

# Kalkbedarfsmessung mit Mittelinfrarot-Spektroskopie (MIRS)

Wiss. Düngekalk-Tagung, Fulda, 27./28. März 2023

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Bodenheterogenität aufgrund...

Dikopshof:

7 ha

Löss über Kies und Sand der Mittelterrasse

Pätzold & Welp, 2009

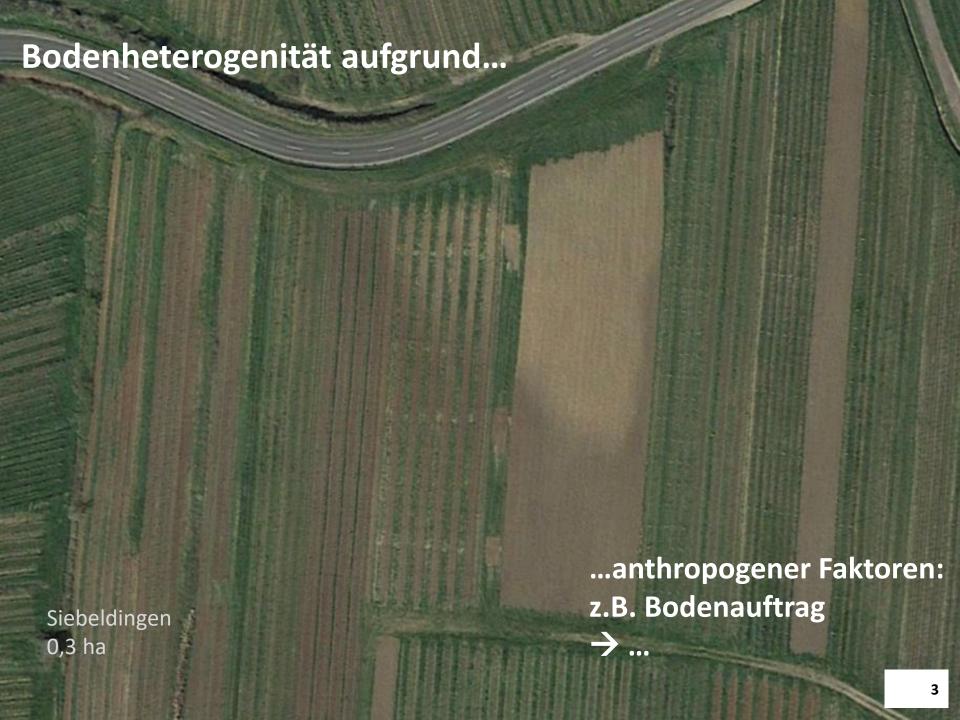
Mertens et al., 2008

...der Geologie:

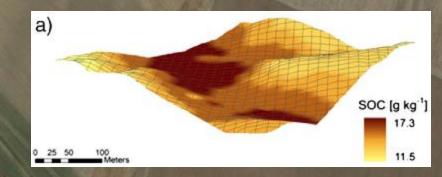
- Schichtung
- **Gesteine/Substrate**
- → Textur, nFK

  Image © 2021 Maxar Technologies
   → Pufferkapazität, pH, Humus...

Dickonshach



# Bodenheterogenität aufgrund...



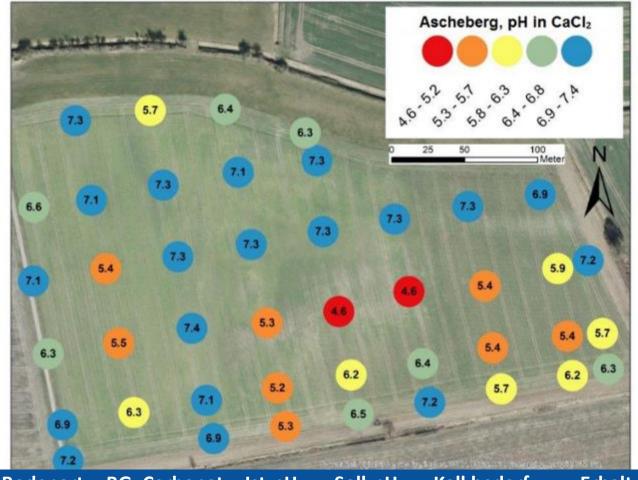
#### Sinsteden:

9 ha, Löss, 5,4 m Reliefunterschied, 1,3 % (0,9 % - 1,5 %) C<sub>org</sub> (n=100)

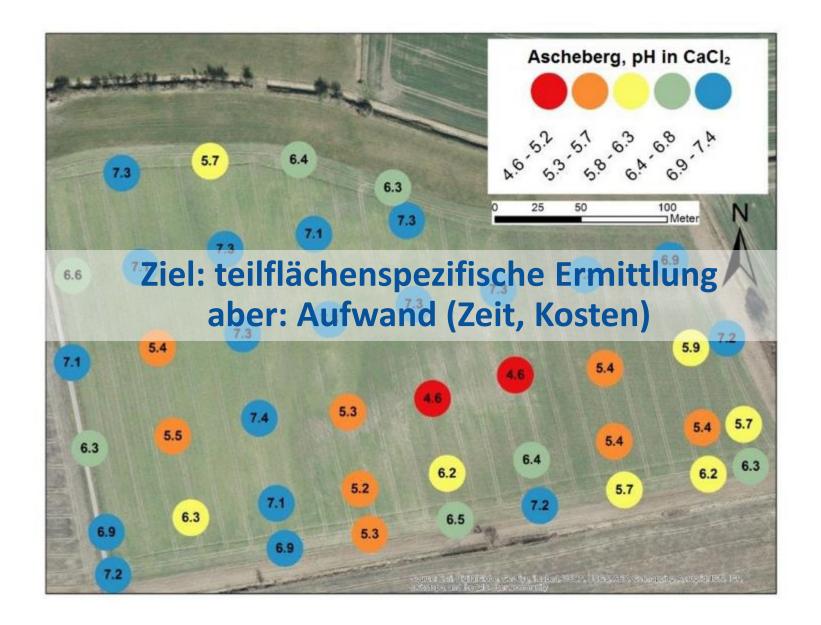
(Hbirkou et al. 2012, Geoderma)

...von Bodenerosion:

→ Humus, pH, Kalk, Nährstoffe...



