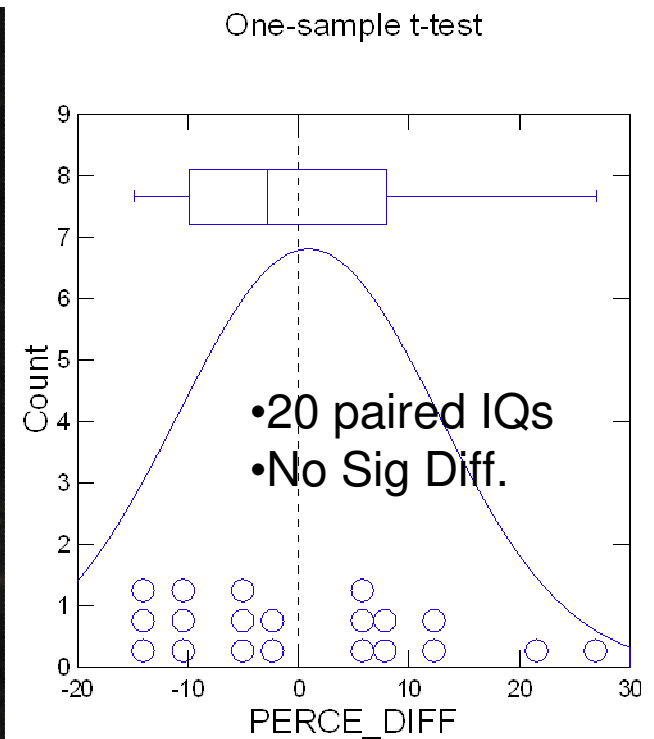# Derivation, Uncertainty, and Variance of the Calibration Factor used in Salt Dilution Flow Measurements

Gabe Sentlinger (ARD), Andre Zimmermann (nhc), Mark Richardson (UBC), John Fraser (ARD)

(11-14 m³/s)

One-sample t-test

Count

•20 paired IQs
•No Sig Diff.

PERCE_DIFF

- – SDIQ measurements CAN be as accurate, or more accurate, than VA measurements.
- – Better when it is unsafe to enter channel and ADCP is not going to work.
- – Extends our ability to measure in poor VA sections (turbulent, boulder controlled, etc)
- – Can work in low flow boulder bed channels that do not have a defined velocity profile.
- – Can be faster than VA but good to get both types if possible.
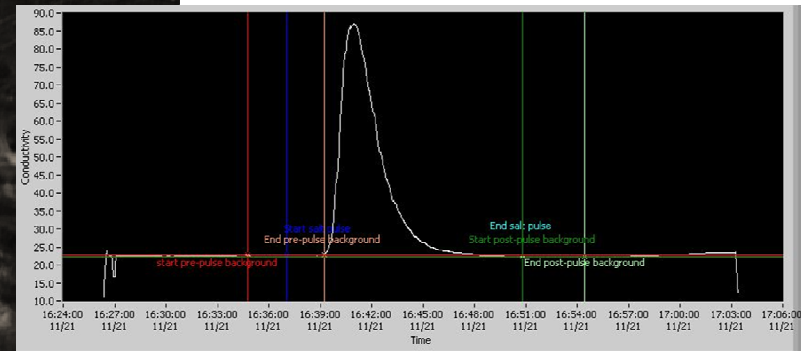- – NaCl easier to use than other tracers (RWT), but requires larger dose.

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Overview of SDIQ

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(11-14 m³/s)

$$Q = \dfrac{Mass}{\sum \left(EC.T(t) - EC.T(bg)\right) * dt * CF.T}$$
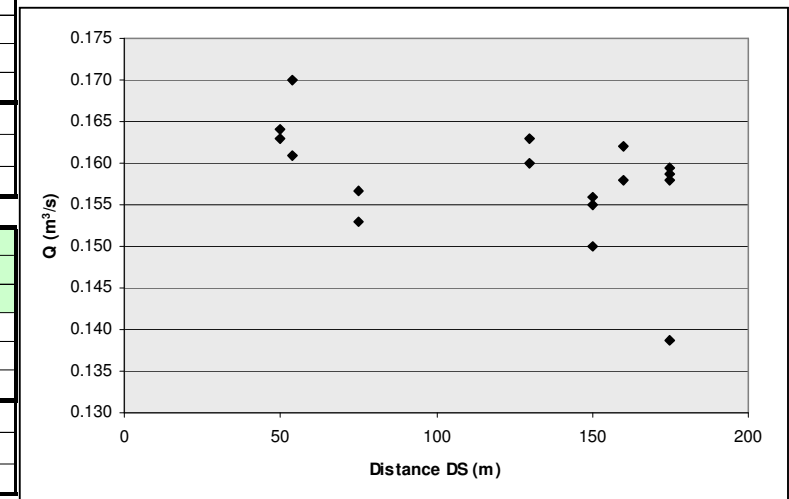
Ensure units cancel out!
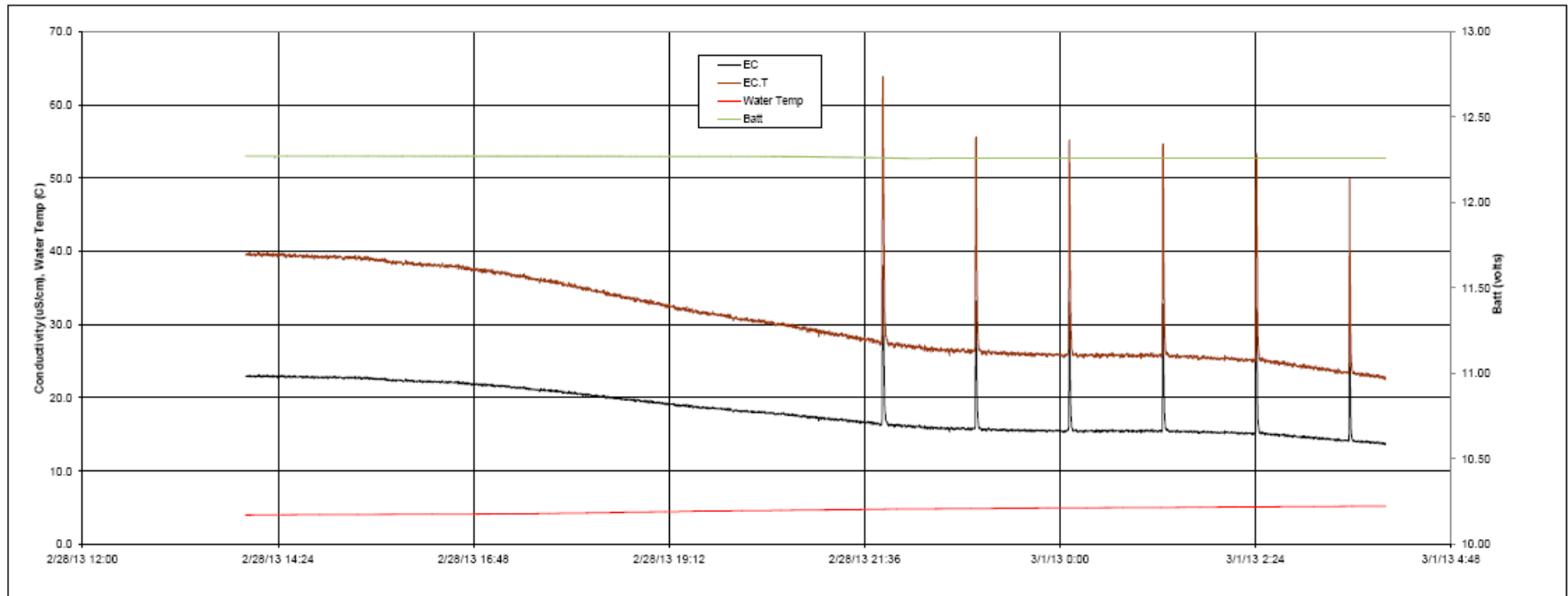
$$\frac{m^3}{s} = \frac{g}{\left(g/m^3\right)\cdot s}$$

