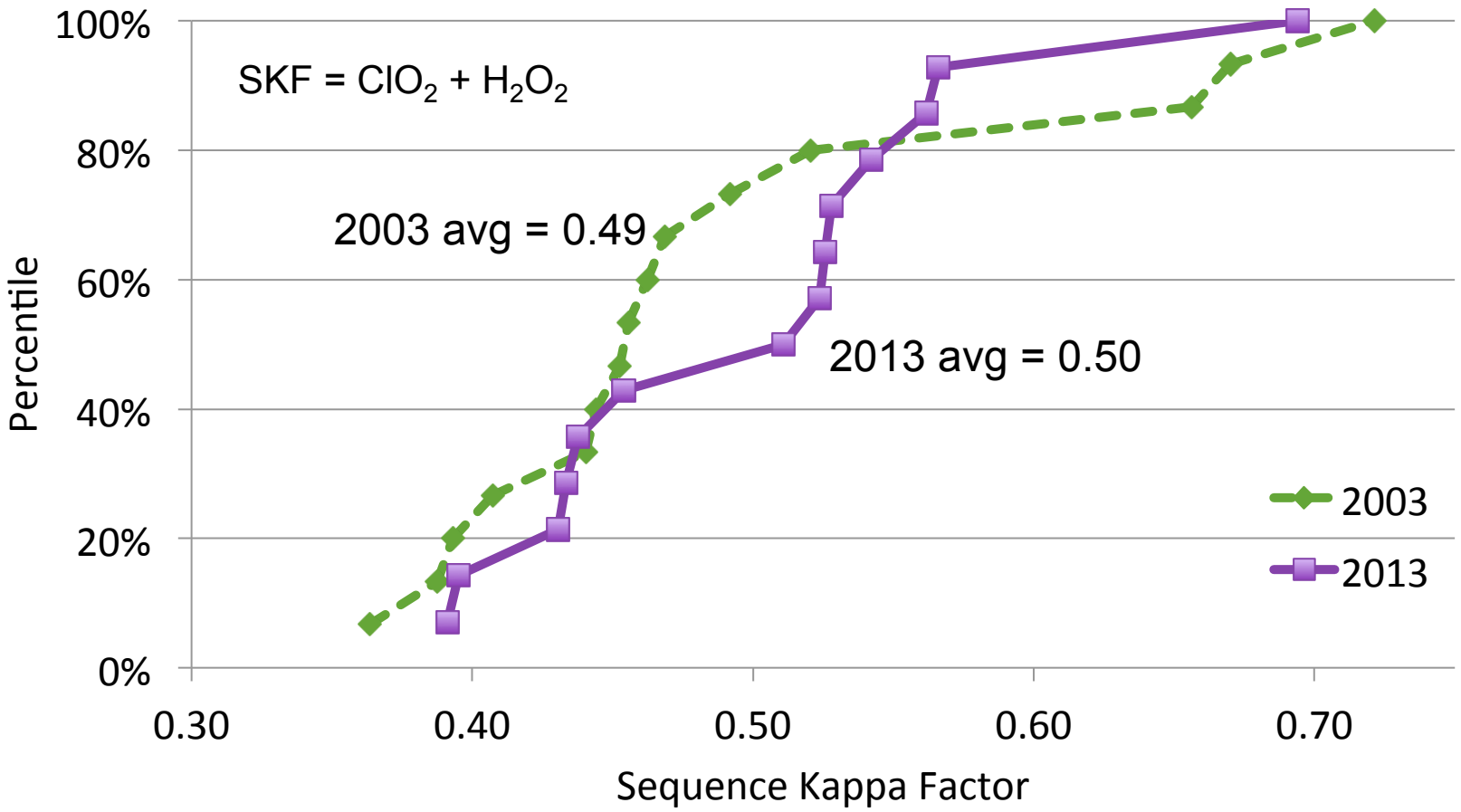
SWD Sequence Kappa Factor



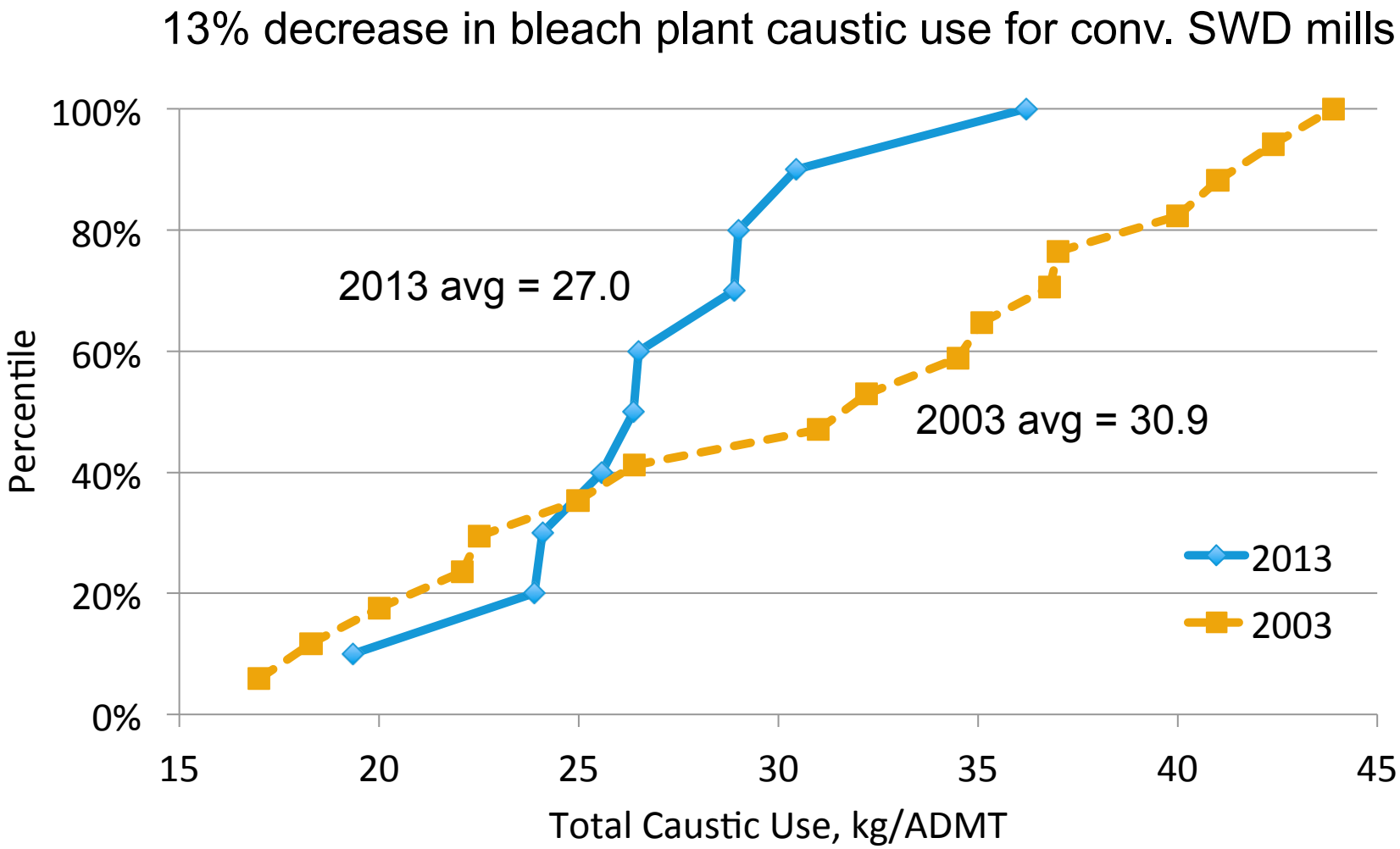
O2-SWD Total H_2O_2 Use



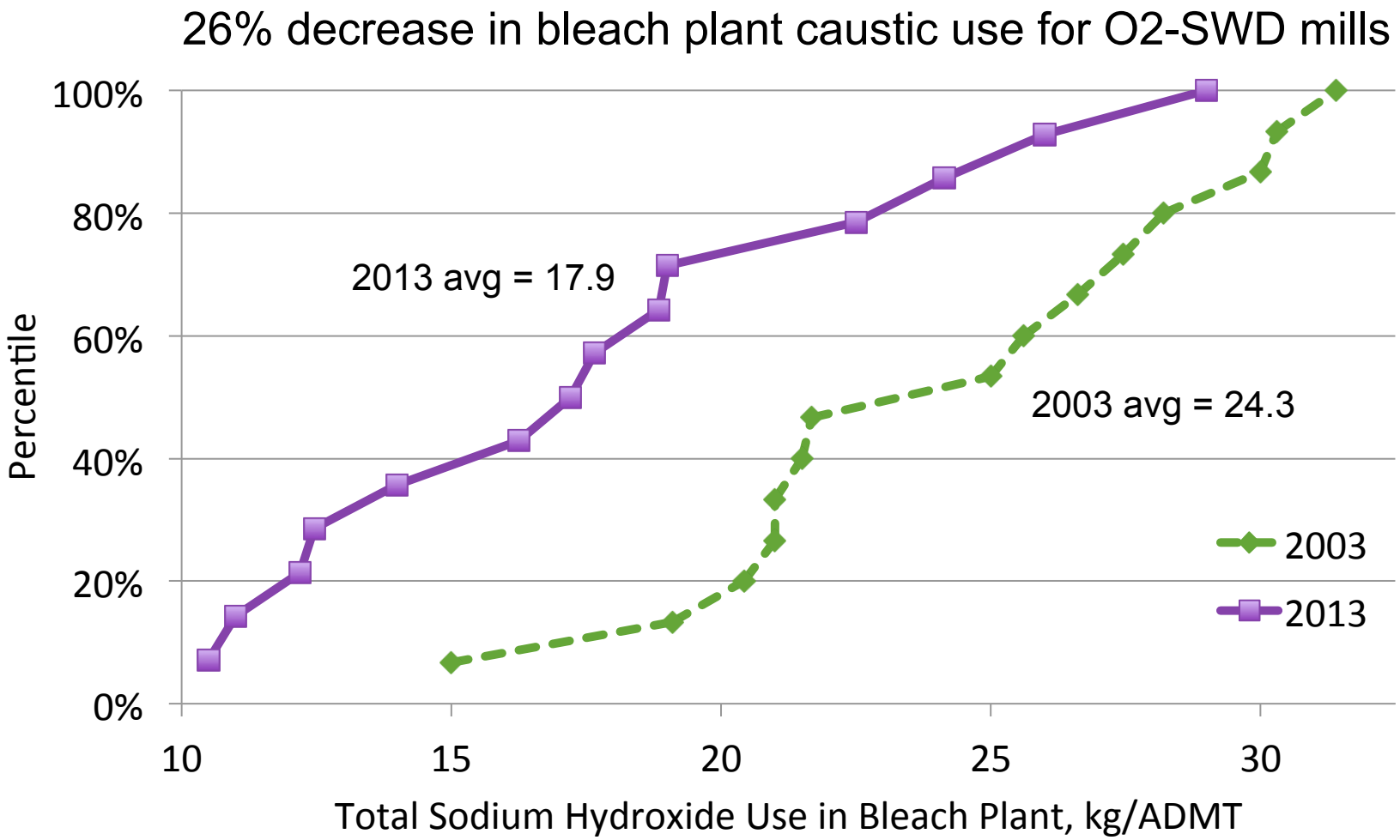
O2-SWD Sequence Kappa Factor



SWD Total Caustic Use



O2-SWD Total Caustic Use



Summary: Conventional Softwood

Since the last survey in 2003, the following changes have been observed for "conventional" (non-O2D) softwood kraft pulp:

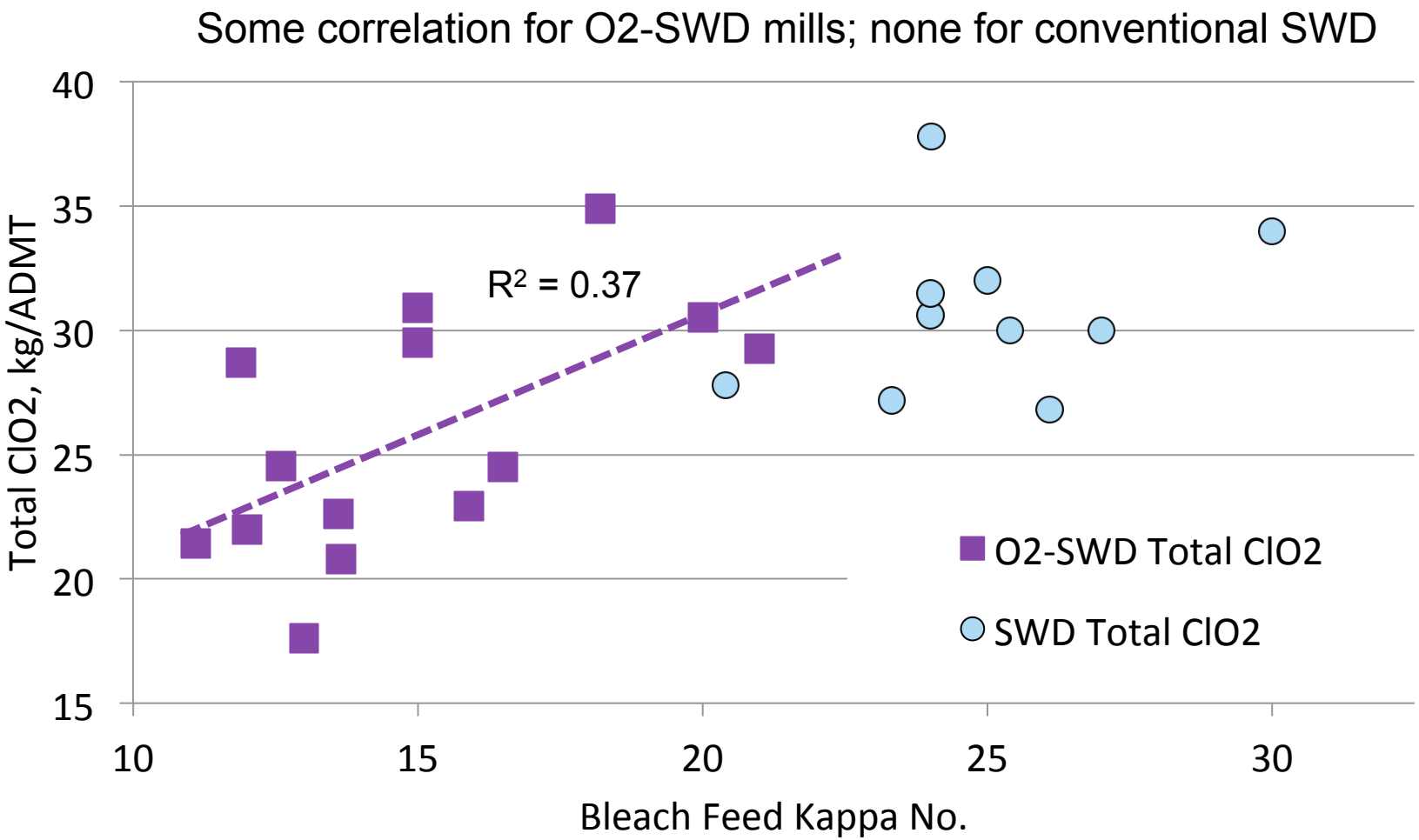
- Pulp production rate?;
- Bleach feed kappa no. has decreased by an average of 1.2 kappa units;
- Final bleach plant brightness has increased by an average of 0.3% ISO;
- Sodium hydroxide use in the bleach plant has decreased by an average of 3.9 kg/ADMT or 13%;
- Chlorine dioxide use has decreased by an average of 3.6 kg/ADMT;
- Hydrogen peroxide use is unchanged.

Summary: O2-Delignified Softwood

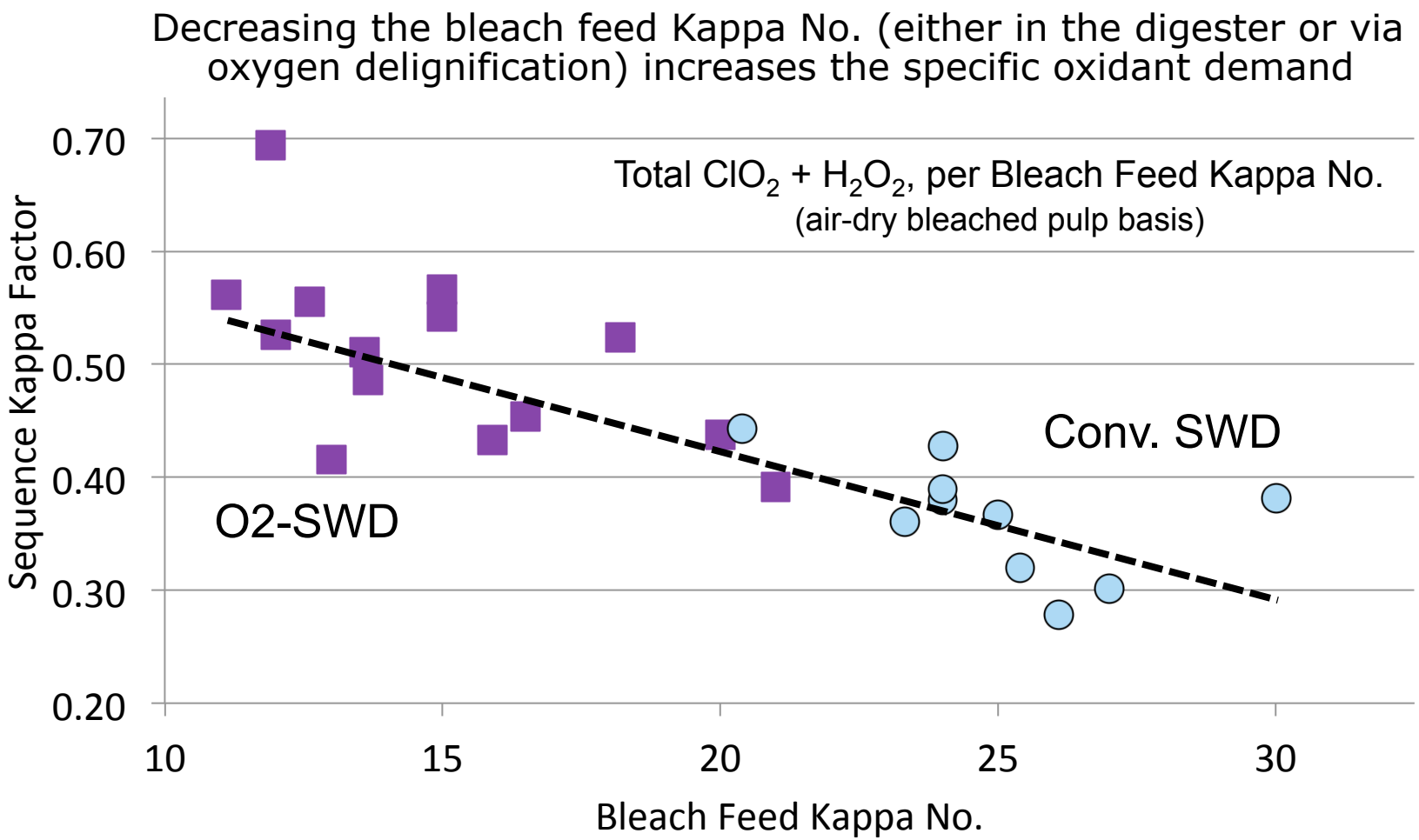
Since the last survey in 2003, the following changes have been observed for oxygen-delignified softwood kraft pulp:

- Pulp production has increased by an average of 6.5%;
- Final bleach plant brightness has increased by an average of 0.5% ISO;
- Digester kappa no. has decreased by an average of 1.3 kappa units, and bleach feed kappa no. has decreased by an average of 1.2 kappa units;
- Sodium hydroxide use in the bleach plant has decreased by an average of 6.4 kg/ADMT or 26%;
- Chlorine dioxide use has decreased by an average of 0.5 kg/ADMT;
- Hydrogen peroxide use has decreased by an average of 0.9 kg/ADMT.

ClO_2 Use vs. Kappa No.

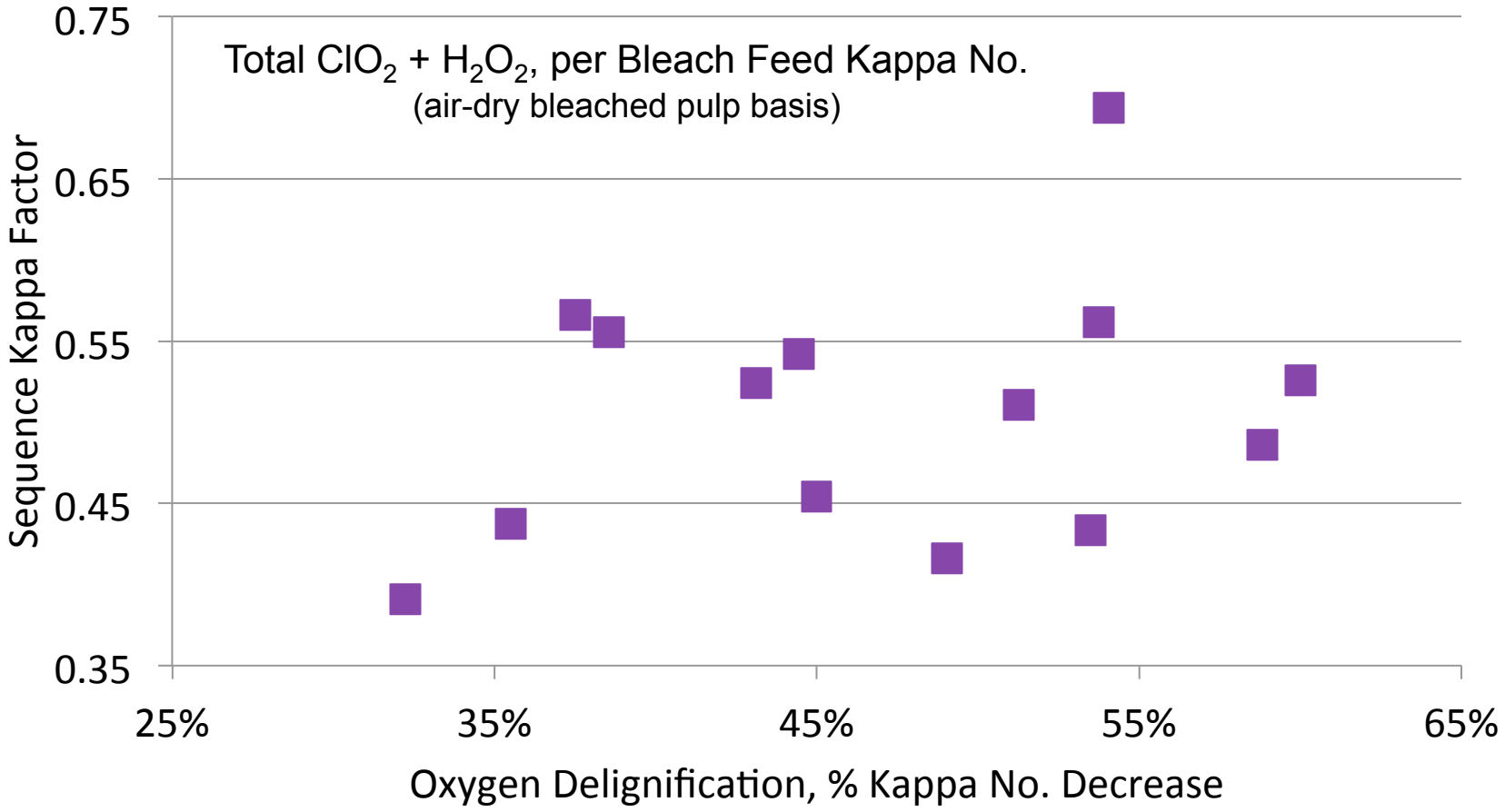


Sequence KF vs. Kappa No.