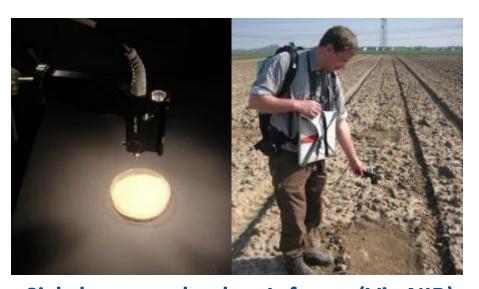
	Bodenart	BG	Carbonat %	Ist-pH	Soll-pH	Kalkbedarf kg CaO/ka	Erhaltungskalkung kg CaO/ha
1	Lu	4	5	7.2	6.8	0	0
2	SI3	2	0	5.5	6.0	2800	1000
3	Ls4	4	0	6.1	6.8	3800	1700
4	Lts	4	0	6.3	6.8	3100	1700
5	Lt3	5	0	6.7	7.0	2800	2000
Mischprobe	Ls3	4	1	7.2	6.8	0	1300







# **IR-Spektroskopie**



Sichtbares und nahes Infrarot (Vis-NIR) 450-2.500 nm



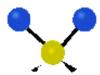


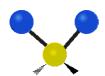
Mittleres Infrarot (MIR) 2.500-25.000 nm

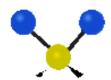


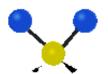
#### Prinzip IR-Spektroskopie

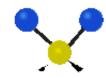
- Anregung einzelner Molekülbindungen durch IR-Strahlung: Absorption
- Ausschläge im Spektrum
- Voraussetzung: Dipolmomente (z.B. in C-H-, O-H- oder N-H-Bindungen in funktionellen Gruppen)
- Molekülgrundschwingung im mittleren Infrarot (2500-25.000 nm)
- Oberton- bzw. Kombinationsschwingungen im nahen Infrarot (400-2500 nm)
- Banden werden nicht direkt interpretiert, sondern mit Hilfe von chemometrischen Verfahren ausgewertet
- (Transmission, Absorption, Reflexion), diffuse Reflexion











Animation: wikipedia





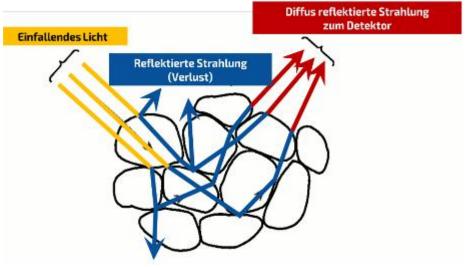
#### Diffuse Reflexions-Spektroskopie

- stark abhängig von Oberflächenbeschaffenheit
  - Feuchte
  - Rauhigkeit
  - (Bedeckung)

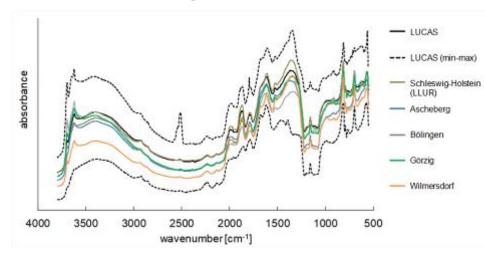
 MIRS noch reine Labormethode, Proben getrocknet und gemahlen, Feldanwendung in Erprobung

wesentlicher Unterschied in der IR-Spektroskopie bei Anwendung an Pflanzen und Boden:

- Pflanzen haben direkte, spezifische Response
- Boden i.a. nicht (spezif. Bande für einzelne funktionelle Gruppen, Verbindungen usw.)



#### **DRIFT-MIRS**



#### → Modellerstellung nötig, meist mit PLSR

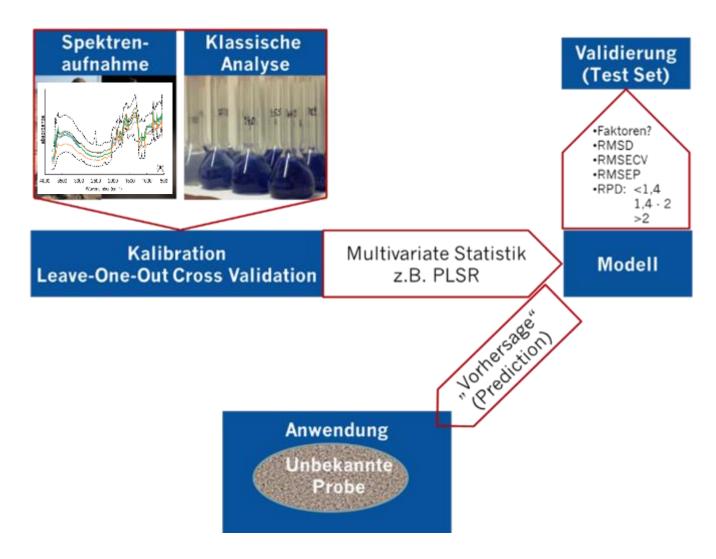
#### d.h. immer:

- Spektren-Aufbereitung und Auswertung mittels <u>multivariater</u> <u>Statistik</u>
- Kalibration anhand von konventionell analysierten Referenzproben: "Ground truth"
- → Methodenauswahl für Ground truth