1. Known amount of salt, or brine, is dumped into a turbulent portion of the river.

2. Mass of dry salt or volume of brine is recorded (can be injected as a brine or dry).

3. Conductivity probe downstream records passage of salt wave.

4. Area under curve is used to quantify amount of salt that passes.

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Overview of SDIQ

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Pulse	Discharge (m3/s)	CF.T (µS/cm)/(mg/L)	Peak over BG (µS/cm)	Distance (m)	Location	Time (PST)
Velocity Area						
ADV	0.164	NA	NA	200	DS Bridge	11:30
PRICE AA	0.209	NA	NA	200	DS Bridge	12:00
Salt dilution						
1	0.164	0.46	9	50	RB	12:30
1	0.170	0.46	9	54	LB	12:30
1	0.153	0.48	5.5	75	LB	12:30
1	0.163	0.45		130		12:30
1	0.150	0.47	4	150	LB	12:30
1	0.162	0.51		160	LB	12:30
1	0.158	0.47	3	175	LB	12:30
1	0.127		3	175	LB	12:30
2	0.161	0.46	30	54	RB	13:10
2	0.163	0.46	30	50	LB	13:10
2	0.157	0.48	28	75	LB	13:10
2	0.160	0.44		130	LB	13:10
2	0.155	0.47		150	LB	13:10
2	0.156	0.47		150	LB	13:10
2	0.158	0.51		160	LB	13:10
2	0.159	0.47	17	175	LB	13:10
2	0.139	0.47	16	175	LB	13:10
2	0.160	0.48	16	175	LB	13:10
Average (m³/s)	**0.160**	**0.471**				
Std Dev (m³/s)=	**0.005**	**0.019**				
CoV	**3%**	**4%**				
Rhodamine dilution						
1	0.139			75	Mid	
1	0.191			75	LB	
1	0.110			175	LB	
2	0.141			75	Mid	
2	0.199			75	LB	
2	0.105			175	LB	
Average (m³/s)	**0.148**					
Std Dev (m³/s)=	**0.040**					
CoV	**27%**					

-19 measurements by 6 independent hydrographers, coefficient of variation ±3%.

-not significantly different from ADV measurement by WSC.

-RWT IQs showed larger CoV.

-In this case, there was no sig. relation to distance downstream.

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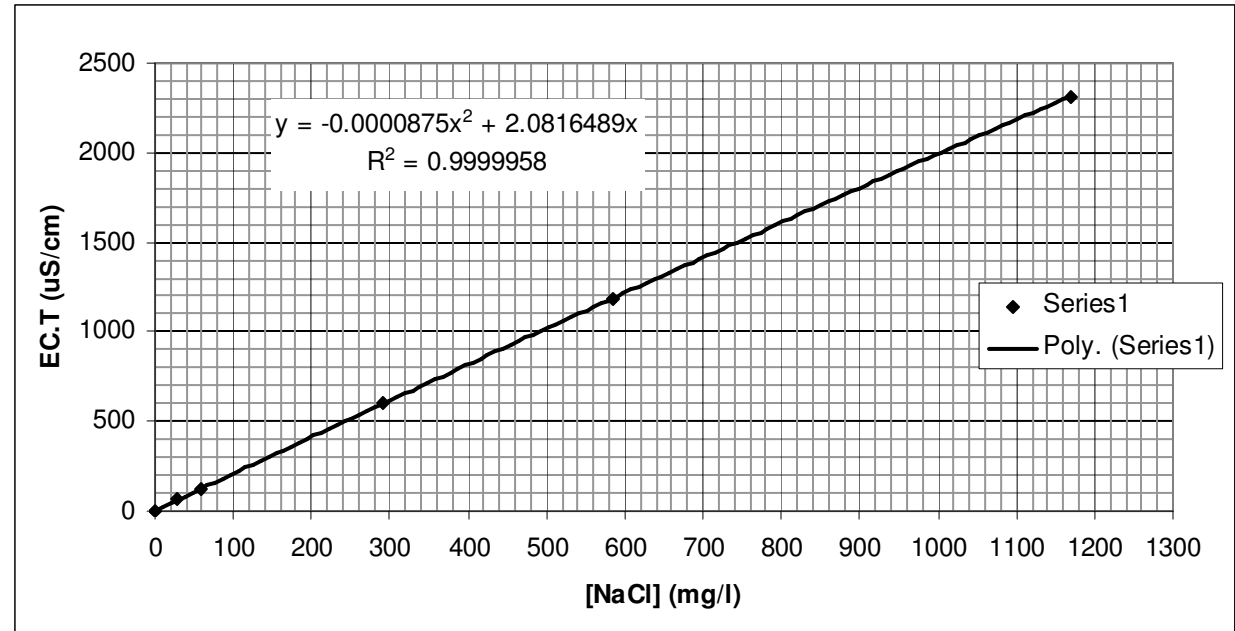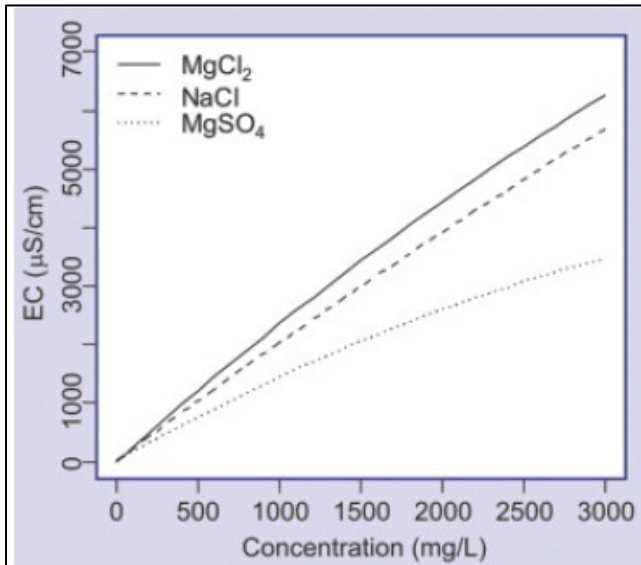
- How much error is introduced by assuming a CF.T for automated measurements?
- Is CF.T a function of BG EC.T or chemical makeup?
- Is CF.T a function of the instrument? (It shouldn't be.)
- Does CF.T vary by region (chemical makeup)?
- Pertains to manual measurements as well.

