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Real-time monitoring of nitrate in soils as a key for optimization of agricultural productivity and prevention of groundwater pollution

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Section - S1 Vadose Zone Monitoring System:

The need for real-time information on the quality of percolating water in the unsaturated zone led to the development of a VMS. The VMS is designed to provide continuous in-situ measurements of the hydraulic and chemical properties of the entire vadose zone, from land surface to the water table. The (VMS) is composed of a flexible sleeve made of thin polyvinyl chloride (PVC) line, hosting several porewater sampling ports (VSPs) made of a customized suction cups. The VMS is installed in the soil at a slanted borehole and the VSPs are facing upward in such way that an undisturbed sediment column is formed between the land surface to the VMS ports. A high-density filling material is poured into the PVC sleeve, which causes an expansion of the sleeve inside the borehole and the attachment of the VSPs to the borehole walls. A filling agent in the form of fine and unconsolidated sand pillow is used in order to achieve hydraulic conductivity between the soil coarse sediments and the VMS ports. Frequent sampling of porewater from the VMS ports is enabled through a series of small diameter access pipes and control valves. In order to extract porewater samples from soil, low pressure (vacuum) is applied to the VSP, and the gained sample is then gathered in a special accumulation chamber. The samples can be then transferred to surface level by introducing high-pressure nitrogen gas on the VSP to push the sample to surface level. The VMS installation procedure can be found in previous publications (Rimon et al., 2007, 2011; Dahan et al., 2009).

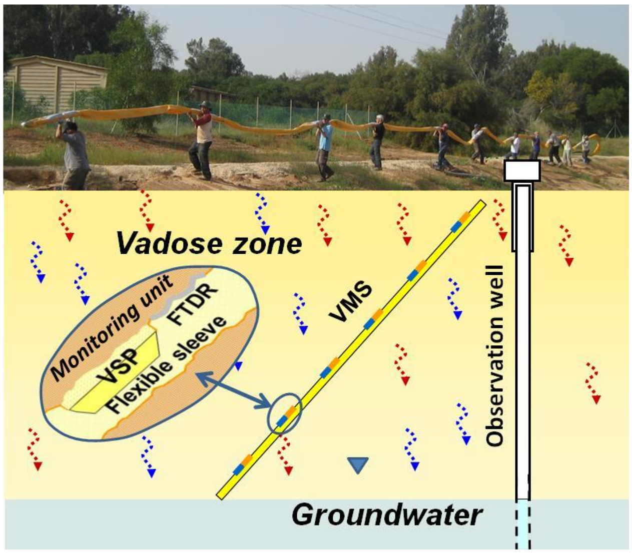


Figure S1 - The Vadose Zone Monitoring System as it is carried prior to its installation (top), and a general layout of the VMS systems when placed in the soil (bottom).

S1.1 Installation

The monitoring systems are installed in uncased, small-diameter (~0.15 m), slanted boreholes (55° to the horizon). The FTDR probes and VSPs are aligned along the borehole's upper side wall facing the undisturbed sediment column, which extends from the probe location on the borehole wall to land surface. Immediately after inserting the sleeve into the borehole, it is filled with non-shrinking cement grout. The hydrostatic pressure generated by the filling material within the sleeve causes its expansion and ensures that it fills the entire void of the borehole. As a result, the FTDR probes and VSPs are pushed against the borehole's upper side wall with sufficient force to achieve good contact with the sediment. The combination of flexible sleeve with high-density filling material ensures tight sealing of the borehole void and elimination of potential preferential flow and cross-contamination along the sleeve.

S1.2 VSP

The VSP enables frequent sampling of the vadose zone pore water. The physical mechanism underlying the sampling is based on creating hydraulic continuity between the sediment pore water and the sampling cell, similar to a standard tensiometer or suction cups. Hydraulic continuity between the VSP and the rough sediments on the borehole sidewall is achieved through an unconsolidated agent made of flexible quartz powder. The VSP is operated through a set of small-diameter access pipes (i.d. (<1 mm) reaching a control panel on the surface. Once hydraulic continuity between the sediment pore water and the VSP is achieved, low pressure (vacuum) is applied to the sampling cell to draw the sediment pore water into the sampling cell. The water sample is then retrieved to land surface using pressurized gas (N2). Finally, the sampling efficiency, as expressed by the water flux into the sampling cell, is controlled by the sediment-water content. The VSP is a patented technology (Deep vadose zone sampling ports, US #12/222,069; EP #07706061.4; IL #193126).