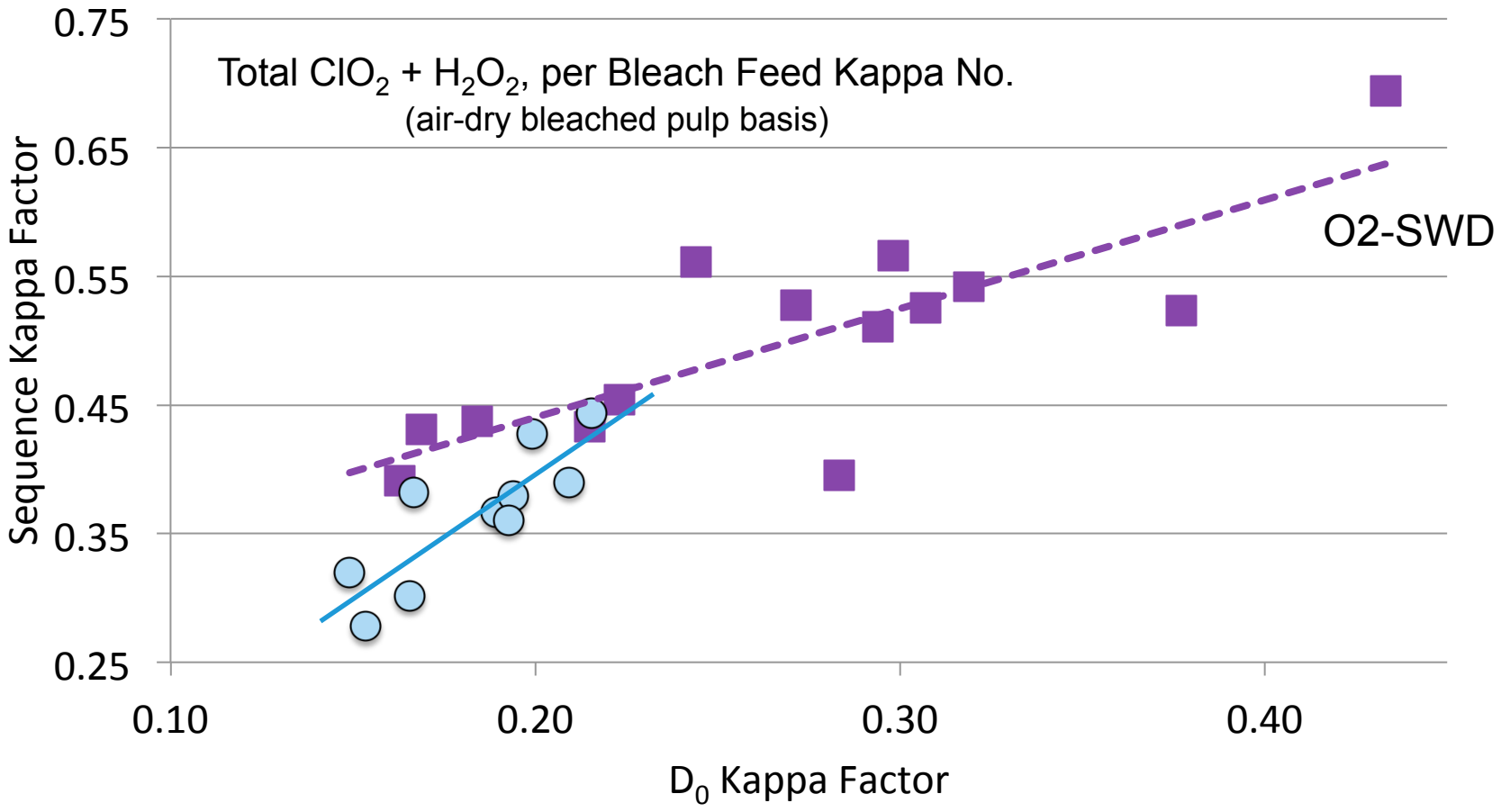
O2 Delignification & Chemical Use

No relationship between *degree* of O2 Delignification and Bleachability; Bleach Feed Kappa No. (*i.e.* free phenolic content) is more significant



SKF vs. D_0 Kappa Factor

A low D_0-stage Kappa Factor correlates will with low overall chemical use



Chemical Use & Kappa No.

- Total specific oxidizing chemical use (Sequence Kappa Factor, ClO_2 + H_2O_2) correlates well with bleach feed kappa no.
  - In general, pulps appear to become more difficult to bleach as the kappa no. is decreased
  - But ClO_2 use (kg/ADMT) has only a weak correlation with kappa no. for O2-SWD pulps, and no correlation for conventional SWD pulps
- There is a strong positive relationship between a low D_0-stage Kappa Factor and a low Sequence Kappa Factor (total oxidizing chemical use per kappa)
- There appears to be no relationship between the *extent* of oxygen delignification (% kappa n0. decrease) and relative oxidizing chemical use
  - Speculation: the degree of oxygen delignification does not impact the reactivity with chlorine dioxide significantly; instead it is the extent of delignification ahead of the bleach plant (digester plus oxygen delignification) which is the determining factor

Outline

- Background
  - Survey response & methodology
- Results
  - SWD & O2-SWD
    - Comparison with 2003 results
    - Brownstock & Oxygen Delignification
    - Bleaching stages
    - Overall chemical use and bleaching cost
- Analysis
  - Differences between “Low” and “High” relative chemical consumption bleach plants
  - Trends since 2003
  - Identification of bleaching “Best Practices”?

Relative Chemical Consumption: O2-SWD

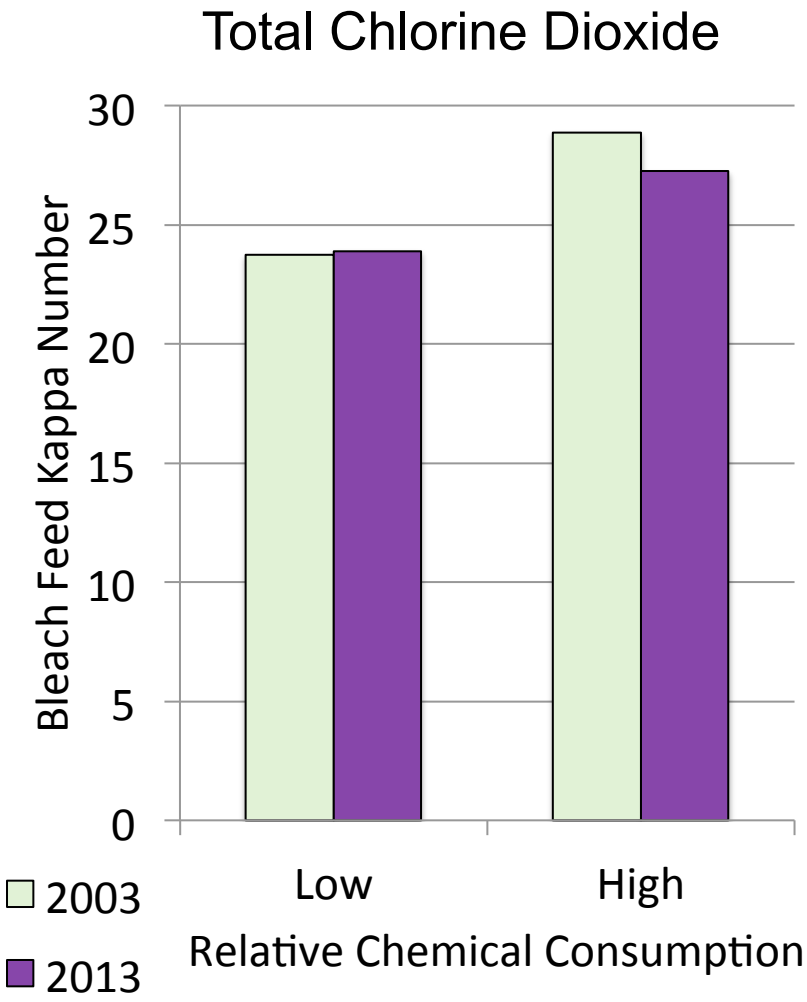
O2-SWD mills sorted by Sequence Kappa Factor & averaged into two groups

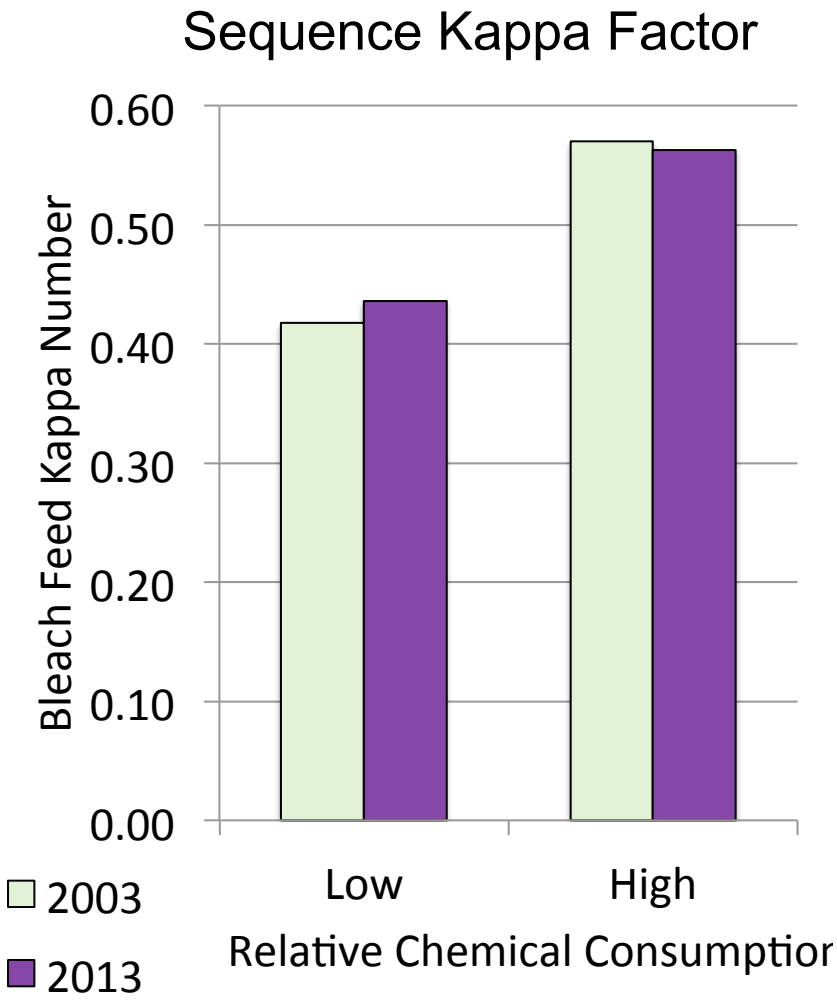
Parameter	Low Relative Chemical Consumption Average	High Relative Chemical Consumption Average
Pre-O_2 Kappa No.	30.4	26.2
Bleach Feed Kappa No.	16.5	13.7
O_2 Delignification	45%	47%
D_0-stage Kappa Factor	0.22	0.32
Eop-stage NaOH, kg/ADMT	13.2	13.6
Eop-stage H_2O_2, kg/ADMT	3.5	1.5
Post-Eop Kappa No.	3.4	3.0
D1-stage ClO_2, kg/ADMT	9.2	8.6
D2-stage ClO_2, kg/ADMT	2.0	1.8
Final Brightness, % ISO	89.2%	88.7%
Total ClO_2, kg/ADMT	23.9	27.2
Total H_2O_2, kg/ADMT	4.1	2.4
Total NaOH, kg/ADMT	17.2	18.6
Sequence Kappa Factor	0.44	0.56

"Low Relative Consumption" O2-SWD mills:

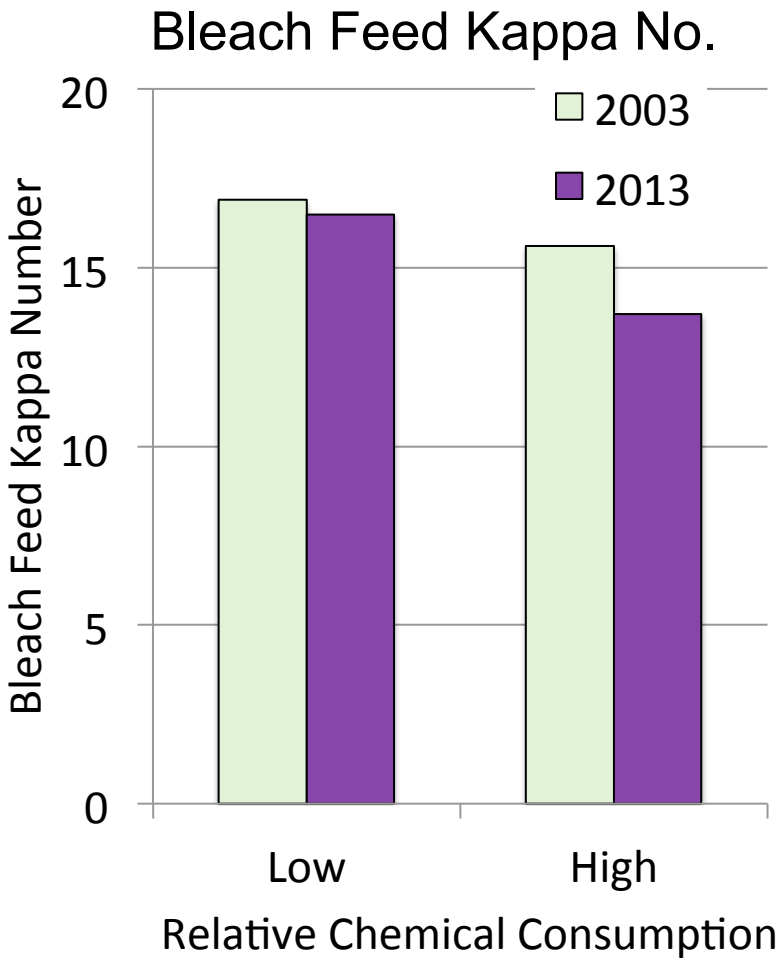
- Have a higher bleach feed kappa no. (by 2.8 points)
- Use 3.3 kg/ADMT less total ClO_2
- Use 1.7 kg/ADMT more peroxide
- Make a higher brightness pulp