Impetus for Study: Automated Gauging
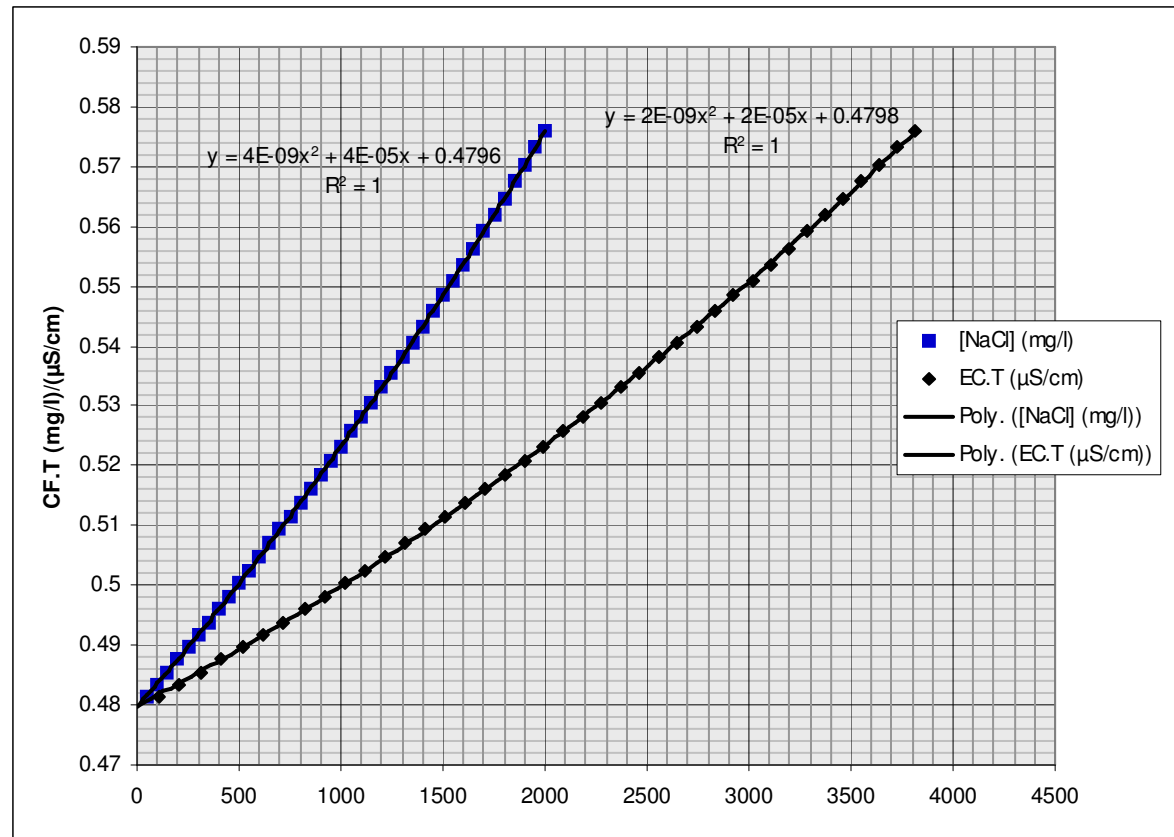
(from Moore, 2008)
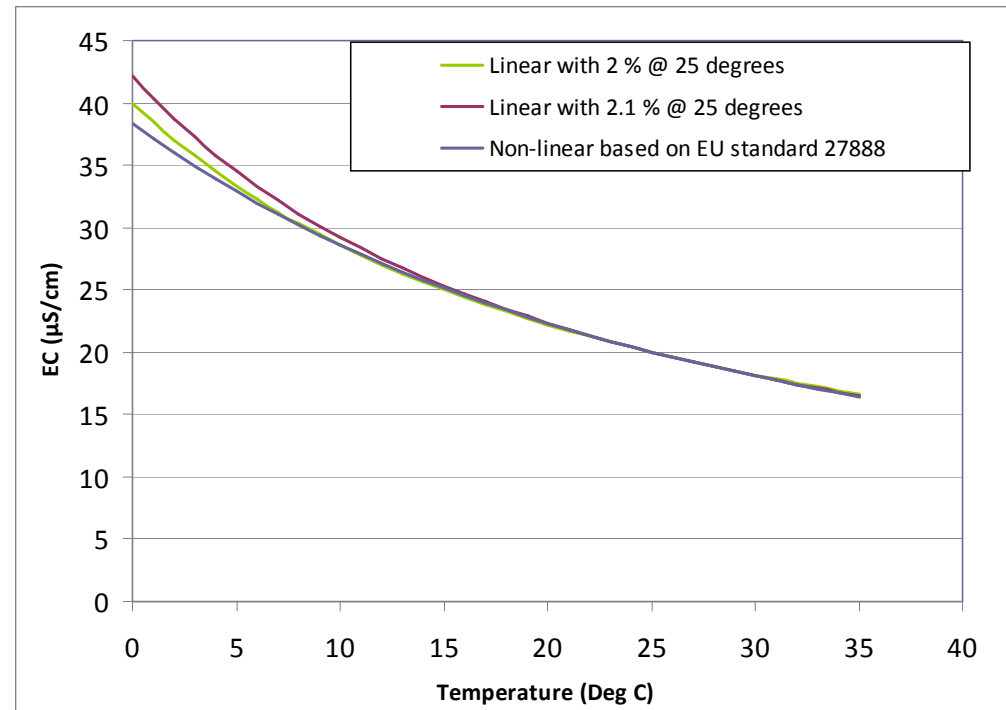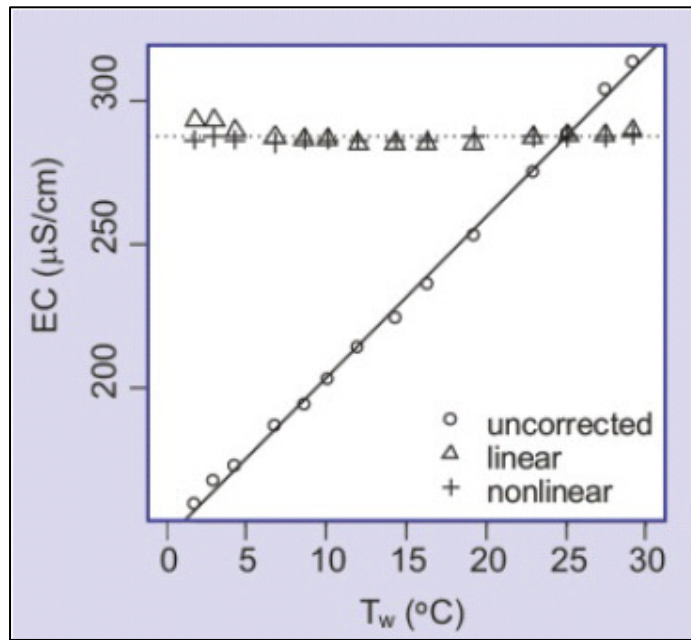
- Different methods. Best is Non Linear Function (nlf) compensation (EU 27888). Not offered on all meters. Next best is linear 2.0%/°C for NaCl.

- Linear departs from actual, and nlf, below 10 °C . This is not an issue for SDIQ if temperature is held relatively constant for CF.T derivation and over course of measurement, BUT this is not often the case (i.e. glacier melt at near zero degrees and calibration done in warm summer weather.

- Using EC.T, and CF.T, is best way to address temperature affect. Also adds layer of QA/QC to ensure linear and repeatable EC.T response. Can reduce time required (assume CF.T) and permit accurate Automated Gauging.

Temperature Compensation

(from Moore, 2008)

$$y = -0.0000875x^2 + 2.0816489x$$
$$R^2 = 0.9999958$$

- Different Salts have different slopes at different concentrations.
- SD measurements should only increase the concentration by 10-20 mg/L, so relationship is ~ linear.
- Theoretical EC.T vs. [NaCl] (from Harned and Owen (1958))
- Polynomial fit is better than linear.
- Possible to estimate [NaCl] from EC.T.
- Temperature compensation is not trivial however

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Theoretical CF.T

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$y = 2E\text{-}09x^2 + 2E\text{-}05x + 0.4798$
$R^2 = 1$

$y = 4E\text{-}09x^2 + 4E\text{-}05x + 0.4796$
$R^2 = 1$

- Theoretical CF.T vs EC.T (from Harned and Owen (1958))
- 0.485 applicable to EC.Ts from 0-500 uS/cm, i.e. this assumption only introduces 1% error into measurement. Our derivation of CF.T is subject to greater uncertainty.
- This assumes that your probe is calibrated, working properly, and there is no interspecies interference, which we have not seen so far.