Section - S2 Selected agricultural sites:

The open crop field and citrus orchards sites are located next to Nir Galim village, Israel (34°41`13`` E long; 31°49`42`` N Lat). Over the past 10 years, the crop field was used for rainfed winter cereal and summer water-melon crops, fertilized mainly with dairy slurry manure. In 2015 the field was converted to irrigated Jojoba crops. The citrus orchard is irrigated during the summer season in addition to the rainfalls during the winter. Further information on these sites may be found at Turkeltaub et al., (2014). Two additional study sites were greenhouses used for rotating vegetable crops. One site practice organic regime that is based on the application of organic compost as the main fertilizer, while the other applied conventional fertigation methods. Detailed Description of the VMS at each site was previously presented at Dahan et al., (2014); Turkeltaub et al., (2014, 2015a, 2016).

Table - S3- Depth of the sampling unit on the VMS sleeve, installed at the study sites.

	Depth to sampling unit center [m]						
Organic greenhouse	1.3	2.3	3.3	5.3	8.3	10.5	13.3
Conventional greenhouse	1	2	3	6	10	15	20
Crop field	1	4	6.3	9.5	12.6	15.7	18
Citrus orchard	1.1	2.7	4.3	6.3	12.6	16.7	21

Table - S4 - Technical properties of the three column experiments:

	Column experiment:	
	Highly controlled environment column experiment	Agricultural soils column experiment
Column volume[L]	18	75
Soil weight [kg]	25	170
Soil type	Fine-sand soil	Clay soil, sandy soil and sandy soil mixed with compost
Column sampling points	Two suction cups placed 20 cm below surface, and the column drainage, 80cm below the surface	Single suction cup placed 40 cm below the surface
Irrigation Pattern	1 L every 24 hours	3 L, for three times every 24 hours
Soil moisture monitoring	Time domain reflectometry (TDR)	N/A
Physical sampling intervals	2-1 times per day	
Selected wavelength	235.00 nm	223.86, 230.63 and 231.82nm
Optical measurement intervals	Every two hours	

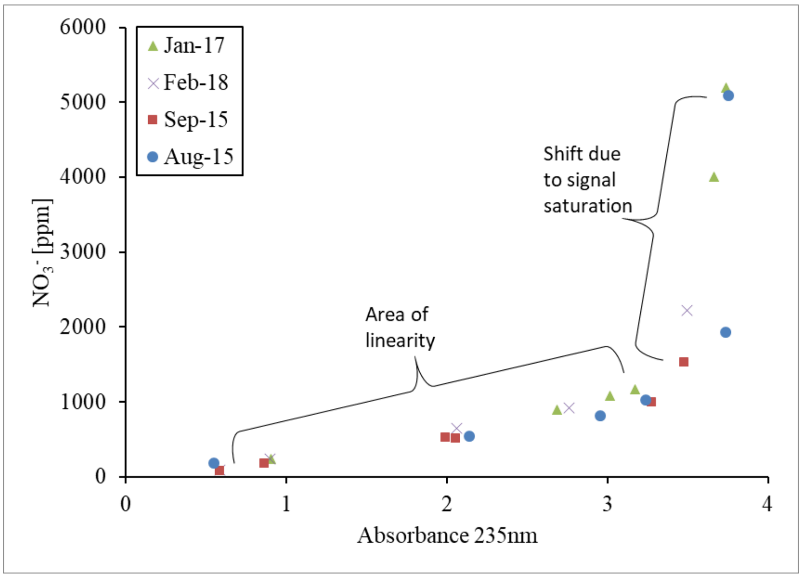


Figure S5 - Shift in measuring high concentrations at 235nm: Open crop field nitrate concentration vs absorbance intensity at 235nm. As can be seen on the graph, until concentration of ~1000 ppm nitrate there is a linear correlation between the nitrate concentration and absorbance intensity. However, when exceeding 1000 ppm nitrate the absorbance signal is found at saturation levels and as a result absorbance intensity is no longer indicative to nitrate concentration values.