O2-SWD: Oxidizing Chemicals





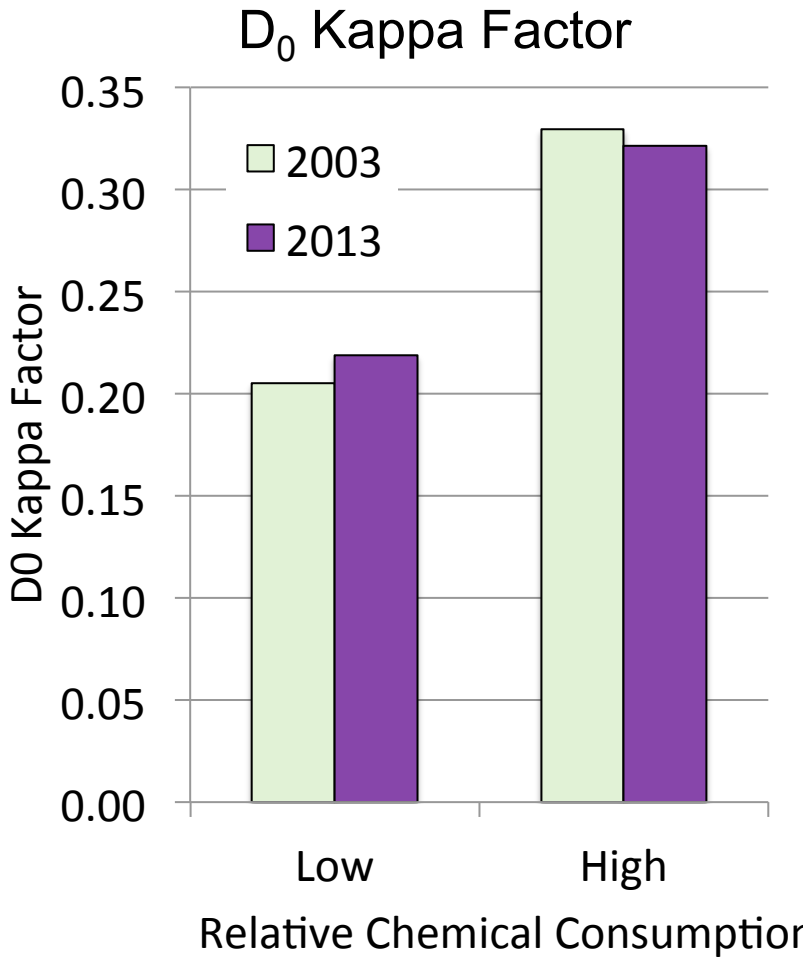
O2-SWD: Kappa No.



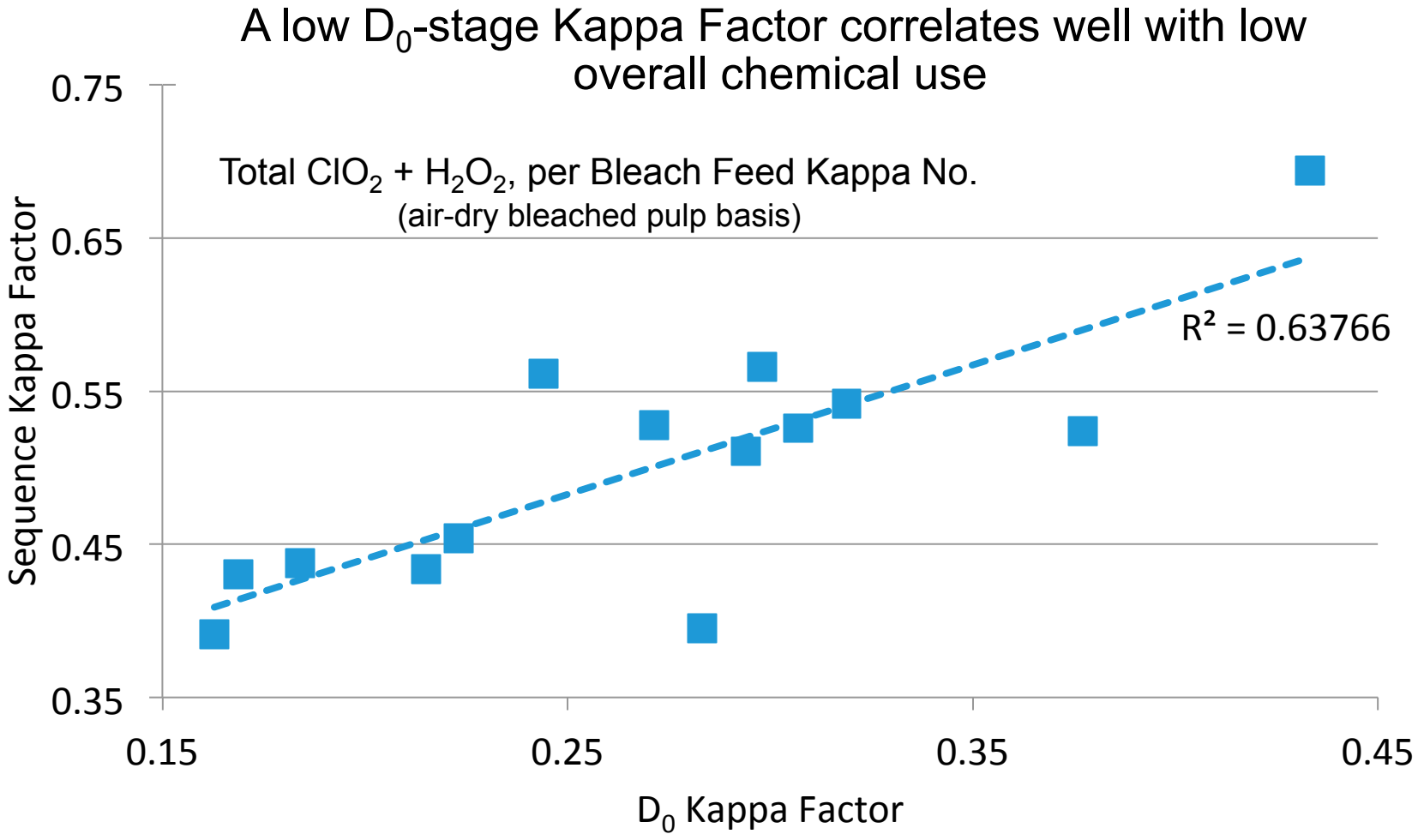
- Low relative chemical consumption mills have a higher bleach feed kappa no.
  - Produce a pulp with 0.5% ISO higher final brightness
- Wood species is not a significant differentiator
- Is higher-kappa pulp easier to bleach?

O2-SWD: D_0 Kappa Factor

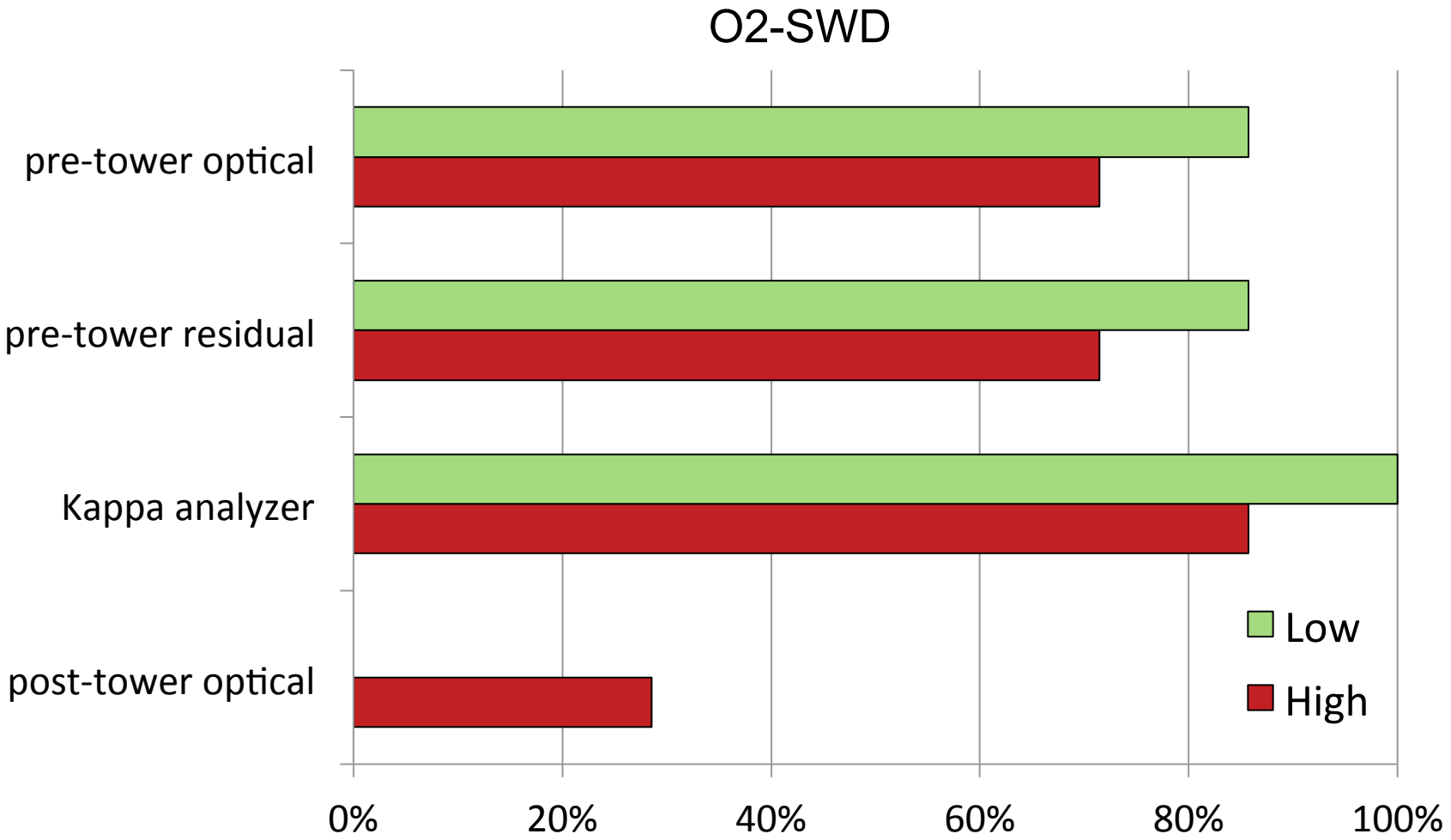
- Low relative chemical consumption bleach plants operate with a significantly lower Kappa Factor in the D_0 stage
  - No difference in carryover
  - Number of bleaching stages was not a factor