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Theoretical CF.T

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- Relationship between dry salt and Temperature Compensated Electrical Conductivity (EC.T aka Specific Conductivity) response is first determined (CF.T)
  - Known amount of dry salt is mixed with known amount of distilled water (not stream water)
  - This solution is then typically diluted to about 1g/L concentration
  - The conductivity of a known amount of the stream water is then measured
  - Then a small amount (e.g. 5 ml) of the ≈ 1g NaCl/L solution is added to the stream water and the conductivity measured again
  - Repeated until the maximum observed conductivity is reached and line consists of ~5 points (4 injections)
  - Slope ~ CF.T (need to account for distilled water)

Overview of Derivation

Increments of Distilled Water (5.4 uS/cm) in Tap Water (~ 65.5 uS/cm)
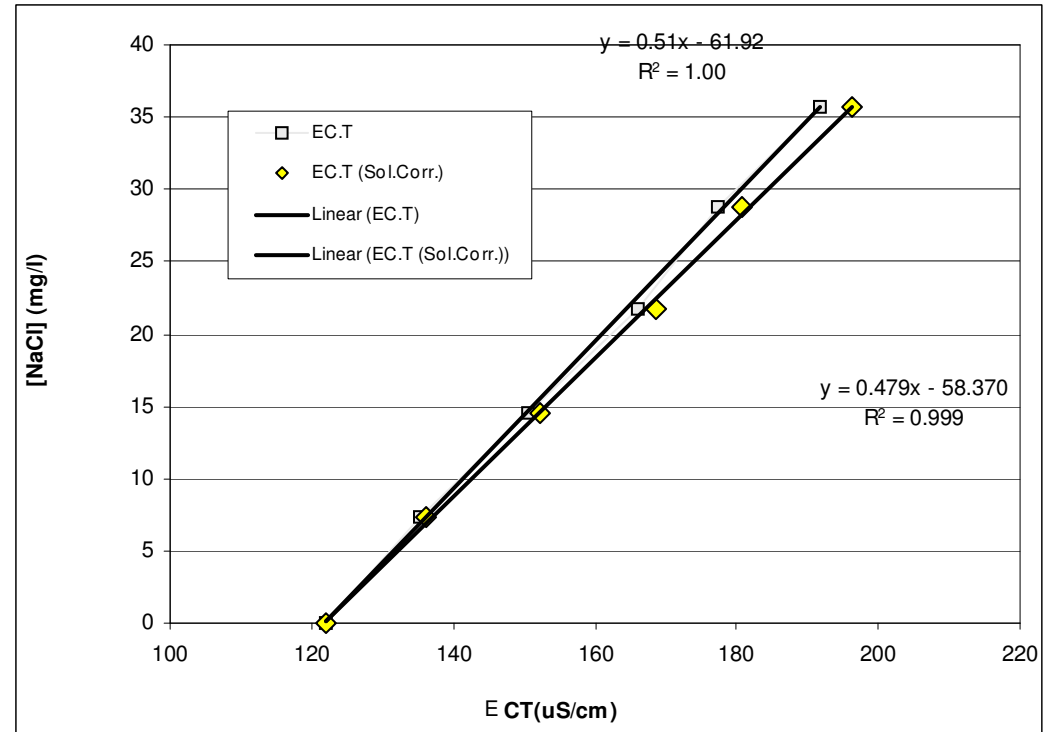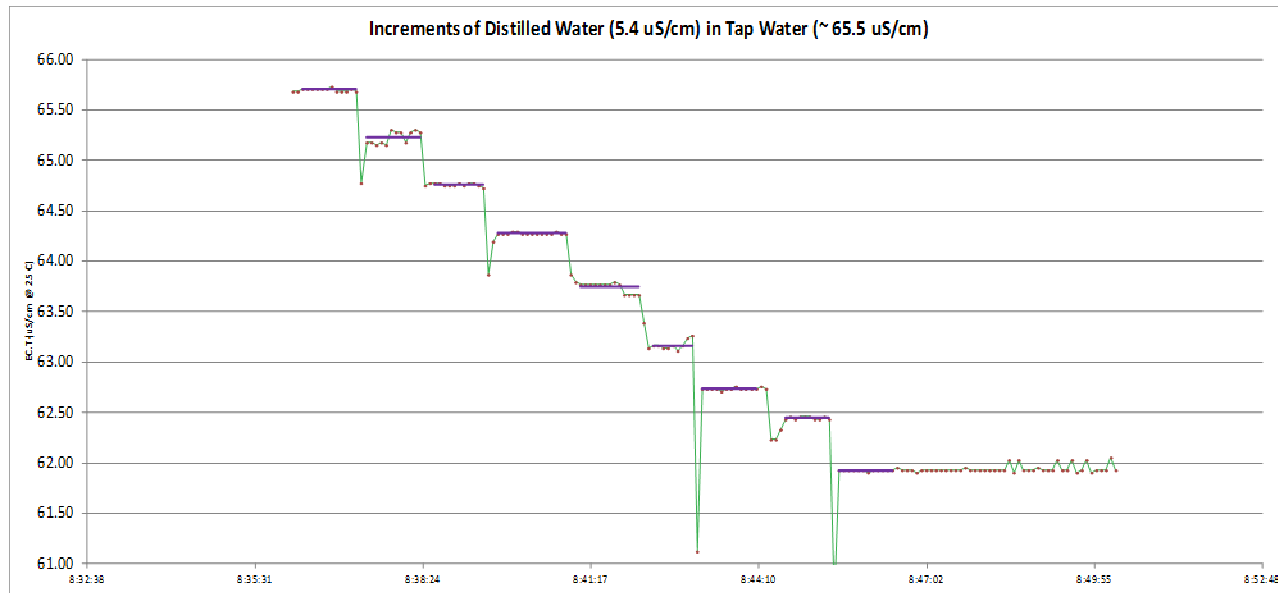
• IF USING A STANDARD: Need to account for the conductivity depression resulting from preparing the calibration solution with distilled water.
• Depression greatest if the background conductivity of the stream water is high.
• The predicted depression in electrical conductivity by adding a known volume of distilled water can be derived from a two-component mixing model:

• ECi   Stream water EC
• ECdw   Distilled water EC
• ECmix   Mixed water EC
• Vi is the initial volume of stream water
• Vdw is the volume of distilled water added.
• The resulting depression of conductivity (ΔEC) can be estimated by rearranging the above terms.
• The ΔEC should be added back onto the EC for the correct slope (CF.T).

$$EC_{mix} = \frac{EC_i V_i + EC_{dw} V_{dw}}{V_i + V_{dw}}$$

Distilled Water CF.T Correction

$$\%E = 1 - \frac{CF.T_{true}}{CF.T_{ms>>}} = 1 - \frac{\left[\dfrac{m_o + m_s + m_d}{V_o + V_s} - \dfrac{m_o}{V_o}\right]}{EC.T' - EC.T_i}$$

$$\dfrac{\dfrac{m_s}{V_o + V_s}}{EC.T' - EC.T_i}$$

$$= 1 - \frac{\dfrac{V_o(m_o + m_s + m_d) - (V_o + V_s)m_o}{(V_o + V_s)V_o}}{\dfrac{m_s}{V_o + V_s}}$$

$$= 1 - \frac{V_o m_o + V_o m_s + V_o m_d - V_o m_o - V_s m_o}{m_s V_o}$$

$$= 1 - 1 + \frac{m_d}{m_s} - \frac{m_o V_s}{V_o m_s}$$

$$= \frac{[d] - [o]}{[s]}$$

- If [d] =[o] no correction (brine method)
- If [s]>> insignificant correction
- If [o] is small, correction small