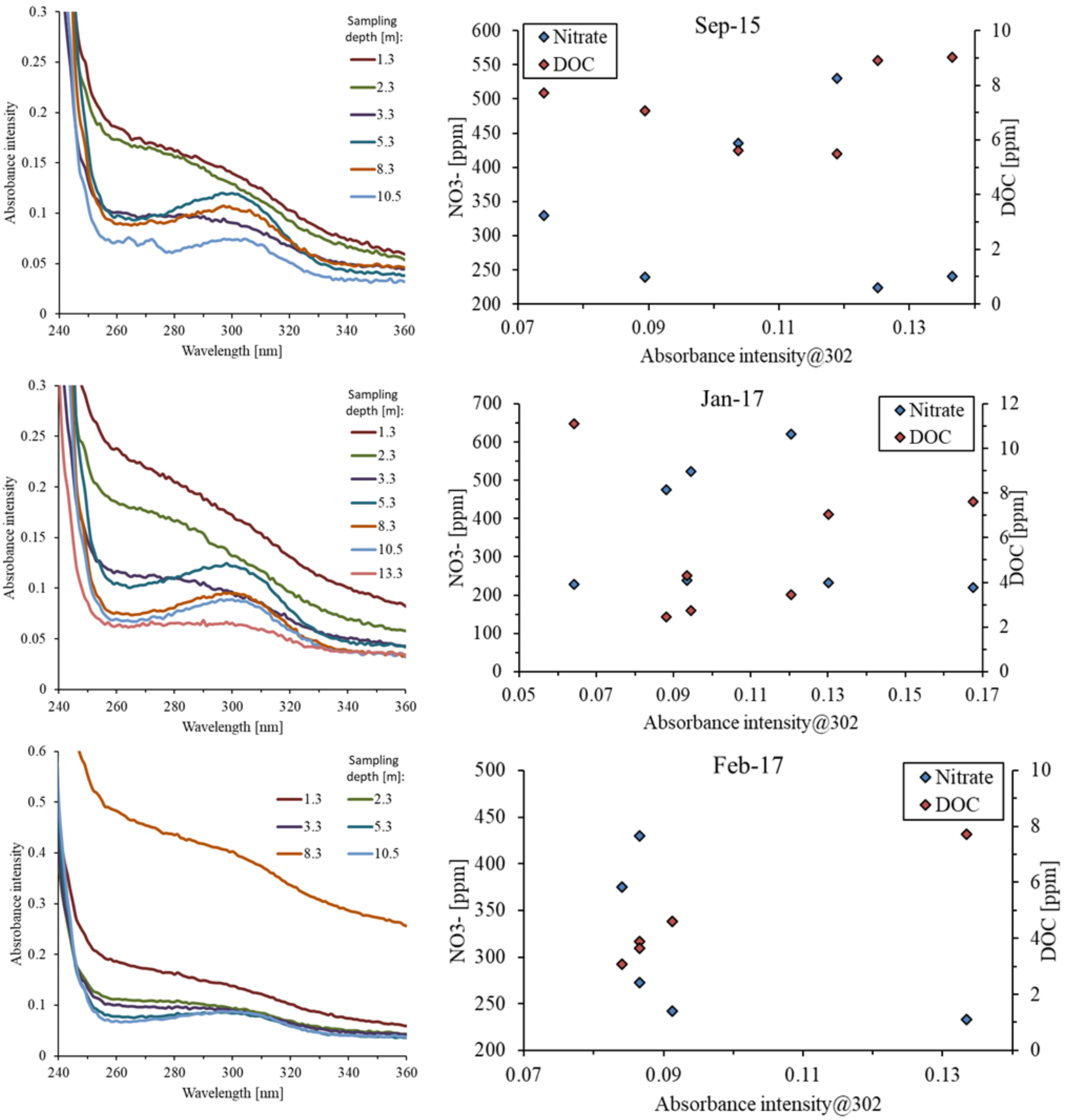


Figure S6 - Anomaly of nitrate spectral analyses at the organic greenhouse samples around 302nm region, during: September – 2015, January and February 2017.