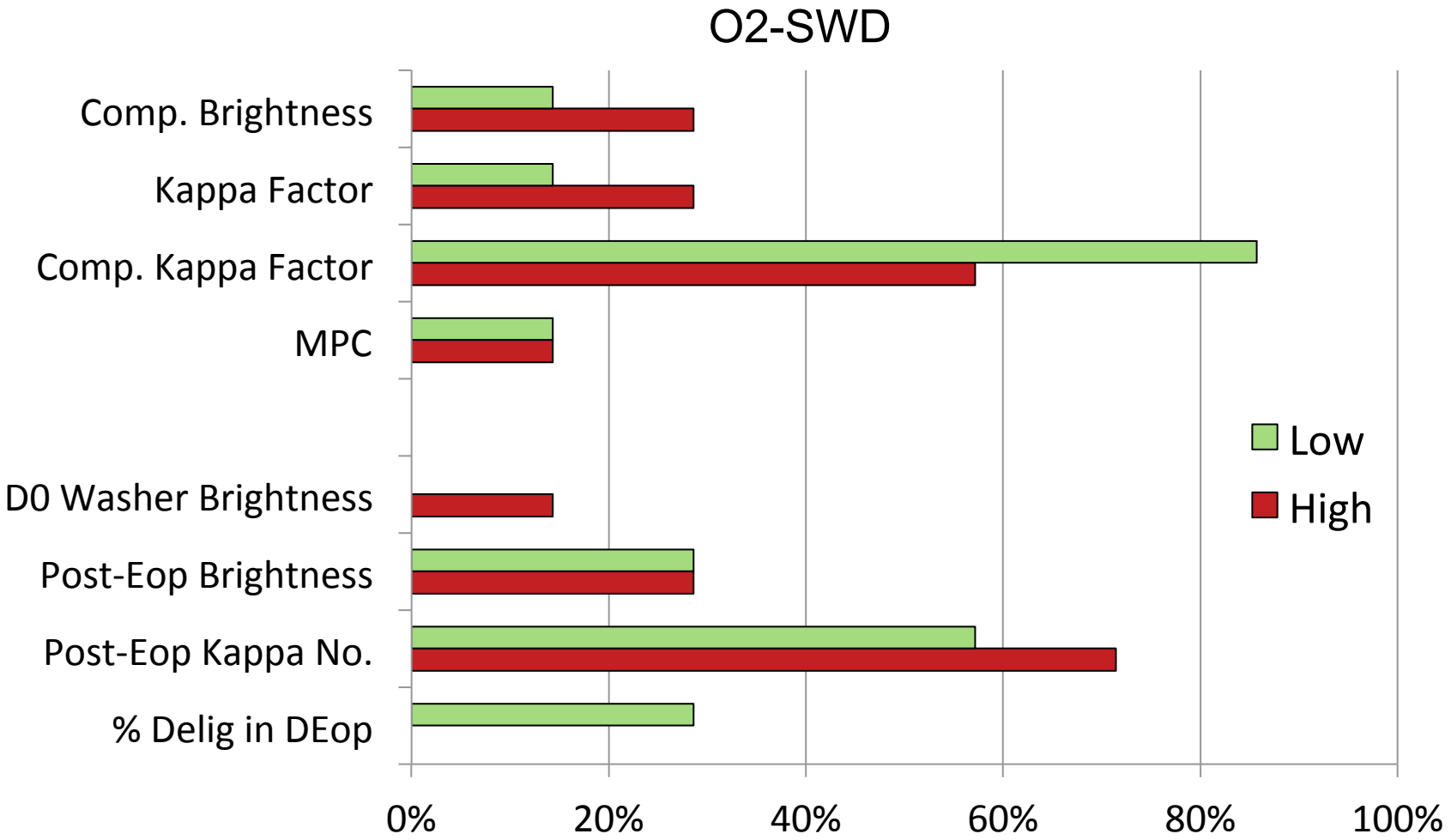
D_0 Kappa Factor & Chemical Use



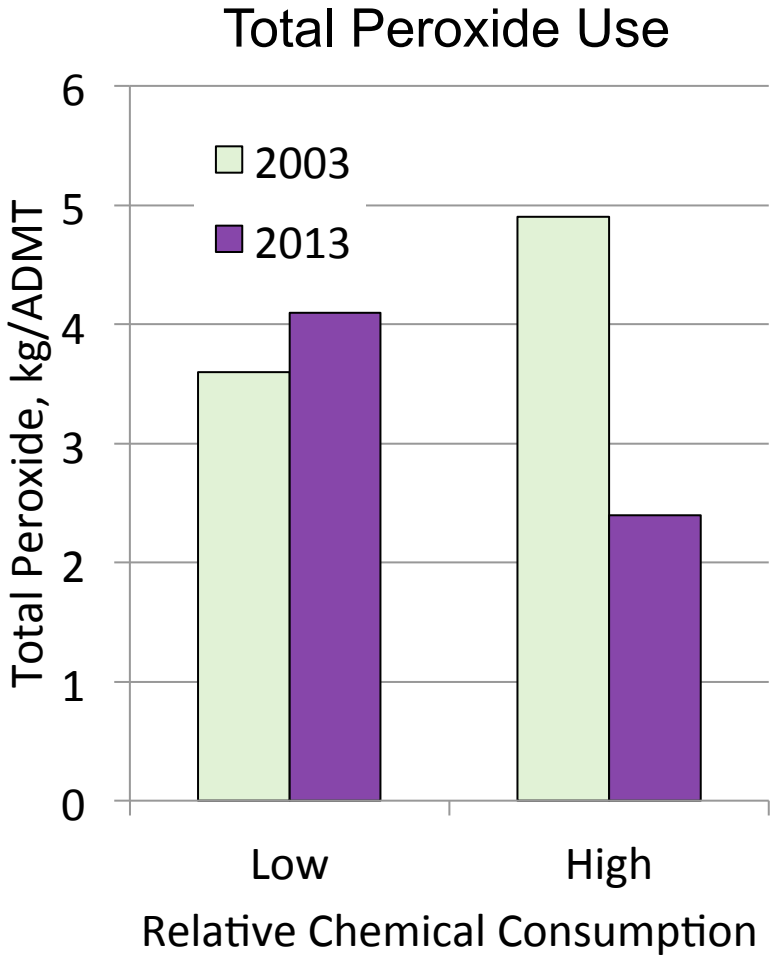
O2-SWD: D0 Sensors & Analyzers



O2-SWD: D0 Process Control



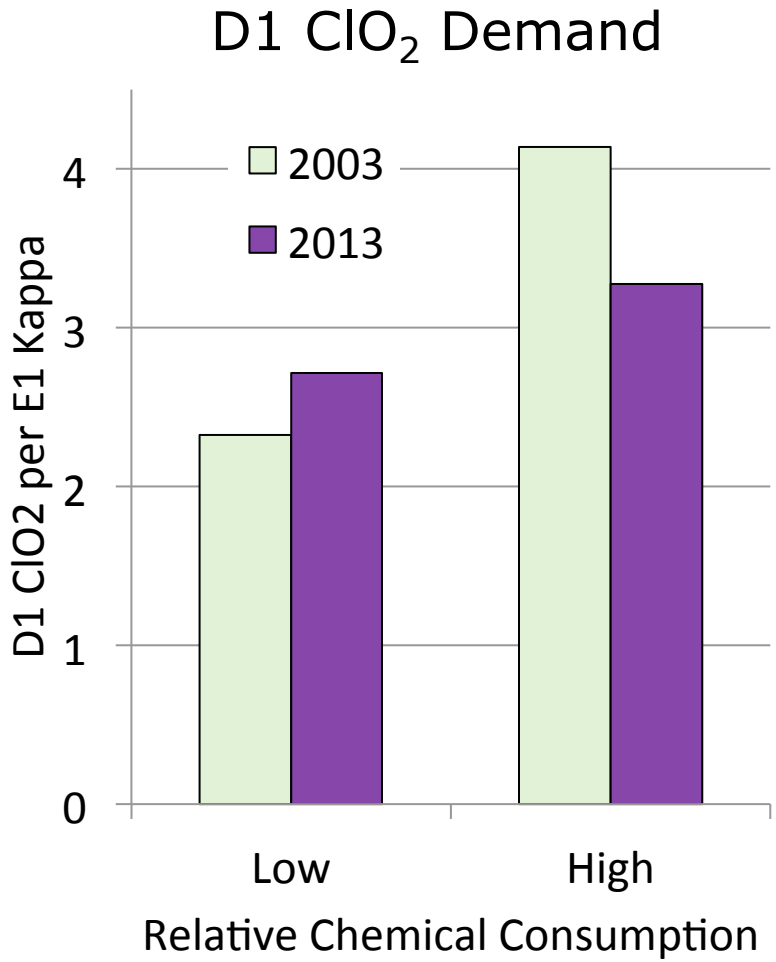
O2-SWD: Peroxide



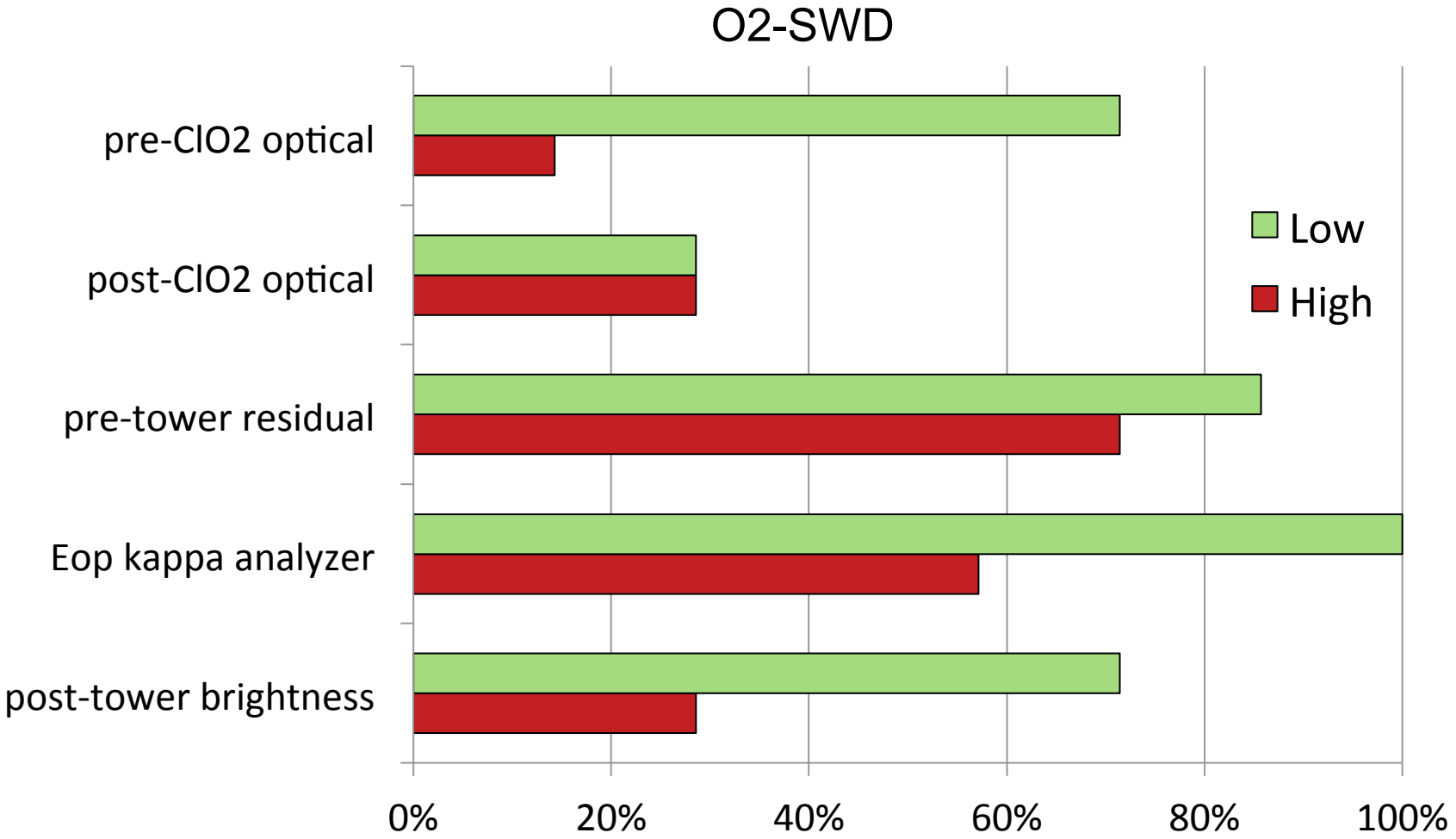
- High relative chemical consumption bleach plants use less peroxide
  - Reversal from 2003
- High D_0 Kappa Factors may leave insufficient lignin in the pulp to react with peroxide?