Approximation to correct archived CF.Ts
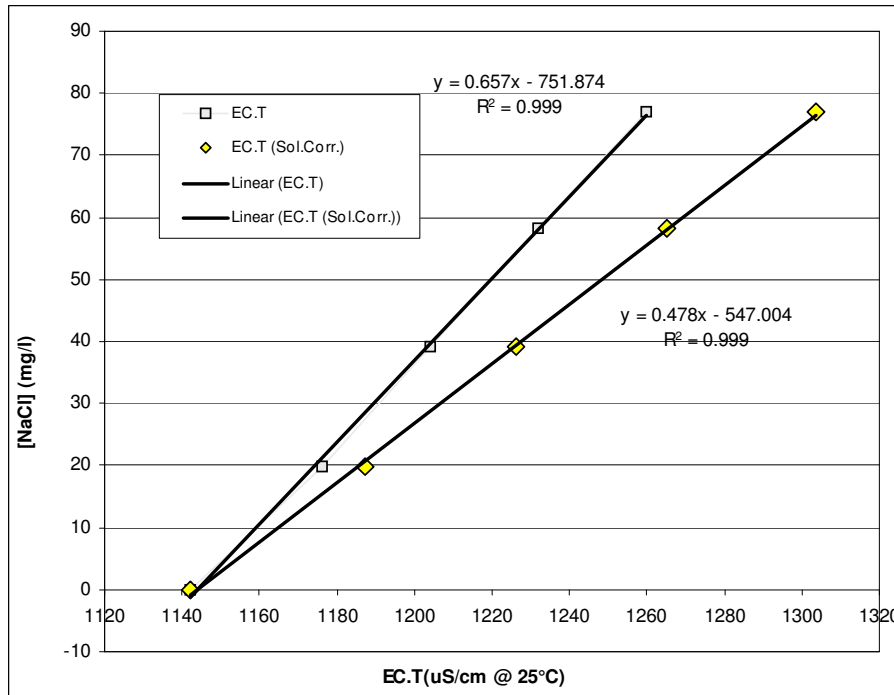
$$CF.T_o \approx \frac{[o]}{EC.T_o} \approx 0.48$$

$$[o] \approx 0.48 \cdot EC.T_o$$

$$[d] \approx 0.48 \cdot EC.T_d$$

$$CF.T_{true} \approx CF.T_{ms>>}\left[1 - \left(\frac{0.48 \cdot (EC.T_d - EC.T_o)}{[s]}\right)\right]$$

$$CF.T_{true} \approx CF.T_{ms>>}\left[1 - \left(\frac{EC.T_d - EC.T_o}{EC.T_s}\right)\right]$$

- The bias is positive, CF.T is overestimated; Q is proportional to 1/CF.T so it produces estimates of Q that are lower than true.
- An approximation can be used to correct archived CF.Ts and Q calcs.

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Distilled Water CF.T Correction:
Analytical Solution

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$$EC.T_{SolCorr} = (EC.T_o - EC.T_{mix}) + EC.T$$

For each injection and find slope

or

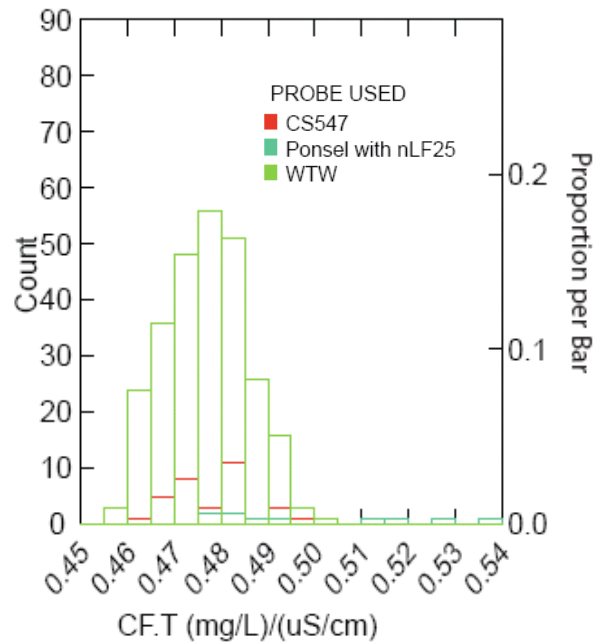$$CF.T_{true} \approx CF.T_{ms>>} \left[1 - 0.48 \cdot \left(\frac{EC.T_d - EC.T_o}{[s]} \right) \right]$$

$$\approx 0.657 \cdot \left[1 - 0.48 \cdot \left(\frac{2.2 - 1142}{1999} \right) \right]$$
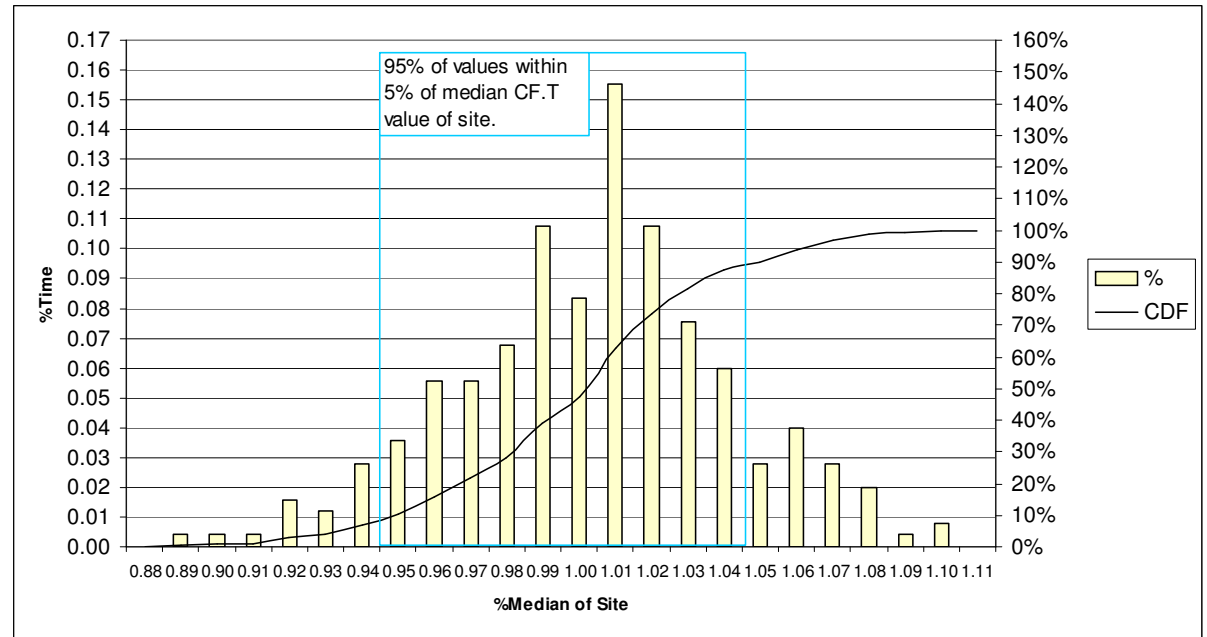
$$\approx 0.657 \cdot [1 - 0.274] = 0.477$$

Chart labels:
- y = 0.657x - 751.874, R^2 = 0.999
- y = 0.478x - 547.004, R^2 = 0.999
- Legend: EC.T; EC.T (Sol.Corr.); Linear (EC.T); Linear (EC.T (Sol.Corr.))
- Y-axis: [NaCl] (mg/l)
- X-axis: EC.T(uS/cm @ 25°C)

• In this example, EC_i was 1142 uS/cm. Distilled Water EC.T was 2.2 uS/cm. This was a reduction of ~27% each injection. If the uncorrected EC.T was used, it would result in a 27% underestimation of Q.