2200	Kaolinita	SSSAJ Minerals in soil Environments	MIN 39	
9690	Kaolinto	Rumpel et al. 2001	MIR 48	2
3620	characteristic for Kaolin among clay minerals!! surface hydroxyl group	Madejova et al. 2002	MIR 34	r
	Kaplin outer hydroxyl	Madejova et al. 2002 Madejova et al. 2002	MIR 34	
		Madejova et al. 2002 Madejova et al. 2002	MIR 34	
	Kaolin outer hydroxyl clay phases	Bertrand et al., 2002	MIR 10	
	Al-rich montmonilionitie		MIR 34	
		Madejova et al. 2002		
	characteristic for Kaolin (Inner hydroxyl)	Madejova et al. 2002	MIR 34	
	Kaolinite	SSSAJ Minerals in soil Environments		
	Gibbsite	SSSAJ Minerals in soil Environments		
	Structural Fe3+ in clay octahedra	Madejova et al. 2002	MIR 34	Pett&Deccareau, 1990
	Nontronit	SSSAJ Minerals in soil Environments		
	Gibbste	SSSAJ Minerals in soil Environments		
3200	clay phases	Bertrand et al., 2002	MIR 10	
	Allophan / Imologit	SSSAJ Minerals in soil Environments		
	Gibbsite	SSSAJ Minerals in soil Environments		
3300	O-H Stretch	Rumpel et al. 2001		Stavenson, 1994
	C-H vibration of Polysaccharides	Nuopponen et al., 2006	MIR 38	
	Stretching of bound and unbound hydroxyl	Haberbauer et al. 1998	MIR 31	Orlov, 1986
3361	Gibbsite	SSSAJ Minerals in soil Environments		
	Boehmite	SSSAJ Minerals in soil Environments		
	Boehmite	SSSAJ Minerals in soil Environments		
	Aromatic groups	Tatzber etal., 2007	MIR 39	
	Diaspor	SSSAJ Minerals in soil Environments		
2900	Aliphatic C-H stretch	Rumpel et al. 2001	MIR 48	Stovenson, 1994
	C-H stretch	Nuopponen et al., 2006	MIR 38	
	Diaspor	SSSAJ Minerals in soil Environments		
	Aliphatic OH of methyl and methylene	Haberbauer et al. 1998	MIR 31	Orlov, 1986
2850	Aliphats	Tatzber etal., 2007	MIR 39	
	CaCO3	SSSAJ Minerals in soil Environments		
	lime (CaCO3)	Bertrand et al., 2002	MIR 10	
2516	lime (CaCOS)	Bertrand et al., 2002	MIR 10	
2519	CaCO3	SSSAJ Minerals in soil Environments		
	Iron oxide (??) Proben Daniel!!	Rumpel et al. 2001	MIR 48	
	AIOH Bend (significant for clays)	,		Clark et al. 1990
	AIOH Bend (significant for clays)			Clark et al. 1990
2115	Carbohydrate overtone frequency near 1050 cm-1	Rumpel et al. 2001	MIR 48	Stavenson, 1994
400	Quartz does NOT show peaks above 2000 cm-1!!	Janik et al. 1998	MIR 1	Control of the Contro
400	Quartz does NO1 snow peaks above 2000 cm-1!!	Bertrand et al., 2002	MIR 10	
			MIN IU	
	CaCO3	SSSAJ Minerals in soil Environments	Name of	
	acetyl groups of xylan / wood resin	Nuopponen et al., 2006	MIR 38	
	carboxylic-protein aromatic	Janik et al. 1998	MIR 1	
1720	C=O	Bachmann et al., 2007		Cell et al. 1997, Günzler and Böck, 1990
	Carboxylic (shoulder)	Haberbauer et al. 1998		Piccolo et al. 1992 / Stevenson 1982
1720	C=O stretch of COOH	Rumpel et al. 2001	MIR 48	Stavenson, 1994
	aromatic carbonyl	Leifeld, 2005	MIR 27	
1640	C=O from carbox, aldehyd, ketone	Leffeld, 2005	MIR 27	
	Carbonylvib. of Carbox, Aldehyd, Ketone	Tatzber etal., 2007	MIR 39	
	C=O vib of carbox acid	Nuopponen et al., 2006	MIR 38	
1690	C=O stretch of amide groups (amid I)	Rumpel et al. 2001	MIR 48	Stavenson, 1994
1000	C=O of Amide and Ketones, Contrib. of Niriles (R-O-NO) and Nitrates (R-O-NO2)	Tatzber etal., 2007	MIR 39	Distriction, 1994
	Amid I maximum (mainly C=O, weak C-N, N-H) mit Schultern bei 1652, 1682	Haris et al. 1992	MIR 50	
	Carboxylic C=Ovib/ aromatic vibration	Haberbauer et al. 1998		Piccolo et al. 1992 / Stavenson 1982
	Allerboxylic CECVID/ aromatic vibration		MIN 31	Piccolo et al. 1992/ Stevenson 1982
1640	Allophan / Imologit	SSSAJ Minerals in soil Environments		Diameter 1991
1600	Aromatic C=C	Rumpel et al. 2001		Stavenson, 1994
	C=O	Bachmann et al., 2007	MIR 49	Cell et al. 1997, Günzler and Böck, 1990
	aromatic C=C	Leifeld, 2005	MIR 27	Cell et al. 1997, Günzler and Böck, 1990
1640	aromatic C=C phenois polysaccharides, lignin	Leifeld, 2005 Nuopponen et al., 2006	MIR 27 MIR 38	
1640	aromatic C=C	Leifeld, 2005	MIR 27 MIR 38	Cell et al. 1997, Günzler and Böck, 1990 Stavenson, 1994
1640	aromatic C=C phenois polysaccharides, lignin COO symmetric stretch, N-H deformation, C=N stretch (amid II)	Leifeld, 2005 Nuopponen et al., 2006 Rumpel et al. 2001	MIR 27 MIR 38 MIR 48 MIR 50	Stavenson, 1994
1640	aromatic C=C phenois polysaccharides, lignin	Leifeld, 2005 Nuopponen et al., 2006	MIR 27 MIR 38 MIR 48 MIR 50	Stavenson, 1994
1640	aromatic C=C phonois polysaccharides, lignin COO symmetric stretch, N=H deformation, C=N stretch (amid II) carboxylata species (COO-) of protein aromatic (shoulder)	Leifold, 2005 Nuopponen et al., 2006 Rumpel et al. 2001 Harts et al. 1992 Rumpel et al. 2001	MIR 27 MIR 38 MIR 48 MIR 50	
1640	aromatic C-C phenols polysaccharides, lignin CDO symmetric structh, N-H deformation, C-N strutch (amid II) carbonylate species (COC-) of protein aromatic (shouldes) COC-, CNC2, C-C-C	Leifeld, 2005 Nuopponen et al., 2006 Rumpel et al. 2001 Harts et al. 1992 Rumpel et al. 2001 Tatrbor etal., 2007	MIR 27 MIR 38 MIR 48 MIR 50 MIR 48 MIR 39	Staverson, 1994 Staverson, 1994
1540	aromatic C-C phenois polysacchardes, ligrin CDO symmetric structh, N-H determation, C-N strutch (amid II) carboxylais specius (CDO-) of protein aromatic (shoulded) CDO-, CND2, C-C CDO, N-H, C-N amidos	Leifeld, 2005 Nuopponen et al., 2006 Rumpal et al. 2001 Harts et al. 1992 Rumpal et al. 2001 Tabbre etal., 2007 Leifeld, 2005	MIR 27 MIR 38 MIR 48 MIR 50 MIR 48 MIR 39 MIR 27	Stavenson, 1994