O2-SWD: D1-stage ClO_2 Demand

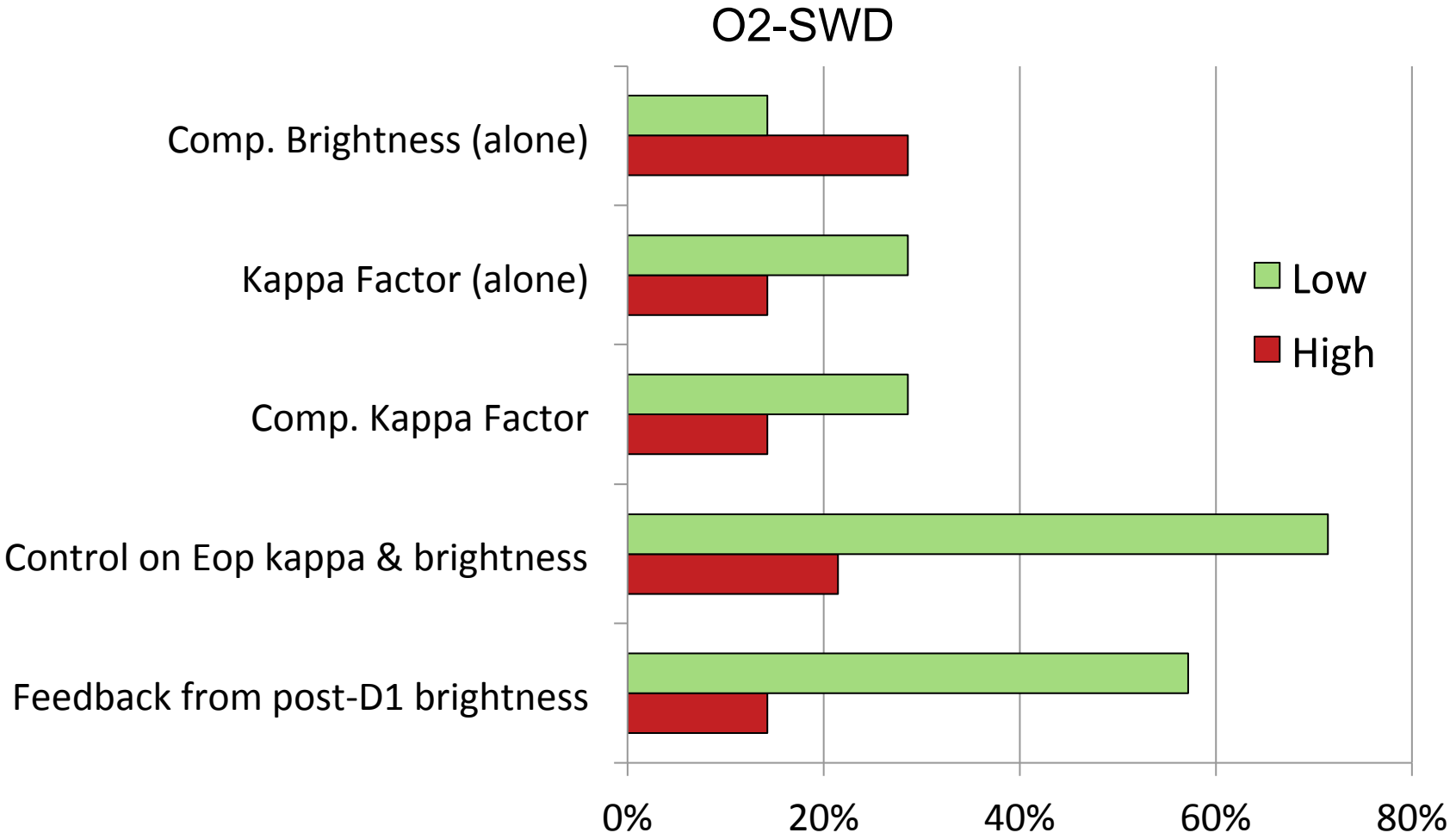
- Low relative chemical consumption bleach plants operate with a lower ratio of D1-stage chlorine dioxide to the Eop kappa number
  - Similar brightness
  - Similar terminal pH
- A high D1 ClO_2/Kappa ratio often indicates poor Eop-stage washing
  - Eop-stage carryover will increase ClO_2 demand



O2-SWD: D1 Sensors & Analyzers



O2-SWD: D1 Process Control



O2-SWD "Best Practices"

Comparison of mills with low and high relative chemical consumption indicates that "low chemical consuming" oxygen-delignified softwood bleach plants:

- Feed the bleach with a pulp having a kappa no. 2.8 units higher than the "high relative consumption" bleach plants;
- Produce pulp with 0.5 points higher final brightness;
- Use 3.3 kg/ADMT less chlorine dioxide, but 1.7 kg/ADMT more hydrogen peroxide;
- ***Operate with a significantly lower D0-stage Kappa Factor***;
- Are more likely to control the D0 stage using an online kappa analyzer in combination with optical and residual sensors;
- Are more likely to control the D1 stage using a combination of post-Eop kappa no. and post-Eop brightness, with feedback from the post-D1 brightness;
- Have a lower ratio of D1-stage chlorine dioxide to the Eop kappa number;
- Operate with a higher pH in the D2 stage

Relative Chemical Consumption: Conventional SWD

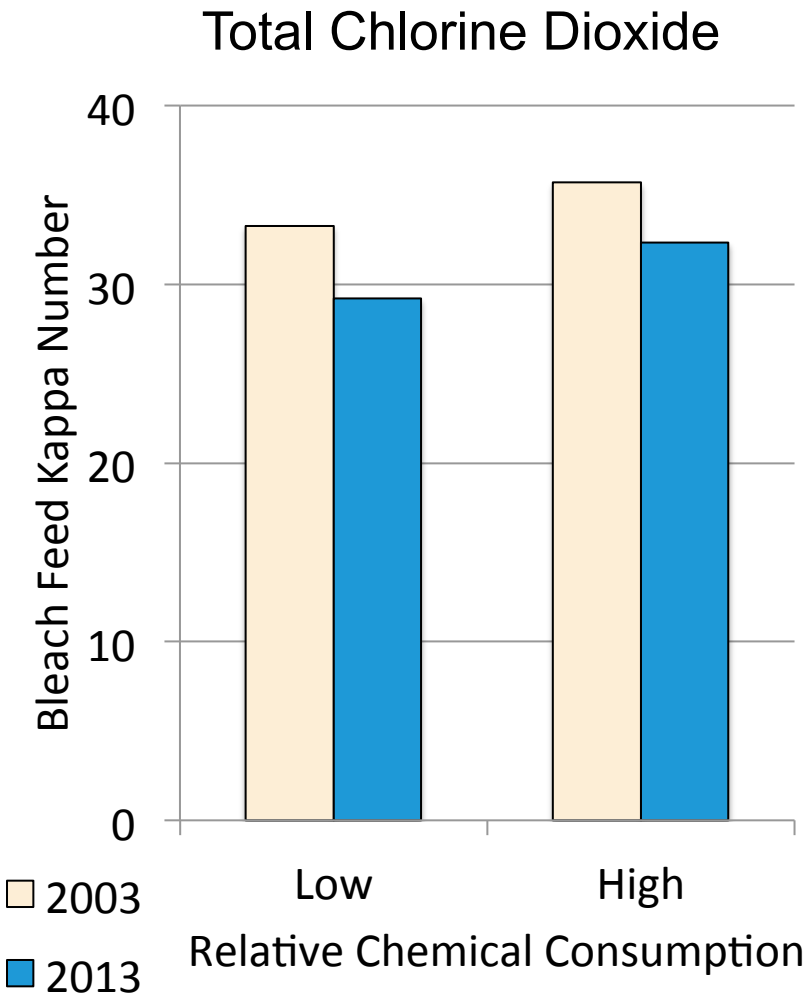
SWD mills sorted by Sequence Kappa Factor & averaged into two groups

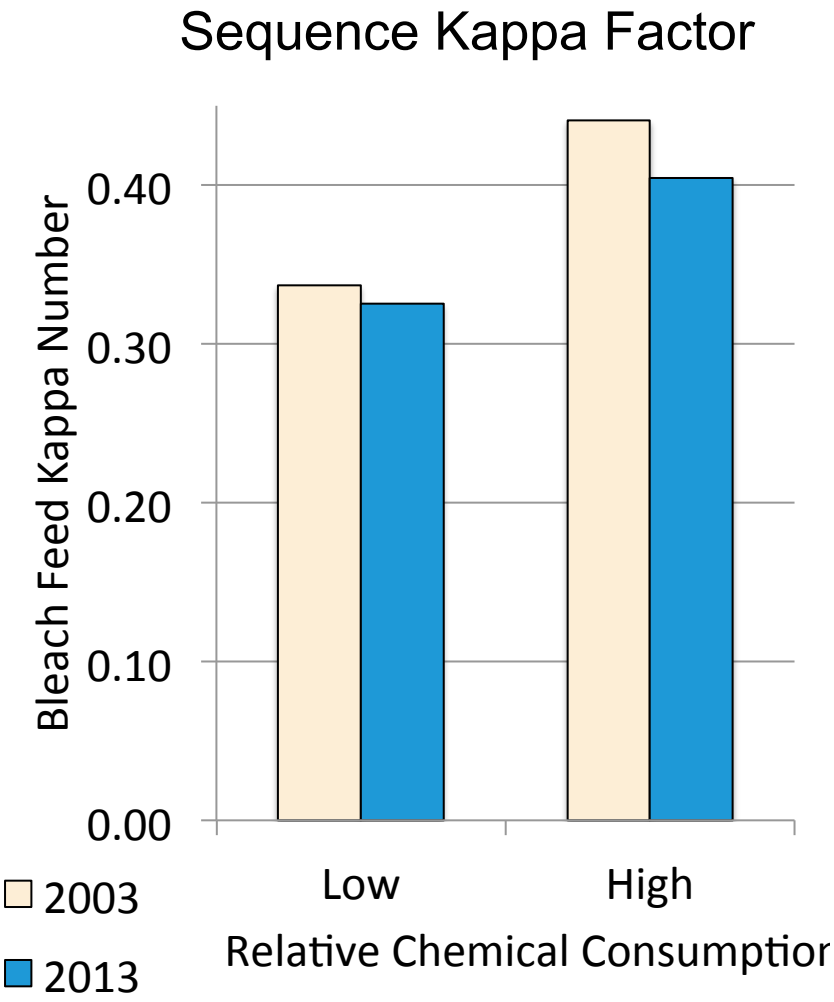
Parameter	Low Relative Chemical Consumption Average	High Relative Chemical Consumption Average
Bleach Feed Kappa No.	25.4	24.5
D_0-stage Kappa Factor	0.17	0.20
Eop-stage NaOH, kg/ADMT	20.6	19.6
Eop-stage H_2O_2, kg/ADMT	1.3	5.6
Post-Eop Kappa No.	5.5	5.1
D1-stage ClO_2, kg/ADMT	10.7	12.6
E2-stage H_2O_2, kg/ADMT	1.3	1.4
D2-stage ClO_2, kg/ADMT	2.1	2.7
Final Brightness, % ISO	88.8%	89.3%
Total ClO_2, kg/ADMT	29.2	32.3
Total H_2O_2, kg/ADMT	2.6	6.4
Total NaOH, kg/ADMT	27.3	26.8
Sequence Kappa Factor	0.33	0.40

"Low Relative Consumption" SWD mills:

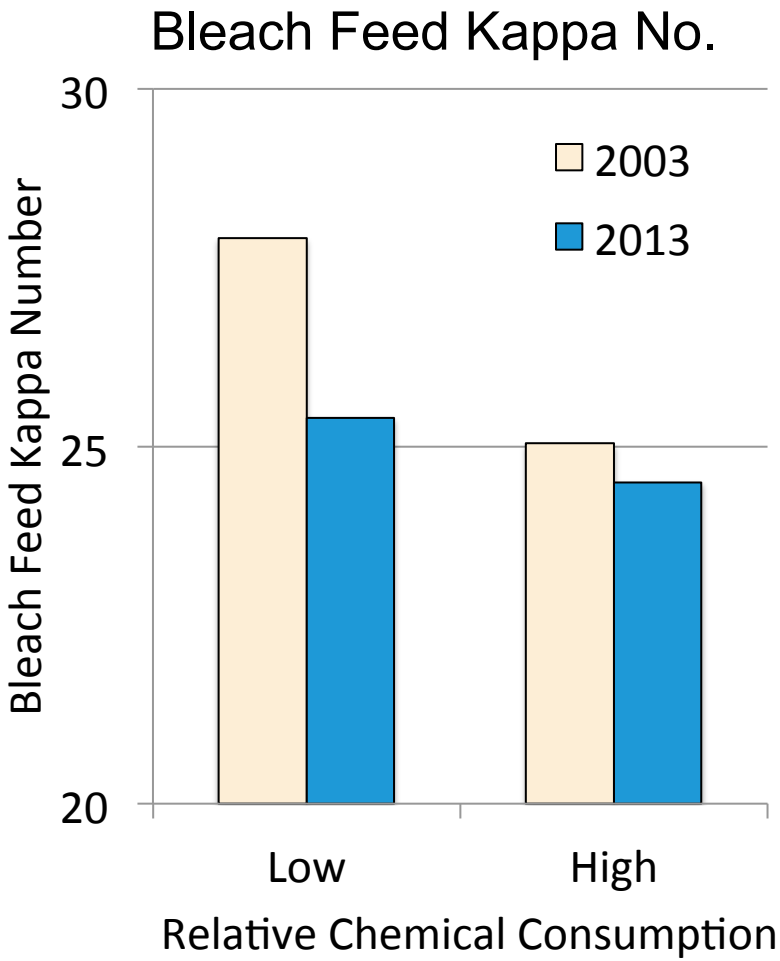
- Use 3.1 kg/ADMT less total ClO_2
- Use 3.8 kg/ADMT less peroxide
- Produce a pulp with 0.5% lower brightness