• Can be corrected for by correcting each injection by EC_{mix} and then recalculating slope (as shown in figure). This method requires reprocessing old calibrations.

• Can also be corrected for using the analytical approximation (-27.4% above).

• Note that any two points may give bias of CF.T; regression slope of 4 injections (5 points) is recommended. R^2 should be 0.99 to 1.00.

AQUARIUS Research & Development Inc.   UBC   Example CF.T Correction   nhc northwest hydraulic consultants

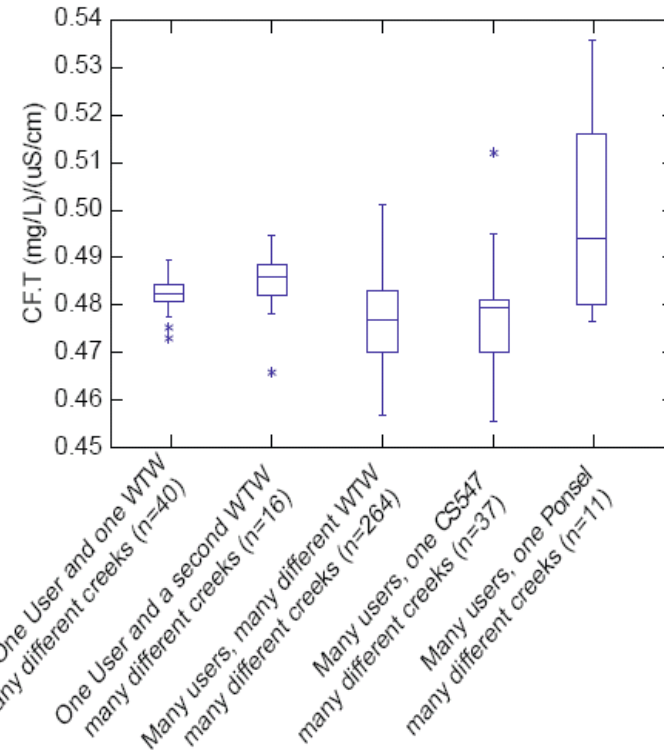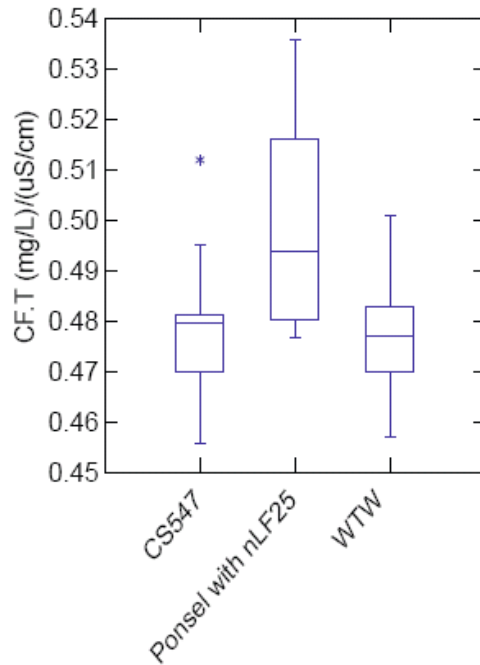From AZ (NHC)   From GS (ARD)

- CF.T Values are typically between 0.48 and 0.49. From NHC, WTW is largest sample, most reliable. For WTW, mean is 0.483 ±0.008 (± 3.3% at 95% confidence)
- From ARD 95% of CF.T values are within 5% of site median.
- Implies that assuming a CF.T of 0.483, with a calibrated probe, introduces up to 5% uncertainty.

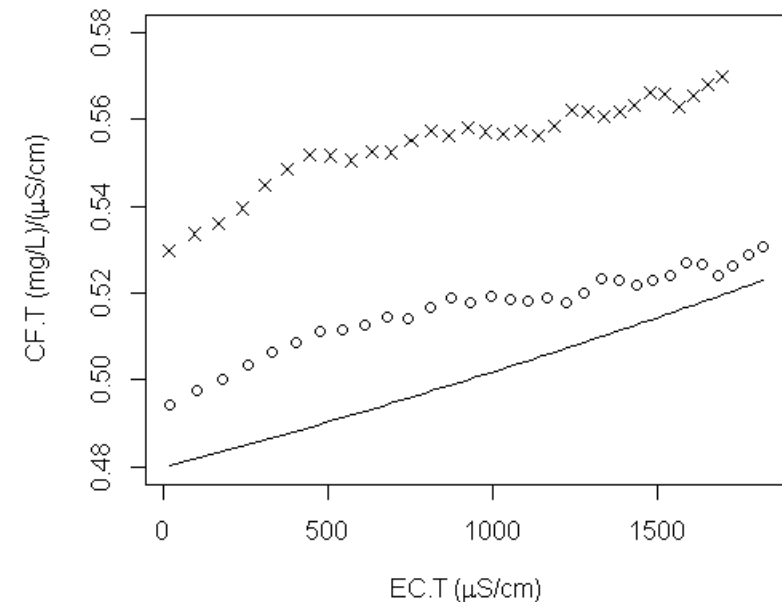Theoretical CF.T

From AZ (NHC)

- NHC has further categorized to user and serial number.
- Smallest variance for single device and user.
- Implies that with training and calibration of a quality instrument, CF.T may vary as little as ±1.6% (at 95% confidence)

Theoretical CF.T

From AZ (NHC)
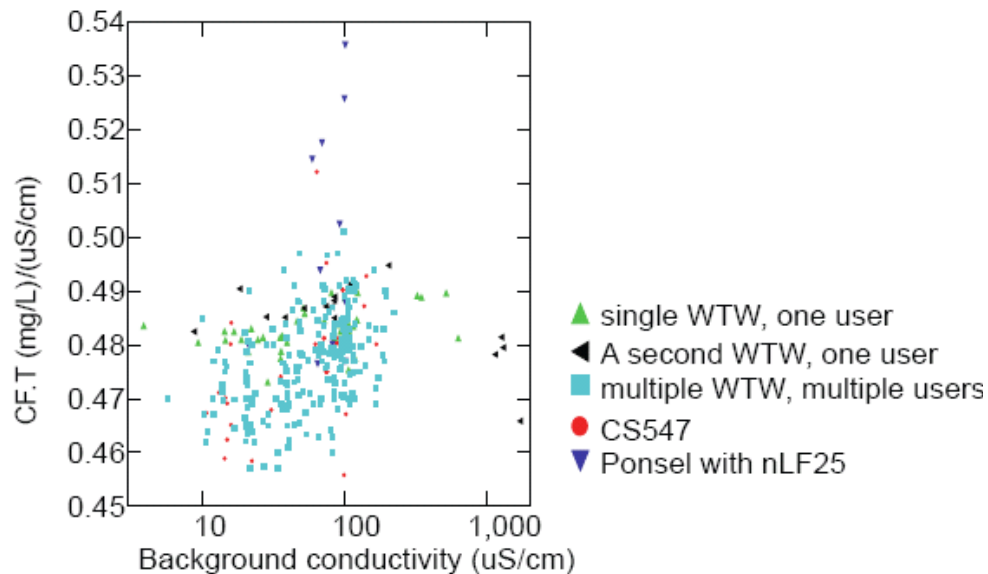
From MR (UBC)

CF.T vs. EC.T (circles) and CF vs. EC (crosses)

- Hongve (1987) suggests it does, but if you apply the distilled water correction to the data: correction = slope of trend; so no trend.
- Szeftel (2011) suggests it does, but also used distilled water.
- Our tests so far suggest that it does not, unless the species present is NaCl.
- Our test suggest that the CF.T does increase with [NaCl], but doesn't quite agree with the theoretical curve