1540	aromatic C-C phonolo polysacchardes, lignin COO symmetric structin, N-H deformation, C-N strutch (amid II) carbonylate species (COO-) of profusi aromatic (shouldes) COO-, CNOZ, C-C COO-, N-H, C-N amids Amid II (indicative for 1½-14 eachange), Malrily N-H band	Lafield, 2005 Nuopponen et al., 2006 Rumpell et al. 2001 Harls et al. 1992 Rumpell et al. 2001 Tatzber etal., 2007 Lafield, 2005 Harls et al. 1992	MIR 27 MIR 38 MIR 48 MIR 50 MIR 48 MIR 39 MIR 27 MIR 50	Stavenson, 1994 Stavenson, 1994 White & Roth, 1986
1540	aromatic C-C phenols polysaccharides, lightin COO symmetric streich, N-H deformation, C-N streich (amid II) carboxylasi specius (COO-) of prolein aromatic (should) COO-, CNO2, C-C COO, N-H, C-N amides Amid II (indicative for "H- <sup>2</sup> H exchange), Mainly N-H bend Plant lightin	Latisti, 2005 Nuopponen et al., 2006 Rumpoi et al. 2001 Harts et al. 1992 Rumpoi et al. 2001 Tatzber etal., 2007 Latisti, 2005 Harts et al. 1992 Rumpoi et al. 2001	MIR 27 MIR 38 MIR 48 MIR 50 MIR 48 MIR 39 MIR 27 MIR 50 MIR 48	Stavenson, 1994 Stavenson, 1994 White & Roth, 1986 7
1540	aromatic C-C phenols polyspaccharides, lignin CDO symmetric stretch, N-H deformation, C-N stretch (amid II) carboxylate species (CDO-) of protein aromatic (shoulded) CDO-, CNDC, C-C-C CDO-, N-H, C-N amids Amid II (Indicative for <sup>1</sup> / <sub>2</sub> . <sup>2</sup> H exchange), Mainly N-H bend Plant (ignin amid II Bland (N-H-Y, C-N)	Latial, 2005 Nucppone et al., 2006 Rumpel et al. 2001 Hars et al. 1992 Rumpel et al. 2001 Tatzber etal., 2007 Latial, 2005 Hars et al. 1992 Rumpel et al. 2001 Hars et al. 1992 Rumpel et al. 2001 Haberbauer et al. 1998	MIR 27 MIR 38 MIR 48 MIR 50 MIR 48 MIR 39 MIR 27 MIR 50 MIR 48 MIR 31	Stavenson, 1994 Stavenson, 1994 White & Roth, 1986 7 Hesse et al. 1995
1540	aromatic C-C phanols polysaccharides, lignin COO symmetric strotch, N-H determation, C-N stretch (amid II) carbonytale species (COO-) of protein aromatic (shoulder) COO-, CNOZ, C-C COO, N-H, C-N amidss Amid II (noticative for "H-2" H exchange), Mainly N-H bend Plant Ilgnin amid II Band (N-H; C-N) amids (Band (N-H; C-N) amids (C N) of the control of	Laffaid, 2005 Nucpponen et al., 2006 Rumpel et al. 2001 Hartis et al. 1992 Rumpel et al. 2001 Tatriber et al., 2007 Laffaid, 2007 Laffaid, 2007 Hartis et al. 1992 Rumpel et al. 2001 Habristoauer et al. 1998 Habristoauer et al. 1998	MIR 27 MIR 38 MIR 48 MIR 50 MIR 48 MIR 39 MIR 27 MIR 50 MIR 48 MIR 31 MIR 31	Stavenson, 1994 Stavenson, 1994 White & Roth, 1986 7
1540	aromatic C-C phenols polyspacchardes, lignin CDO symmetric stretch, N-H deformation, C-N stretch (amid II) carboxylate species (CDO-) of protein aromatic (shoulded) CDO-, CNDC, C-C-C CDO-, N-H, C-N amids Amid II (Indicative for <sup>1</sup> / <sub>2</sub> . <sup>2</sup> H exchange), Mainly N-H bend Plant lignin amid II Bland (N-H; C-N) aromatic CO Vibration gualasty (lignin to otherwood	Laffeld, 2005 Nucpponen et al., 2006 Rumpel et al. 2001 Harris et al. 1992 Rumpel et al. 2001 Tabbre et al., 2007 Laffeld, 2005 Harris et al. 1992 Rumpel et al. 2001 Harris et al. 1992 Rumpel et al. 2001 Habortzauer et al. 1998 Habortzauer et al. 1998 Nucpponen et al., 2006	MIR 27 MIR 38 MIR 48 MIR 50 MIR 48 MIR 39 MIR 27 MIR 50 MIR 48 MIR 31 MIR 31 MIR 31	Stavenson, 1994 Stavenson, 1994 White & Roth, 1986 7 Hesse et al. 1995
1640 1517 1550	aromatic C-C phorols polysaccharides, ligrin COO symmetric streich, N-H determation, C-N streich (amid II) carbonylate species (COO-O) protein aromatic (shoulder) COO-, CNOZ, C-C COO, N-H, C-N amidis Amid II (indicative for "H-"H exchange), Mainly N-H bend Plant Ilgrin amid II Band (N-H; C-N) samatic CO Withoution gualasty (lignin of softwood aromatic CO Withoution gualasty (lignin of softwood	Laffait, 2005 Nucpponen et al., 2006 Rumpel et al. 2001 Haris et al. 1992 Rumpel et al. 2001 Tatrise et al. 2001 Tatrise et al., 2007 Laffait, 2007 Laffait, 2007 Laffait, 2007 Haris et al. 1992 Rumpel et al. 2001 Habertosuer et al. 1998 Nucpponen et al., 2006 Laffait, 2005	MIR 27 MIR 38 MIR 48 MIR 50 MIR 48 MIR 39 MIR 27 MIR 50 MIR 31 MIR 31 MIR 31 MIR 31 MIR 33 MIR 37	Stavenson, 1994 Stavenson, 1994 White & Roth, 1986 7 Hesse et al. 1995 Ancoena et al. 1995 / Niemayer et al. 1992
1640 1517 1550	aromatic C-C phenols polyspaccharides, lignin COO symmetric stretch, N-H deformation, C-N stretch (amid II) carboxylate spaces (COO-) of protein aromatic (shoulded) COO, CNOZ, C-C COO, N-H, C-N amides Amid II (indicative to *1-2* H exchange), Mainly N-H bend Plant lignin amid II Band (Pi-H; C-N) aromatic CC Vibration gualasy) (lignin to orthwood aromatic carbony) aromatic C-C stretch	Lafisti, 2005 Nucpponen et al., 2006 Rumpaol et al. 2001 Tarbber et al., 2007 Lafisti, 2005 Rumpaol et al. 2001 Haris et al. 1992 Rumpaol et al. 2001 Haris et al. 1998 Haris et al. 1998 Haris et al. 1998 Lafisti, 2005 Lafisti, 2005 Lafisti, 2005 Lafisti, 2005	MIR 27 MIR 38 MIR 48 MIR 50 MIR 27 MIR 50 MIR 48 MIR 31 MIR 31 MIR 31 MIR 38 MIR 27 MIR 27	Stavenson, 1994 Stavenson, 1994 White & Roth, 1986 7 Hesse et al. 1995
1640 1517 1550	aromatic C-C phonols polyspocharides, lignin COO symmetric strotch, NH deformation, C-N stretch (amid II) cattorpolis polyspocharides (COO-) of profesin aromatic (shouldar) COO-, CNO2, C-C COO-, N-H, C-N amidiss Amid II (noticative for "H-2" aschange), Mainly N-H bend Plant Iignin amid II Band (N-H; C-N) amidiss (Band (N-H; C-N) amonatic CO Vibration guilassy) (ignin of softwood aromatic Cot Vibration guilassy) (ignin of softwood aromatic carried- imme (CaOCO)	Laffeld, 2005 Nucpponen of at., 2006 Rumpaol of at. 2001 Harts of at. 1992 Rumpaol of at. 2001 Tathre of at., 2007 Laffeld, 2007 Laffeld, 2007 Laffeld, 2007 Harbor of at., 2007 Harbortosus of at., 1998 Hasbortosus of at., 1998 Nucpponen of at., 2006 Laffeld, 2005 Senfrand of at., 2005	MIR 27 MIR 38 MIR 48 MIR 50 MIR 48 MIR 39 MIR 27 MIR 50 MIR 31 MIR 31 MIR 31 MIR 31 MIR 33 MIR 37	Stavenson, 1994 Stavenson, 1994 White & Roth, 1986 7 Hesse et al. 1995 Ancoena et al. 1995 / Niemayer et al. 1992
