Modeling and Prediction of Soil Water Vapor Sorption Isotherms

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Introduction

- Soil water vapor sorption isotherms (SI) describe the relationship between water activity (a_w) and soil water content along adsorption or desorption paths
- SIs are important for modeling numerous soil biological and physical processes, as well as estimating several soil properties (e.g., specific surface area, clay content)
- Although several theoretical and empirical models exists to characterize SIs for food and engineering products, their applicability to soil SIs is not known
- Measurement of SIs are either time consuming, or require expensive equipment, thus the ability to estimate SIs from readily available soil properties is crucial

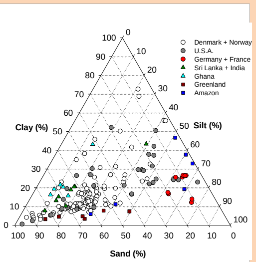
Objectives

- Evaluate the potential of theoretical and empirical isotherm models to accurately characterize measured vapor sorption isotherms for a wide range of soils
- Develop and test regression models for estimating the isotherms from clay content

Methods

- **Investigated soils**

  207 top-soils varying in texture, organic matter (0.2 to 50%), and clay mineralogy (kaolinite, smectite, mixed clays) across five continents



- **Water vapor sorption isotherms**

  Measured with a Vapor sorption analyzer at 25°C

  Water activity range: 0.03 to 0.93 for both adsorption and desorption paths

- **Models**

Theoretical models

i. Guggenheim-Anderson-Boer[1] (GAB)

$$M = M_0 C K a_w / [(1 - K a_w)(1 - K a_w + C K a_w)]$$

ii. Modified BET[2] (MBET)

$$M = a_w (1 - a_w^{\ n}) / [(k_1 + k_2 a_w)(1 - a_w)]$$

iii. Lewicki[3] (LEW)

$$M = F\{[1/(1 - a_w)^G] - [1/(1 + a_w^{\ H})]\}$$

M = soil water content (g g^{-1})

Free model parameters in blue font

Empirical models

(i) Oswin[4] $M = A[(a_w / 1 - a_w)]^B$

(ii) Double Log Polynomial[5](DLP)

$$M = b_0 + b_1\chi + b_2\chi^2 + b_3\chi^3$$

$$\chi = \ln[-\ln(a_w)]$$

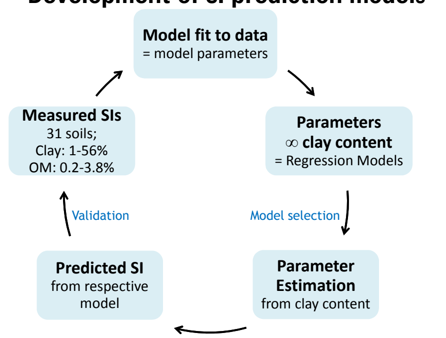
(iii) Peleg[6] $M = K_1 a_w^{\ n_1} + K_2 a_w^{\ n_2}$

Model fitting and performance evaluation

Model parameterization by nonlinear least squares method with measured SIs (adsorption and desorption separately)

Performance evaluation: Mean relative percentage deviation modulus (E) and Akaike Information Criterion (AIC)

Development of SI prediction models



31 selected soils:
Mixed clay mineralogy
OM <4%

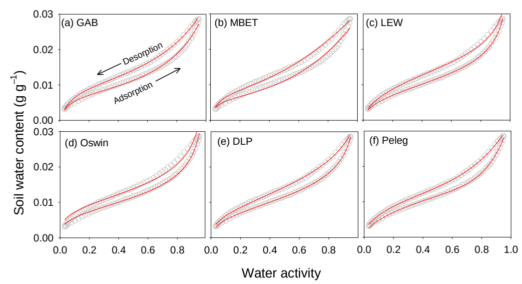
Considerations
Accuracy of model fit
Sorption direction
Relationship with clay
OM contribution

Six soils for validation
Group A (4 soils)
mixed clay mineralogy
Clay: 10-42%, OM: 0.3-3.3%

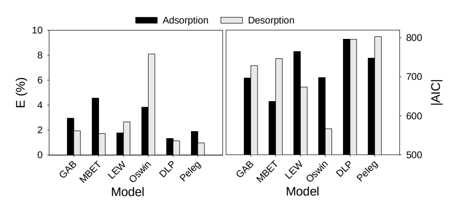
Group B (2 soils)
1 soil /only kaolinite
1 soil /only smectite
Clay: 16,43%, OM: 2.0,1.55%

Results

Model fits to measured SI for a selected soil



Model performance (average of 207 soils)



Best models

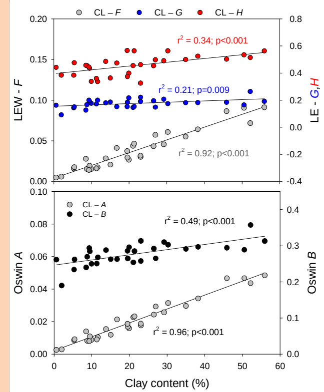
Adsorption
theoretical - **LEW**
empirical- **DLP**

Desorption
theoretical - **MBET**
Empirical - **Peleg**

*Oswin model not suited for desorption isotherms

Relationship between model parameters and clay

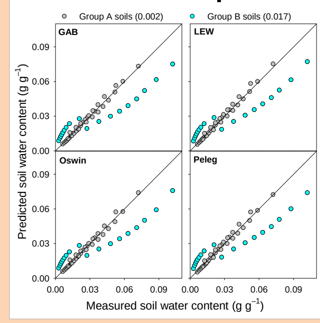
LEW and Oswin model parameters (adsorption data) versus clay content



Regression equations for estimating model parameters (adsorption data)

Model Parameters		Regression equation (x = clay content)	p-value
GAB	M_0	0.00158 + 0.000582x	<0.001
	K	50.2 − 0.56x	0.003
	C	0.657 + 0.0016	0.002
MBET	k_1	7.69x$^{-0.50}$	<0.0001
	k_2	7.69x$^{-0.50}$	<0.0001
	n	3.24 + 0.02x	<0.001
LEW	F	0.0041 + 0.0016x	<0.001
	G	0.155 + 0.00097x	0.009
	H	0.396 + 0.00279x	<0.001
Oswin	A	0.0021 + 0.00085x	<0.001
	B	0.246 − 0.00142x	<0.001
DLP	b_0	0.0023 + 0.00071x	<0.001
	b_1	0.000125 − 0.00042x	<0.001
	b_2	−0.000237 − 0.000013x	0.002
	b_3	−0.000119 − 0.0000048x	0.061
Peleg	K_1	0.00115 + 0.00123x	<0.001
	K_2	0.00110 + 0.00094x	<0.001
	n_1	0.354 + 0.00275x	<0.001
	n_2	5.662 + 0.00283x	0.863

Validation of equations for SI prediction



- Predictions of water content for nine a_w levels (0.10 to 0.90) based on estimated model parameters
- RMSE values provided in bracket after legend
- Poor prediction of two Group B soils due to significantly smaller and larger water contents, respectively, for kaolinitic and smectitic soils
- Number of model parameters (2, 3, 4) have no impact on prediction accuracy

Conclusions

- All tested models, except the Oswin model for desorption data, accurately characterized the sorption isotherms
- Reasonably accurate prediction of SI from clay content but significant errors for kaolinitic or smectitic soils

Acknowledgments

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Reference

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