Does CF.T depend on background EC.T?
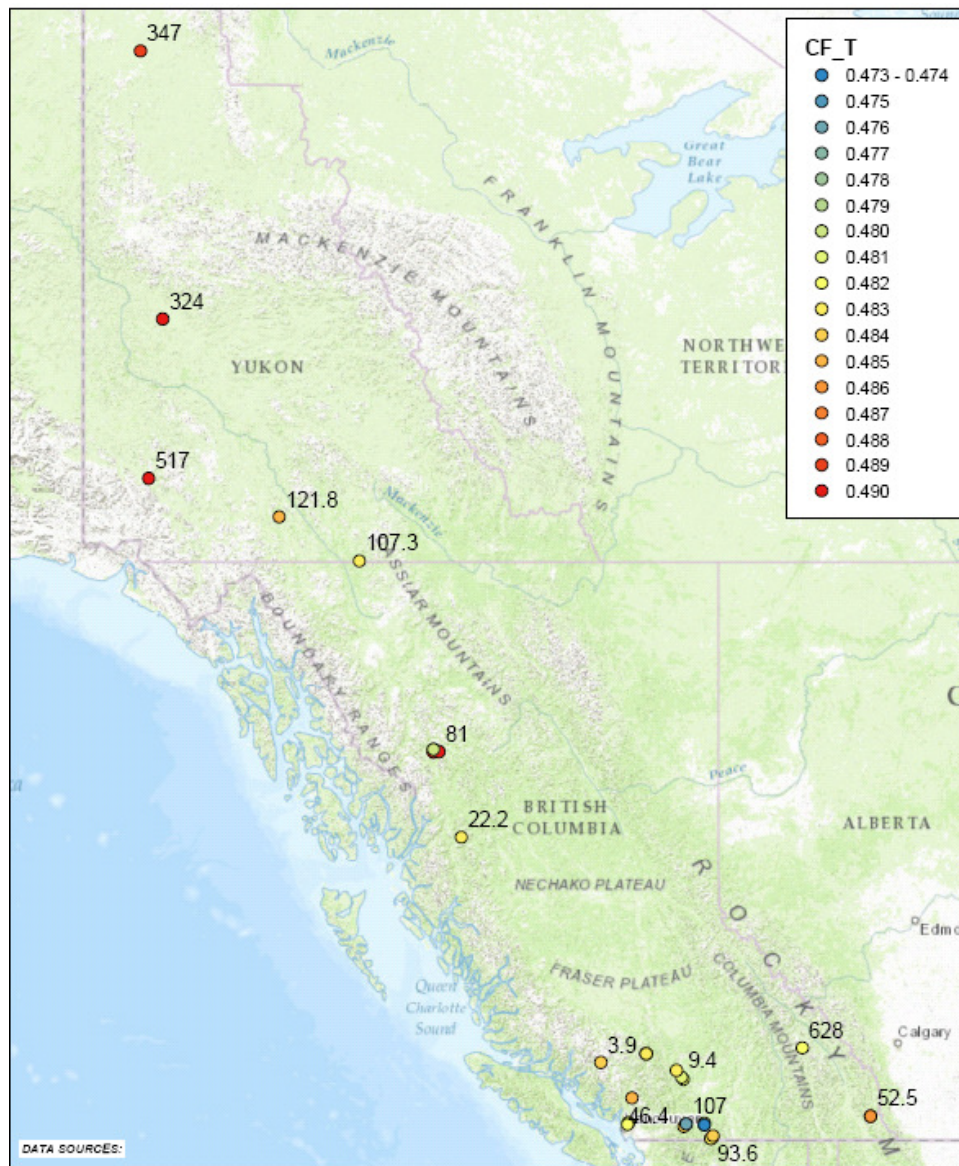
- 40 samples from WSC from BC and Alaska with BG EC.T spanning from 3.9 µS/cm to 1142 µS/cm.

- No apparent correlation to BC locations.

- Higher BG EC.T sites in Yukon yield larger CF.T, but only by 1% from the average.

Does CF.T depend on Region?
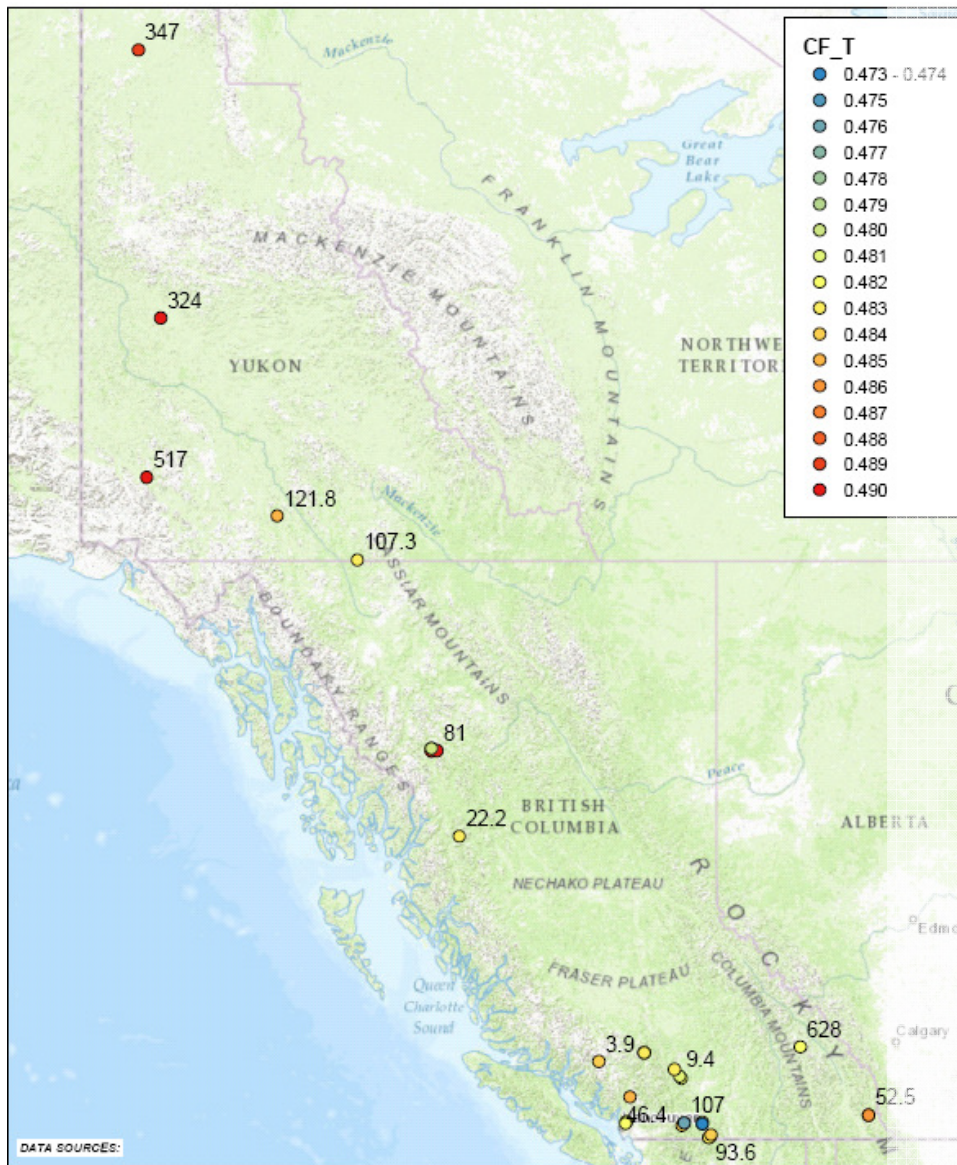
1. Use EC.T, nlf if possible and 2.0%/°C if not, compensated to 25 °C.
   - Promotes consistency across measurements, devices, and sites.
   - Reduces uncertainty due to temperature changes during measurement or CF.T.
2. Calibrate your meters and record calibration. Use CF.T to track calibration.
3. Not all meters are appropriate.
4. Our study suggests that CF.T is 0.483 ±1.6% at 95% confidence for samples tested.
5. If using diluent in std other than stream water, correction should be applied.