1517 1517 1550	aromatic C-C phenols polyspaccharides, lignin CDO symmetric stretch, N-H deformation, C-N stretch (amid II) curboxylate spacies (CDO-) of protein aromatic (shoulded) CDO, CNDC, C-C CDO, N-H, C-N amides Amid II (indication to ft <sup>-2</sup> H exchange), Mainly N-H bend Plant lignin amid II Band (N-H; C-N) aromatic CC Vibration guilassyl (lignin of ortherod aromatic carbony) aromatic C-C stretch lime (CBCOS) Aragentia (COTronbornbia CBCOS)	Laffeld, 2005 Nucpponen et al., 2006 Rumpel et al. 2001 Rumpel et al. 2001 Rumpel et al. 2001 Harris et al. 1992 Rumpel et al. 2001 Tabber et al., 2007 Laffeld, 2005 Harris et al. 1992 Rumpel et al. 2001 Harbortbauer et al. 1998 Nucpponen et al. 2006 Laffeld, 2005 Borffard et al., 2005 Borffard et al., 2005 Borffard et al., 2005 Borffard et al., 2005 SSSAJ Minerals in soil Environments	MIR 27 MIR 38 MIR 48 MIR 50 MIR 27 MIR 50 MIR 48 MIR 31 MIR 31 MIR 38 MIR 27 MIR 27 MIR 10	Stavenson, 1994 Stavenson, 1994 White & Roth, 1986 7 Hosse et al. 1995 / Niemayer et al. 1992 Stavenson, 1994
1517 1517 1550	aromatic C-C phonois polysaccharides, ligriin COO symmetric stroich, NH delomation, C-N stretch (amid II) catbonylate species (COO-) of protein aromatic (phonoides) COO-, CNO-C, C-C COO-, N-H, C-N amidiss Amid II (noticative for "H-2"H) amid II Band (N-H; C-H) amid II Band (N-H; C-H) amid II Band (N-H; C-H) amomatic CO Vibration guilassyl (pinin of softwood aromatic Co Stratich Imme (CaCOS) Aragoniae (Critichonomibic CaCOS) Aragoniae (Critichonomibic CaCOS) Aragoniae (Critichonomibic CaCOS)	Lafleti, 2005 Nucpponen et al., 2006 Rumpal et al. 2001 Rumpal et al. 2001 Harris et al. 1992 Rumpal et al. 2001 Tatrber et al., 2007 Lafleti, 2005 Harris et al. 1992 Rumpal et al. 2001 Harris et al. 1992 Harris et al. 1993 Haberbaser et al. 1998 Haberbaser et al. 1998 Lafleti, 2005 Lafleti, 2005 Lafleti, 2005 SISAA Minerals in soil Environments Rumpal et al., 2002	MIR 27 MIR 38 MIR 48 MIR 48 MIR 39 MIR 27 MIR 50 MIR 48 MIR 31 MIR 31 MIR 31 MIR 31 MIR 31 MIR 31	Stavenson, 1994 Stavenson, 1994 White & Roth, 1986 7 Hesse et al. 1995 Ancoena et al. 1995 / Niemayer et al. 1992
1517 1517 1550	aromatic C-C phenols polyspocharides, lignin COO symmetric streich, N-H deformation, C-N streich (amid II) controlypida spocies (COO-) of protein aromatic (shoulded) COO, CNOZ, C-C COO, N-H, C-N amides Amid II (Indicatate for <sup>1</sup> / <sub>2</sub> <sup>2</sup> H aschange), Mainy N-H bend Plant lignin amid II Band (Ph-H; C-N) aromatic CO Vibration gualasty (lignin of sorthwood aromatic carbony) aromatic C-C streich lime (CGOC9) Aliphatic C-H C-H Bond	Lafisti, 2005 Nucpponen et al., 2006 Rumpaol et al. 2001 Tabber et al., 2007 Lafisti, 2005 Rumpaol et al. 2001 Hariss et al. 1992 Rumpaol et al. 2001 Haborteaure et al. 1998 Nucpponen et al., 2006 Lafisti, 2005 Lafisti, 2005 Berfrand et al., 2006 SSSAJ Minerals in soil Environments Rumpaol et al. 2006 Rumpaol et al. 2006 Rumpaol et al. 2006	MIR 27 MIR 38 MIR 48 MIR 39 MIR 27 MIR 31 MIR 31 MIR 31 MIR 31 MIR 32 MIR 27 MIR 10	Stavenson, 1994 Stavenson, 1994 White & Roth, 1986 7 Hosse et al. 1995 / Niemayer et al. 1992 Stavenson, 1994
1517 1517 1550	aromatic C-C phonois polysaccharides, ligriin COO symmetric stroich, NH delomation, C-N stretch (amid II) catbonylate species (COO-) of protein aromatic (phonoides) COO-, CNO-C, C-C COO-, N-H, C-N amidiss Amid II (noticative for "H-2"H) amid II Band (N-H; C-H) amid II Band (N-H; C-H) amid II Band (N-H; C-H) amomatic CO Vibration guilassyl (pinin of softwood aromatic Co Stratich Imme (CaCOS) Aragoniae (Critichonomibic CaCOS) Aragoniae (Critichonomibic CaCOS) Aragoniae (Critichonomibic CaCOS)	Lafleti, 2005 Nucpponen et al., 2006 Rumpal et al. 2001 Rumpal et al. 2001 Harris et al. 1992 Rumpal et al. 2001 Tatrber et al., 2007 Lafleti, 2005 Harris et al. 1992 Rumpal et al. 2001 Harris et al. 1992 Harris et al. 1993 Haberbaser et al. 1998 Haberbaser et al. 1998 Lafleti, 2005 Lafleti, 2005 Lafleti, 2005 SISAA Minerals in soil Environments Rumpal et al., 2002	MIR 27 MIR 38 MIR 48 MIR 48 MIR 39 MIR 27 MIR 50 MIR 48 MIR 31 MIR 31 MIR 31 MIR 31 MIR 31 MIR 31	Stavenson, 1994 Stavenson, 1994 White & Roth, 1986 7 Hosse et al. 1995 / Niemayer et al. 1992 Stavenson, 1994
1517 1517 1550	aromatic C-C phenols polyspocharides, lignin COO symmetric streich, N-H deformation, C-N streich (amid II) controlypida spocies (COO-) of protein aromatic (shoulded) COO, CNOZ, C-C COO, N-H, C-N amides Amid II (Indicatate for <sup>1</sup> / <sub>2</sub> <sup>2</sup> H aschange), Mainy N-H bend Plant lignin amid II Band (Ph-H; C-N) aromatic CO Vibration gualasty (lignin of sorthwood aromatic carbony) aromatic C-C streich lime (CGOC9) Aliphatic C-H C-H Bond	Lafisti, 2005 Nucpponen et al., 2006 Rumpaol et al. 2001 Tabber et al., 2007 Lafisti, 2005 Rumpaol et al. 2001 Hariss et al. 1992 Rumpaol et al. 2001 Haborteaure et al. 1998 Nucpponen et al., 2006 Lafisti, 2005 Lafisti, 2005 Berfrand et al., 2006 SSSAJ Minerals in soil Environments Rumpaol et al. 2006 Rumpaol et al. 2006 Rumpaol et al. 2006	MIR 27 MIR 38 MIR 48 MIR 50 MIR 39 MIR 27 MIR 50 MIR 31 MIR 31 MIR 38 MIR 27 MIR 10 MIR 38 MIR 38	Stavenson, 1994 Stavenson, 1994 White & Roth, 1986 7 Hosse et al. 1995 Ancona et al. 1995 / Niemayer et al. 1992 Stavenson, 1994 Hesse et al. 1995
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#### Verfahrensablauf







