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## Feasibility of On-the-go Mapping of Soil Nitrate and Potassium Using Ion-Selective Electrodes

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“The sensing of soil variability is probably the most important step in site-specific management. Without accurate maps, varying application rates are no more appropriate than an average, uniform rate. Obtaining this descriptive information about a field is expensive using today’s techniques.”

(Schueller et al., 1993)

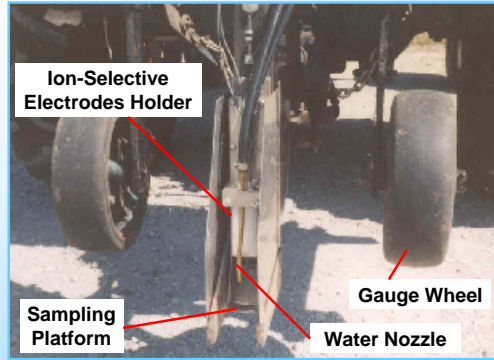
- Soil pH
- Macronutrients **N-P-K**
- Organic matter
- Clay content
- Soil moisture



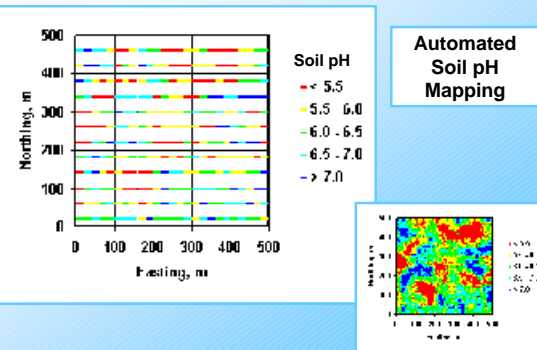
## Automated Soil pH Mapping Systems



## Soil Sampling Mechanism



## Simulated 25 ha Field



## Background

- Soil pH can be mapped on-the-go with an average of 12 s between samples (17 m spacing at 5 km/hr travel speed).
- Previous research has shown 0.4 pH standard measurement error
- Agroecomic analysis has indicated a potential benefit of \$6/ha/year while comparing with 1 ha grid point sampling
- Mapping soil pH only may not be justifiable in many sites



## Objectives

- Verify feasibility of using **polymer membrane combination ion-selective electrodes** to measure residual nitrate and potassium ion activity
- Address the following issues:
  - Stability
  - Calibration
  - Repeatability
  - Accuracy
  - Reliability



## Reference Methods

- Nitrate
  - Colorimetric (Cadmium Reduction)
    - 2:5 Soil Water Solution
- Potassium
  - Atomic Absorption Spectroscopy (AAS)
    - Ammonium Acetate Extraction (Exchangeable)
    - 1:1 Soil/Water Solution (Soluble)



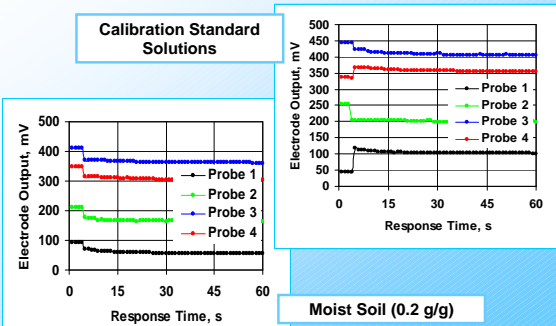
## Tested Measurements Methods

- Using Ion-Selective Electrodes (ISE)
  - Direct Soil Measurements (DSM)
    - Gravimetric Moisture Content 0.2 g/g
  - Soil Solution Measurements (SSM)
    - 1:1 Soil/Water Solution

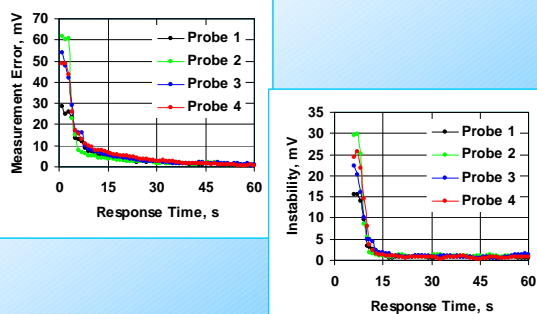
No extraction  
No equilibrium time  
No ionic strength adjustment