*This study suggests that insitu calibration (CF.T) may not be required for every measurement. Calibration to absolute reference standards in the lab, proper device settings (EC.T), user training, and appropriate corrections may result in LOWER error in derived Q and faster measurements in the field.

CF_T
- 0.473 - 0.474
- 0.475
- 0.476
- 0.477
- 0.478
- 0.479
- 0.480
- 0.481
- 0.482
- 0.483
- 0.484
- 0.485
- 0.486
- 0.487
- 0.488
- 0.489
- 0.490

Recommendations
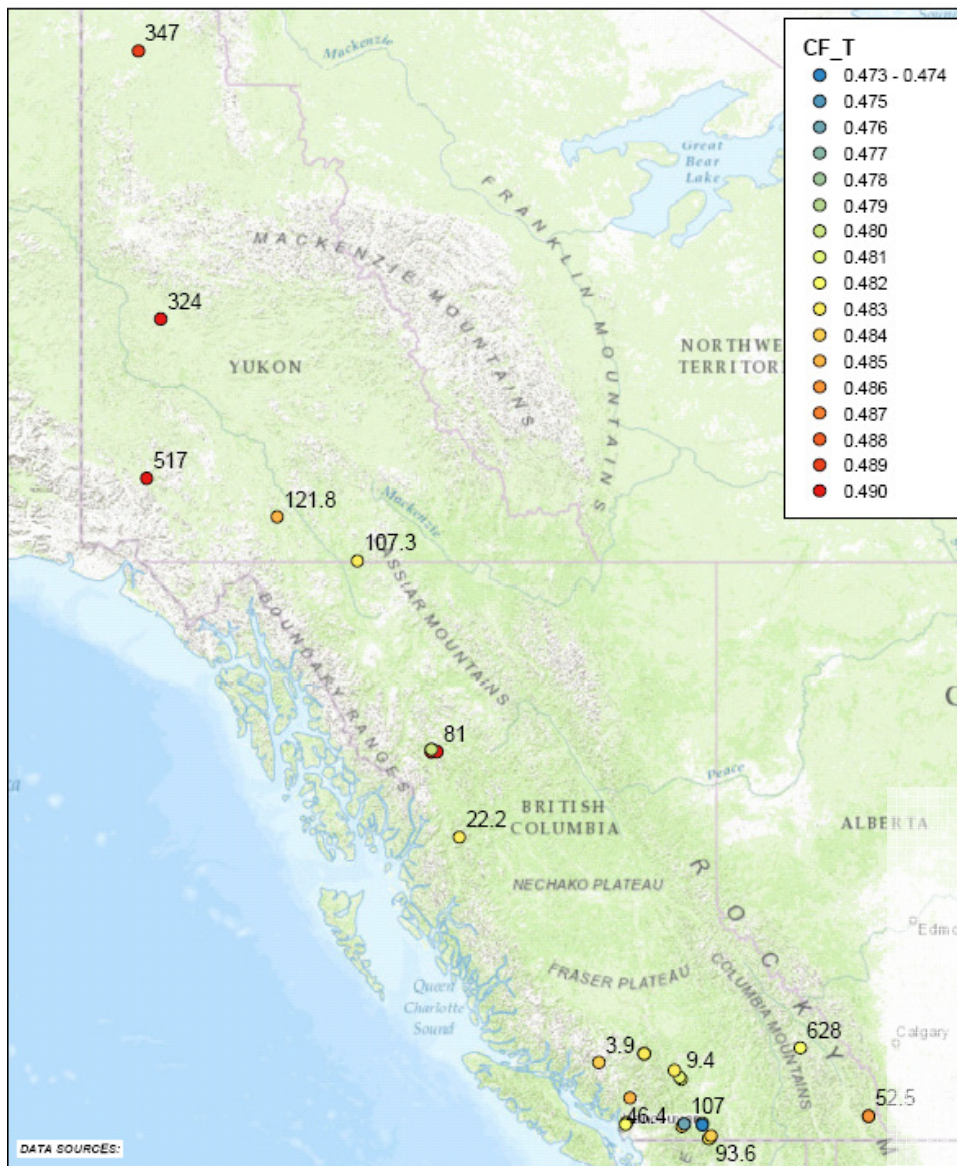
Thank you

Jane Bachman, EDI Yukon
Dave Hutchinson, WSC
Robin Pike, BC MOE
Dan Moore, UBC

Questions?

References:

H. S. Harned and B. B. Owen (1958) Physical Chemistry of Electrolytic Solutions, 3rd edn, Appendix A, 697, Reinhold, New York.

Moore, R.D. G.Richards, (2008) and A.Story "Electrical Conductivity as an Indicator of Water Chemistry and Hydrologic Process" Streamline Watershed Management Bulletin Vol. 11/No. 2 Spring 2008 29, Victoria, B.C.

Moore, R.D. (2005) "Slug Injection Using Salt in Solution" Streamline Watershed Management Bulletin Vol. 8/No. 2 Spring 2005, Victoria, B.C.

Acknowledgements

Class A	7%	Class B	15%	Class C	30%
Glass	1%	Plastic	2%	none	
CF.T in field	1%	site specific CF.T	5%	constant CF.T	10%
pre-weighed bagged salt	1%	off the shelf salt	3%	"bunch of"	20%
two probes (US-DS or LB,Thal)	<30%	one probe	?	"tasts salty"	?
several measurements	$H/\sqrt{2}$	one measurement	H	no measurements	
dosing >1kg/cms	var	dosing <1kg/cms	var		
sensor accuracy 0.05% FS	0.05%	sensor accuracy 1uS/cm	<5%		
baseline, averaging, sloped	var	constant baseline	var		
standard using streamwater	var	standard using distilled water	var		

Plasticware

Notes	V Std (ml)	Calibration Factor — Distilled Water Sample	Value	%Unc.
Stream	0	Vol. Dist. H_2O (l)	1.00	0.4%
	5	Mass NaCl (mg)	1000	1.0%
	10	[NaCl] (mg/l)	1000	1.4%
	15	Vol. Str. H_2O (l)	0.500	0.40%
Using Plastic Syringe		EC.T Std. (µS/cm)@25°C	1994	0.5%
		EC.T Sol. (µS/cm)@25°C	2.200	0.5%
Uncertainty	0.5%		**Total**	**2.3%**

Glassware

Notes	V Std (ml)	Calibration Factor — Distilled Water Sample	Value	%Unc.
Stream	0	Vol. Dist. H_2O (l)	1.00	0.2%
	5	Mass NaCl (mg)	1000	1.0%
	10	[NaCl] (mg/l)	1000	1.2%
	15	Vol. Str. H_2O (l)	0.500	0.04%
Using Glass Pipette		EC.T Std. (µS/cm)@25°C	1994	0.5%
		EC.T Sol. (µS/cm)@25°C	2.200	0.5%
Uncertainty	0.2%		**Total**	**1.4%**

- In B.C. we are in the process of developing a Standard Operating Protocol (SOP) to guide Salt Dilution gauging. We are proposing different Data Classes based on our testing and field experience. Class system recognizes the Accuracy : $$Cost balance.
- For example, tests with Glassware vs Plasticware yields a difference of 0.9% uncertainty in CF.T. Does it justify using Glassware? Depends on requirements.

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Uncertainty Budget

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