### Bestimmung von Humus, Ton und pH mit MIRS

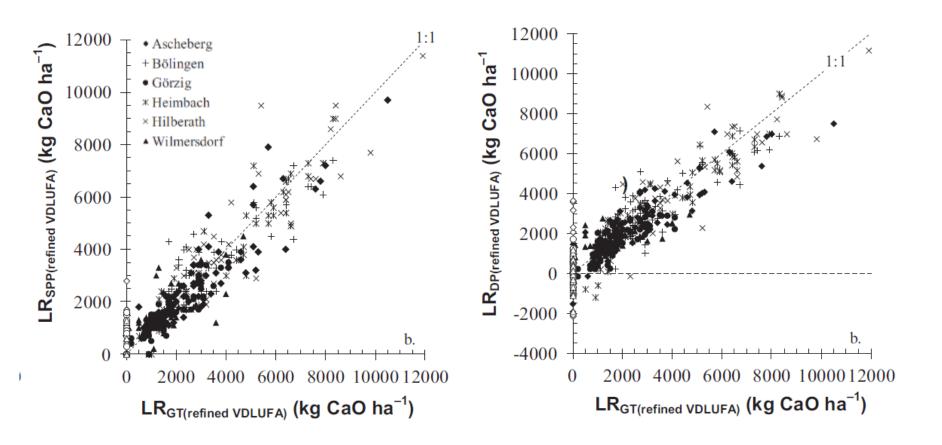
Location n		SOM				Clay				pH (CaCl <sub>2</sub> )			
		(g kg <sup>-1</sup> )			(%)								
		R <sup>2</sup>	RMSECV	RMSEP	RPD	R <sup>2</sup>	RMSECV	RMSEP	RPD	R <sup>2</sup>	RMSECV	RMSEP	RPD
		Leave-one-out cross validation											
Aschehera	115	0.93	24	_	3 65	0.98	17	_	6.74	0.90	0.25	_	3 23
							Test-set v	alidation					
Ascheberg	43	0.92	-	2.7	3.50	0.98	-	2.0	6.72	0.93	-	0.22	3.70
Bölingen	21	0.97	-	0.9	5.38	0.98	-	1.4	7.17	0.63	-	0.21	1.73
Görzig	33	0.79	_	2.2	2.19	0.67	_	1.0	1.75	0.88	_	0.14	2.84

Leenen et al. 2019, JPNSS



- → korrekte Klassenzuordnung möglich
- → Kalkbedarf aus Einzelparametern ableitbar