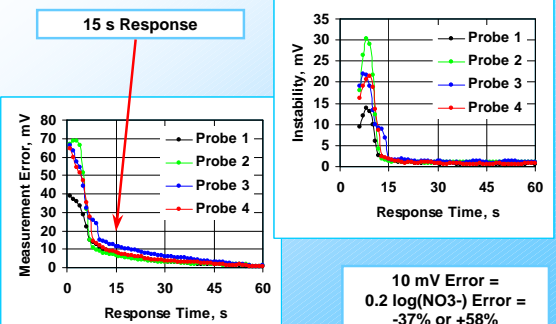
## Ion-selective Electrode Response



## Calibration Standard Solutions



## Moist Soil Samples



10 mV Error =  
0.2 log(NO<sub>3</sub><sup>-</sup>) Error =  
-37% or +58%

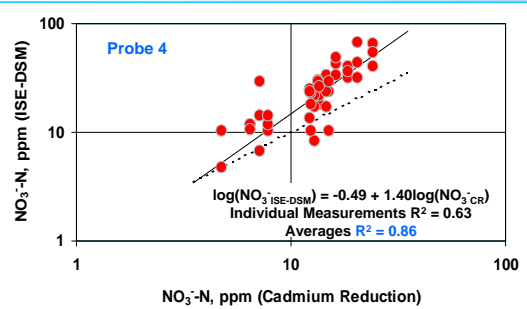


## Repeatability (Random Error)

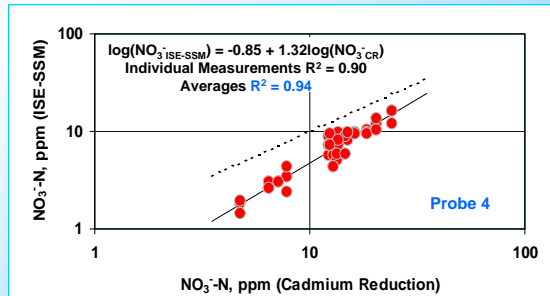
	Probe 1	Probe 2	Probe 3	Probe 4	Probe 1	Probe 2	Probe 3	Probe 4
	ISE-DSM Test				ISE-SSM Test			
Calibration Standards								
MSE, mV	7.04	6.73	6.09	7.90	9.05	9.16	6.05	4.35
MSE, log(NO <sub>3</sub> )	0.19	0.19	0.13	0.16	0.32	0.27	0.13	0.10
Soil Samples								
MSE, mV	0.19	0.19	0.13	0.16	0.32	0.27	0.13	0.10
MSE, log(NO <sub>3</sub> )	0.31	0.31	0.28	0.21	0.14	0.20	0.08	0.07
- MSE, %	51%	51%	47%	39%	27%	37%	18%	15%
+ MSE, %	105%	103%	90%	63%	38%	59%	21%	17%



## Nitrate (ISE-DSM vs. CR)



## Nitrate (ISE-SSM vs. CR)



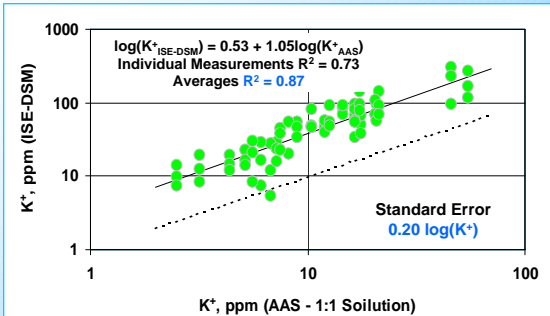
## Nitrate ISEs R<sup>2</sup>

	Probe 1	Probe 2	Probe 3	Probe 4	Probe 1	Probe 2	Probe 3	Probe 4
	ISE-DSM Test				ISE-SSM Test			
Calibration Standards								
Individual R <sup>2</sup>	0.93	0.93	0.97	0.96	0.89	0.92	0.98	0.99
Averages R <sup>2</sup>	0.97	0.97	0.99	0.99	0.96	0.97	1.00	1.00
Soil Samples								
Individual R <sup>2</sup>	0.52	0.38	0.45	0.63	0.54	0.42	0.84	0.90
Averages R <sup>2</sup>	0.77	0.57	0.74	0.86	0.68	0.56	0.92	0.94

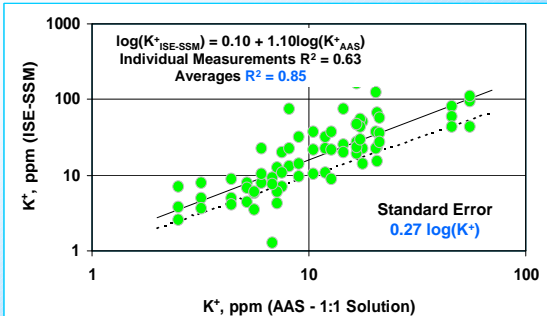
15 Soil Samples X 3 Replications  
 Range of NO<sub>3</sub><sup>-</sup>-N: 5 – 24 ppm



## Potassium (ISE-DSM vs. AAS)



## Potassium (ISE-SSM vs. AAS)





## Potassium ISEs R<sup>2</sup>

Method	ISE-DSM	ISE-SSM	AAS (1:1)	AAS (sat. paste)	AAS (col. displ.)	AAS (0.01 N CaCl <sub>2</sub> )
AAS (NH <sub>4</sub> OAc)	0.37	0.39	0.54	0.49	0.35	0.76
AAS (0.01 N CaCl <sub>2</sub> )	0.78	0.78	0.89	0.89	0.75	
AAS (col. displ.)	0.80	0.76	0.90	0.91		
AAS (sat. paste)	0.88	0.86	0.96			
AAS (1:1)	0.87	0.85				
ISE-SSM	0.85					

24 Soil Samples X 3 Replications  
 Range of K<sup>+</sup> (1:1 Soil/Water Solution): 3 – 55 ppm  
 Range of K<sup>+</sup> (Ammonium Acetate Extraction): 61 – 506 ppm



## Conclusions

- On-the-go mapping of residual nitrate and potassium content is feasible
- Random error of about 0.3 log can be expected when using ISE
- Moisture and sampling depth will affect automated measurements of NO<sub>3</sub><sup>-</sup>-N
- Plant available K<sup>+</sup> itself does not allow for prescribing appropriate fertilizer rate
- Soil-sensor contact is the greatest concern



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