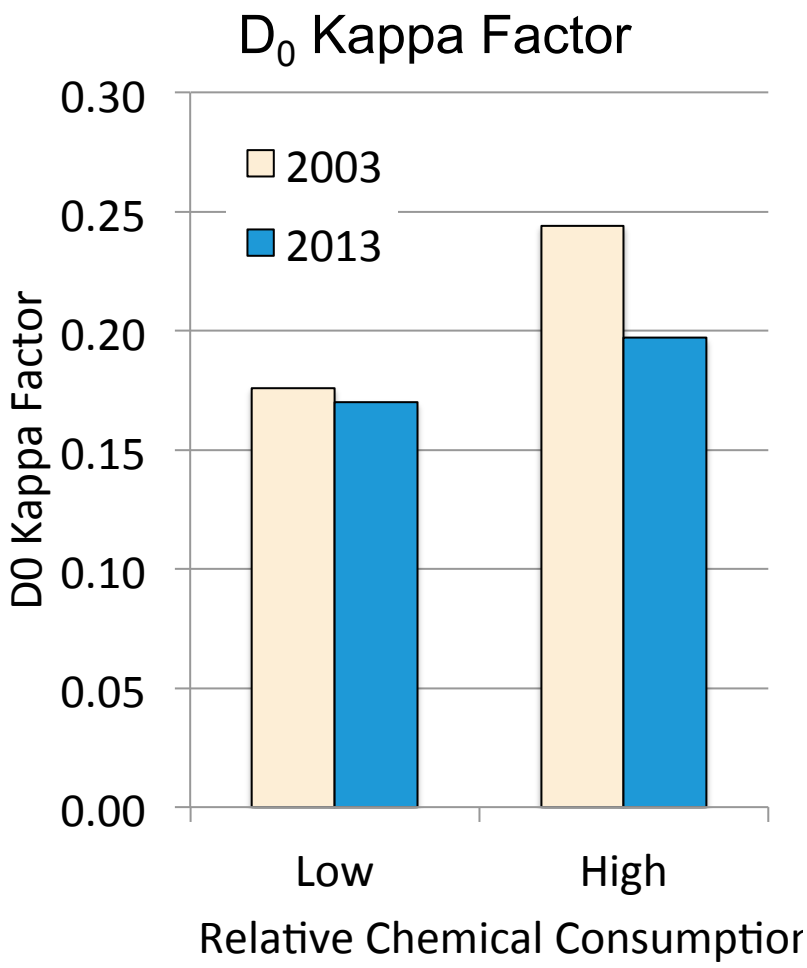
Conv. SWD: Oxidizing Chemicals



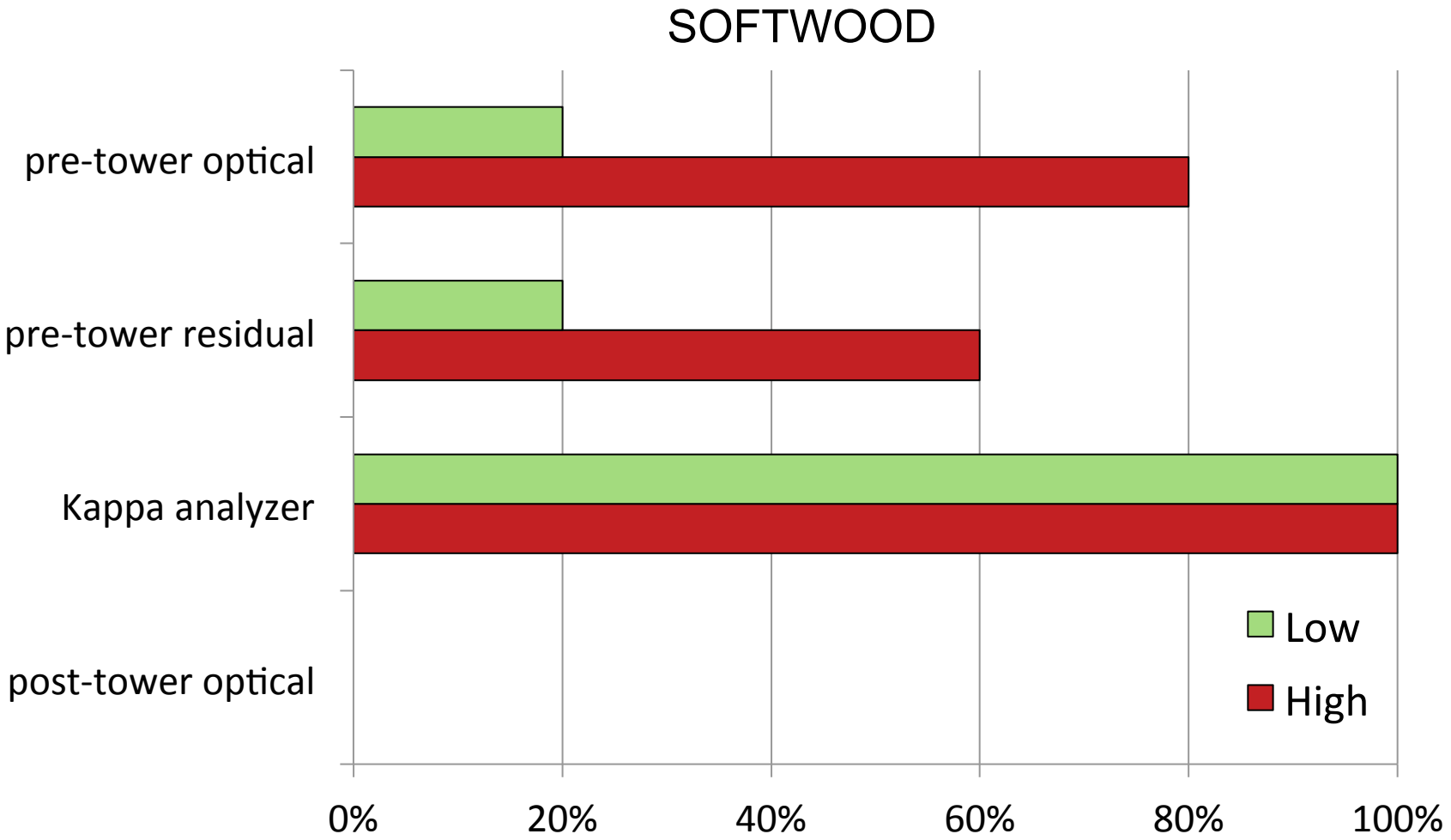


Conv. SWD: 2013 vs. 2003

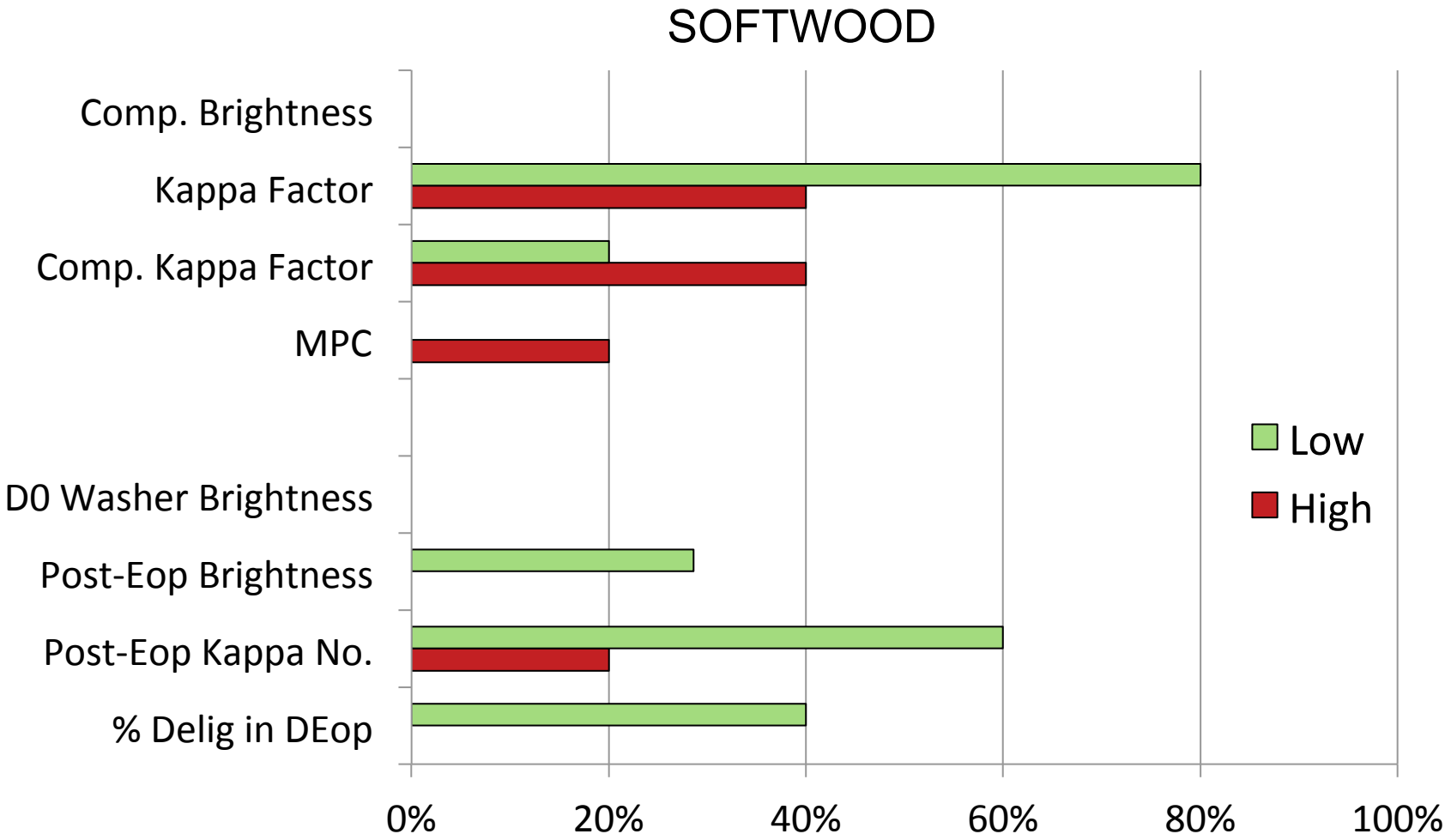




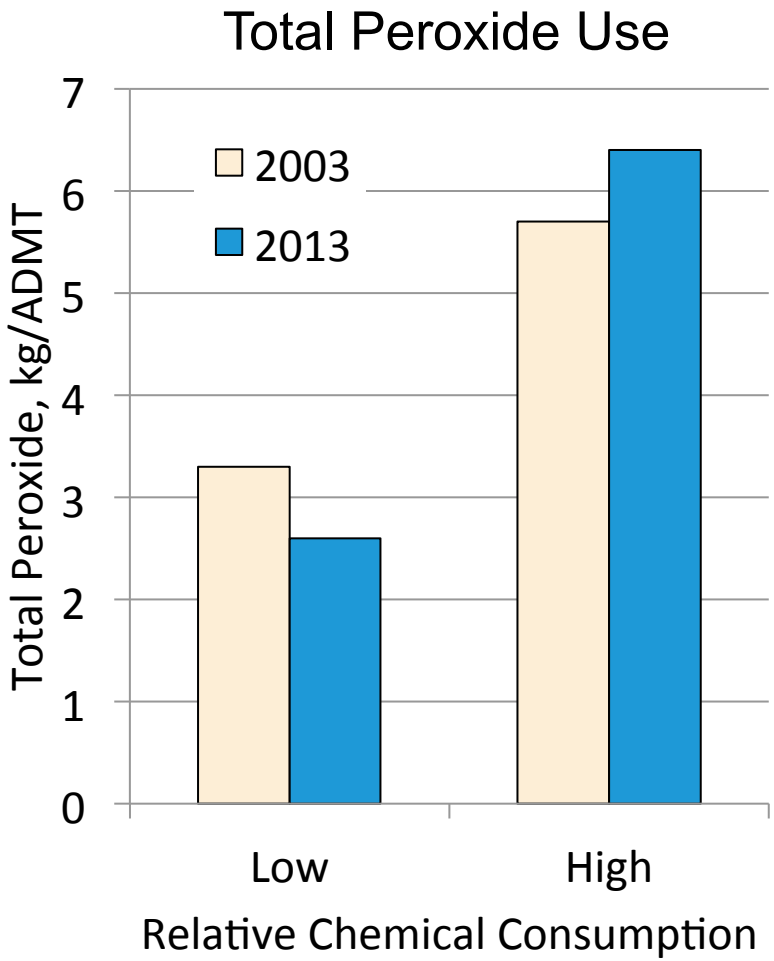
SWD: D0 Sensors & Analyzers

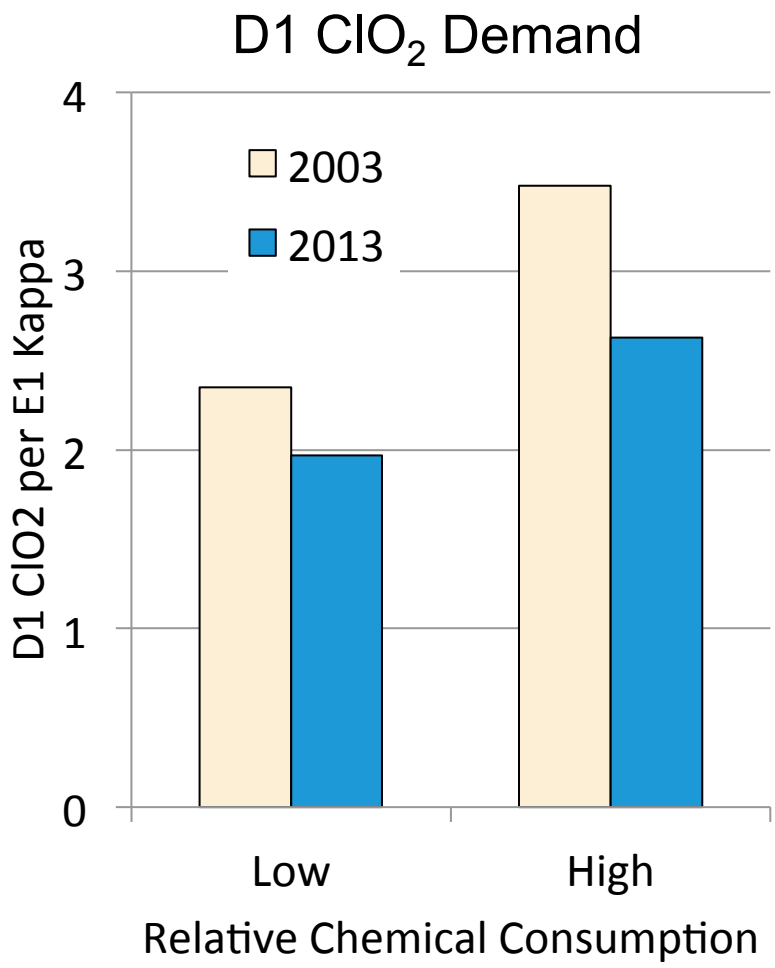


SWD: D0 Process Control

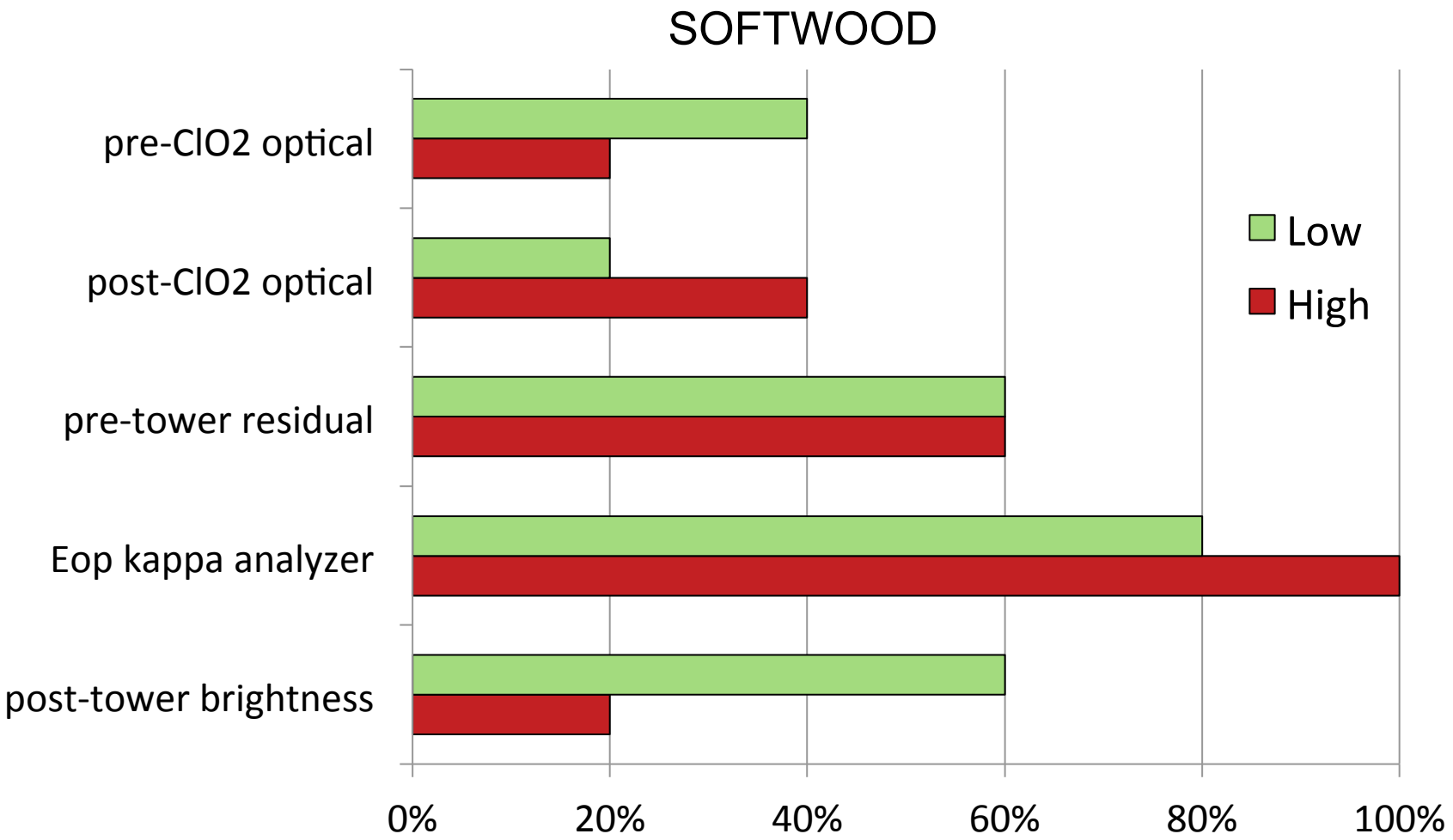


Conv. SWD: 2013 vs. 2003

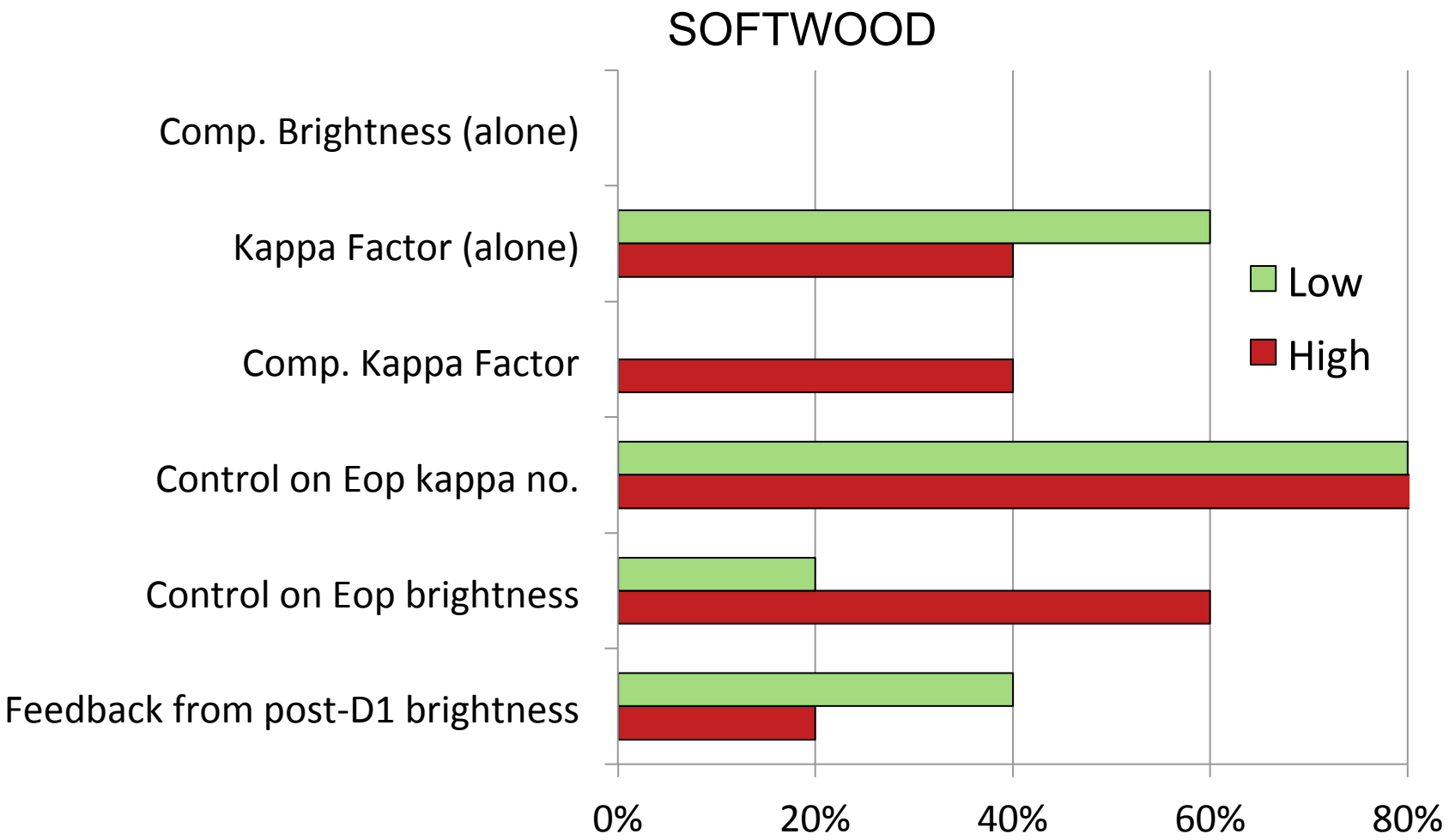




SWD: D1 Sensors & Analyzers



SWD: D1 Process Control



SWD "Best Practices"

Difference (spread) between "low" and "high" relative chemical consumption softwood bleach plants has decreased since 2003

- Improvement in high chemical consumers? Or mill shut-downs?

Comparison of mills with low and high relative chemical consumption indicates that "low chemical consuming" softwood bleach plants:

- Produce pulp with 0.5 points ***lower*** final brightness;
- Use 3.1 kg/ADMT less chlorine dioxide and 3.8 kg/ADMT less hydrogen peroxide;
- ***Operate with a lower D0-stage Kappa Factor***;
- Are more likely to control the D0 stage using Kappa Factor control (alone);
- Are more likely to operate a high-temperature/high-pressue "EO" stage; 40% of the "low chemical consuming" mills use "oxygen bleaching", *i.e.* DODEpD
- Have a lower ratio of D1-stage chlorine dioxide to the Eop kappa number.

And that's all for now…

These slides and coded spreadsheets will be posted on the new Bleaching Committee website

- Updates will be posted as available

Next steps:

- O2-SWD results to be presented (again) at 2015 TAPPI PEERS
  - Same presentation as at 2014 IPBC and 2015 PaperWeek
- O2-HWD results and analysis to be presented at Fall 2015 Bleaching Committee meeting