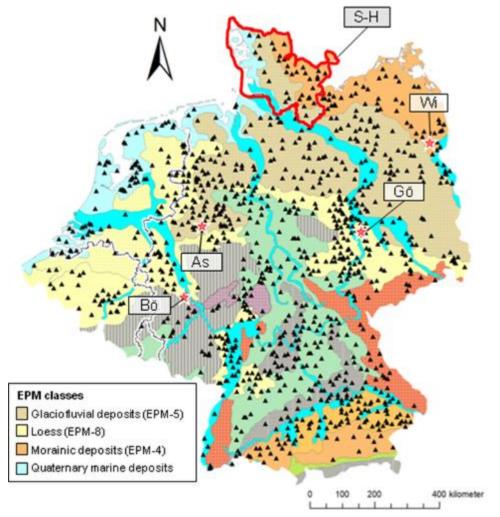
## Kalkbedarf über Einzelparameter und direkt



#### Kalkbedarf stufenlos



# Ziel: Lokale Anwendung standortunabhängiger Vorhersagemodelle

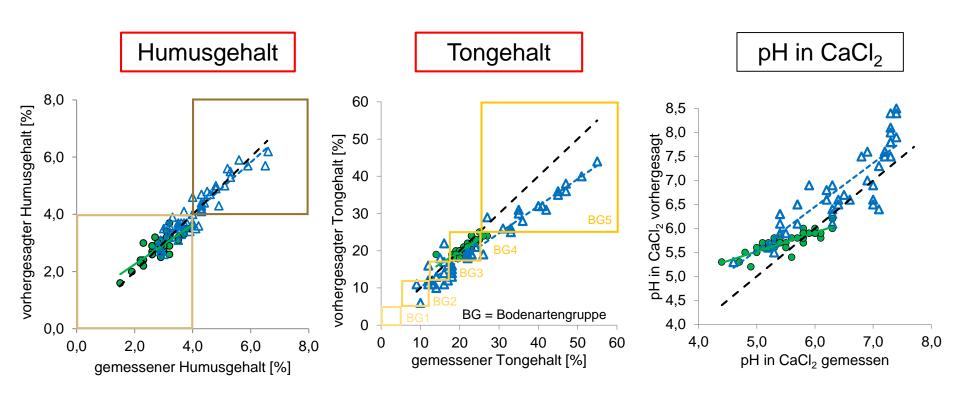


1013 Ackerbodenproben des europäischen JRC-LUCAS Topsoil Surveys (▲)

	R²	RPIQ	RMSE <sub>cv</sub>
Humus [%]	0,89	3,5	0,39
Ton [%]	0,95	6,7	2,4
pH in CaCl <sub>2</sub>	0,84	4,0	0,35

**PLSR-LOOCV** 

#### Vorhersagen mit standortunabhängigen Modellen



▲ Ascheberg ● Hilberath



## Lokale Anwendung des Datenbank-Modells

	Ascheberg	Bölingen	Görzig	Wilmersdorf					
	n = 115	n = 71	n = 110	n = 217/59 <sup>(1)</sup>					
Ton [%]									
R <sup>2</sup>	0.91	0.89	<del>0.36</del>	0.88					
RMSEP [%]	4.5	3.5	<del>1.2</del>	1.2					
Bias [%]	1.8	0.5	<del>-0.1</del>	-0.6					
RPIQ	2.9	3.4	<del>0.8<sup>(2)</sup></del>	3.3 <sup>(2)</sup>					
Corg [g/kg]									
R <sup>2</sup>	0.86	0.78	<del>0.61</del>	0.72					
RMSEP [g kg <sup>-1</sup> ]	1.8	1.5	<del>2.0</del>	1.7					
Bias [g kg <sup>-1</sup> ]	0.0	1.1	<del>1.6</del>	0.0					
RPIQ	3.3	1.9	<del>1.0<sup>(2)</sup></del>	1.4					
		pH in CaCl <sub>2</sub>							
R <sup>2</sup>	0.83	0.62	0.82	0.85					
RMSEP	0.49	0.28	0.20	0.47					
Bias	-0.36	-0.17	0.06	-0.14					
RPIQ	3.2	1.0	3.3	4.5					

<sup>(1)</sup>sample subset: sand, silt, and clay content were only analyzed for 59 of the 217 topsoil samples from Wilmersdorf (2)fields with unsuccessful prediction of soil property associated with low within field heterogeneity



# **Ausblick: Feldanwendung**

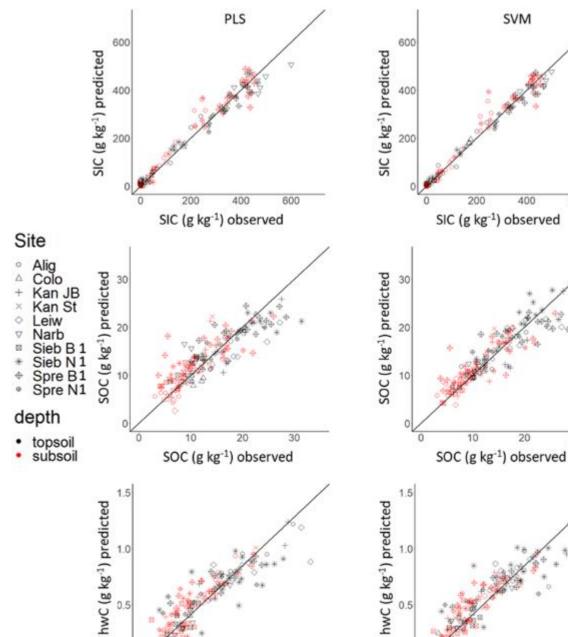








# C-Bestimmung mit pMIRS-SVM



1.5

1.0

0.5

hwC (g kg-1) observed

30

1.5

1.0

0.5

hwC (g kg-1) observed

Wehrle et al. 2022, Biosyst. Engin.



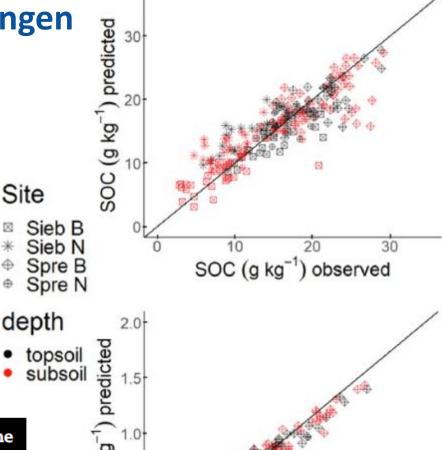
# Ausblick: Spektrale Veränderungen im Laufe der Zeit?

- $\rightarrow$  C<sub>org</sub>, C<sub>hwl</sub>
- → portable MIRS

Wehrle et al. 2022

Table 7 — Results of pMIRS SVM prediction models for the follow-up sampling dataset 2 (n = 243) of top and subsoils in four vineyards for SOC and hwC.

Property (g kg <sup>-1</sup> )	RMSE	$R^2$	RPIQ
SOC	2.98	0.75	3.03
hwC	0.08	0.93	4.79



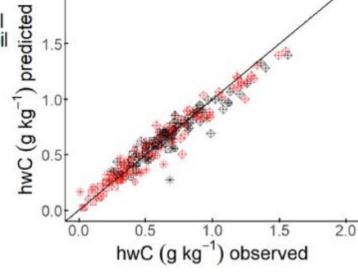
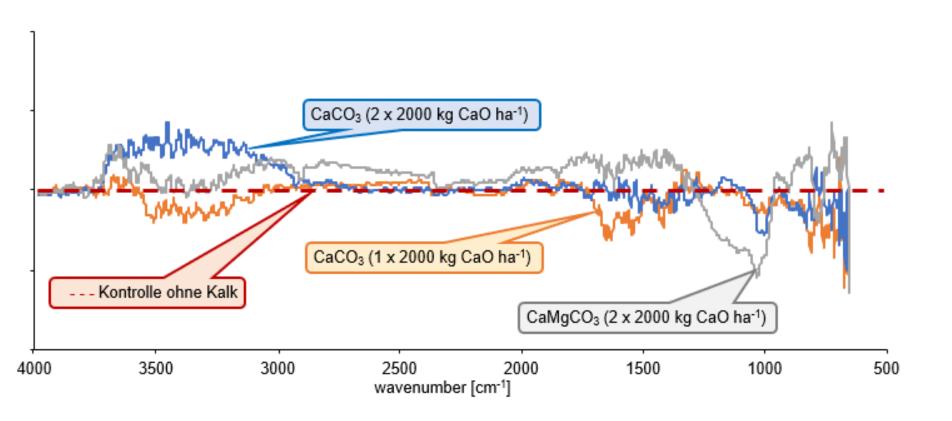






Fig. 6 — Predicted and observed values (n = 243) and 1:1-line of pMIRS SVM models for the monitoring of SOC and hwC for top and subsoils of four vineyards (Dataset 2).

## Spektrale Veränderungen nach Kalkung?





#### Kalkversuch Hilberath

#### Versuchsfrage:

 Veränderung des Boden-pH-Wertes und humuschemischer Parameter auf einer heterogenen Fläche (sandiglehmig bis lehmig-tonig) sensorisch verfolgbar?





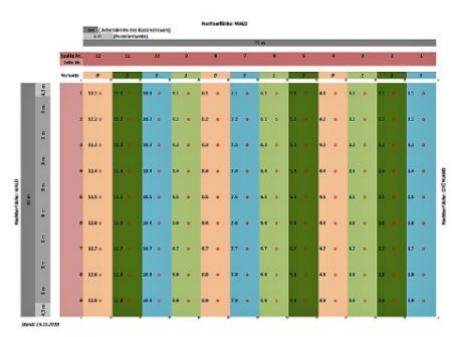
#### Varianten:

- 0 keine Kalkung
- 1 Kohlensaurer Kalk (2000 kg CaO/ha)
- 2 Kohlensaurer Kalk (4000 kg CaO/ha)
- 3 Kohlensaurer Magnesiumkalk (2000 kg CaO/ha]



# **Ausblick:**

### Modelle nach Kalkung valide? → Kalkversuch Hilberath







	рН	S	U	Т	Corg	C/N
min	4.18	22	30	12	1.6	10
max	4.85	49	49	25	4.9	16
MW	4.51	38	41	19	3.2	13
Sd	0.14	7.1	4.9	2.8	0.4	1.2

Bodenarten: SI4, Slu, Ls4, Ls3, Ls2, Lt2 Kalkbedarf der Versuchsfläche (0,6 ha)

- 600 5700 kg CaO/ha (n=108)
- Mittelwert (n=108): 1688 kg CaO/ha





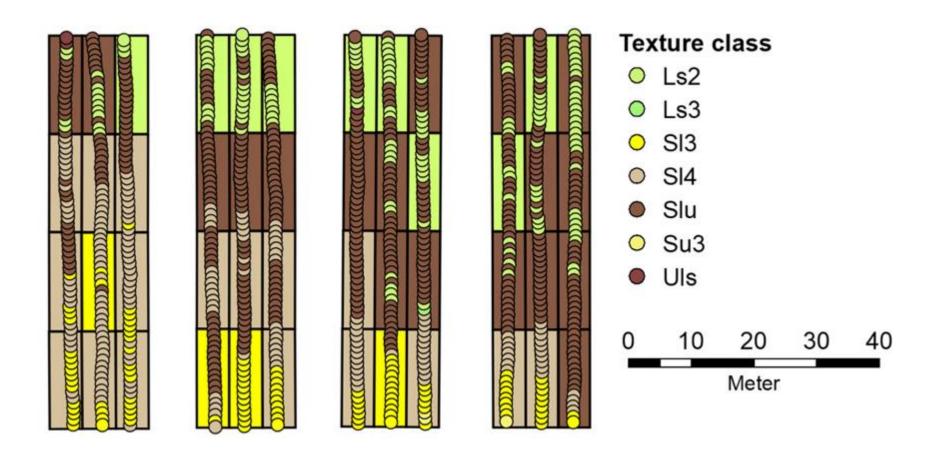
## **Perspektive: Sensor-Fusion**







### Flächenhafte Texturdaten über Gamma-Spektrometrie





Standort Hergarten Pätzold et al. 2020, Soil Syst.

#### Kalkbedarf über MIRS? → Fazit

- (noch) keine Routinemethode
- Modelle für komplexe Parameter grundsätzlich möglich
- nach Modellerstellung (Kalibrierung) und Prüfung (Validierung) keine Kosten für Verbrauchsmaterial, schnell, → Teilflächen
- Präzision noch verbesserungsbedürftig
- Perspektiven:
  - Datenbanken
  - maschinelles Lernen
  - Feldanwendung
  - Sensor Fusion