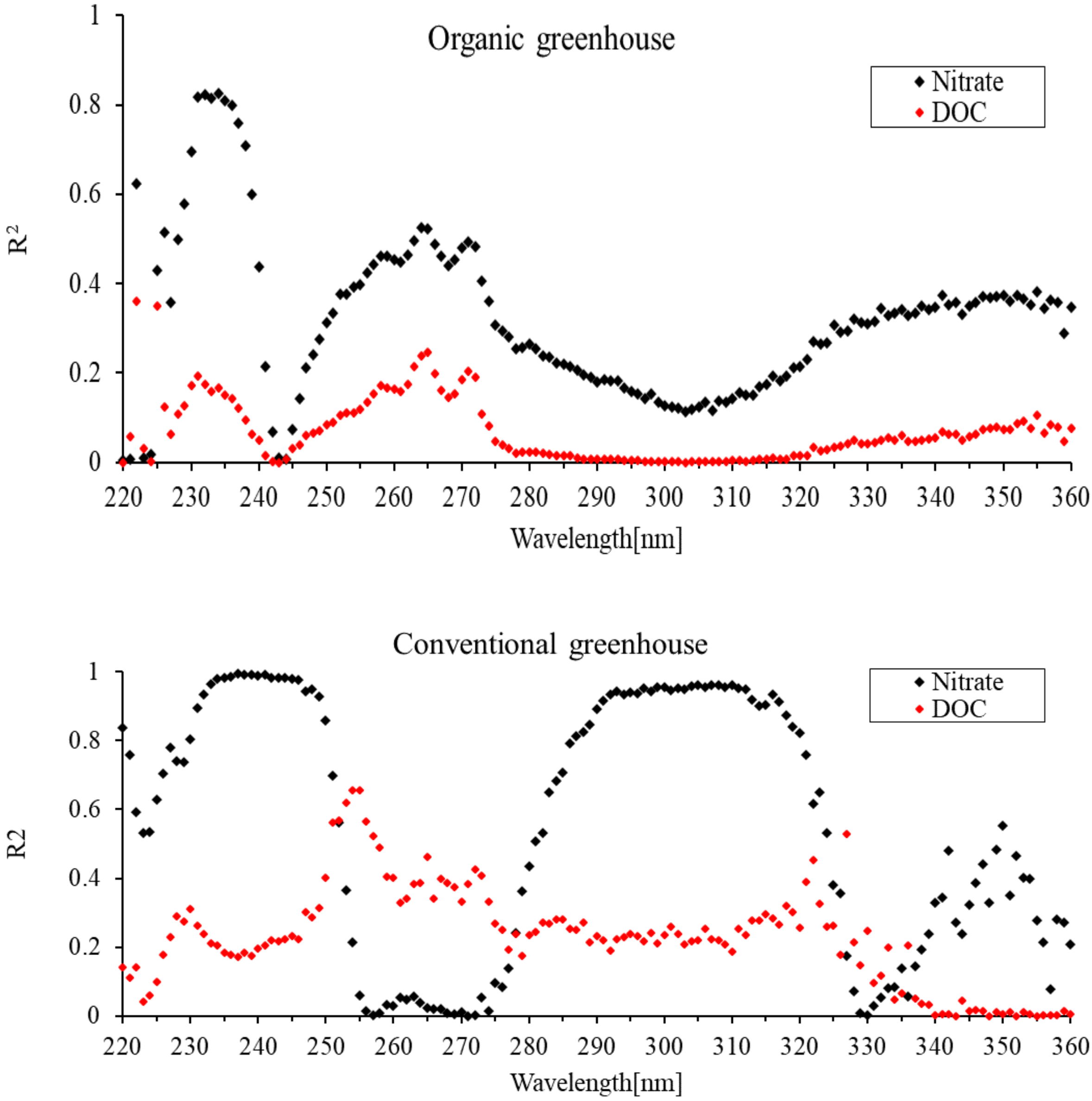
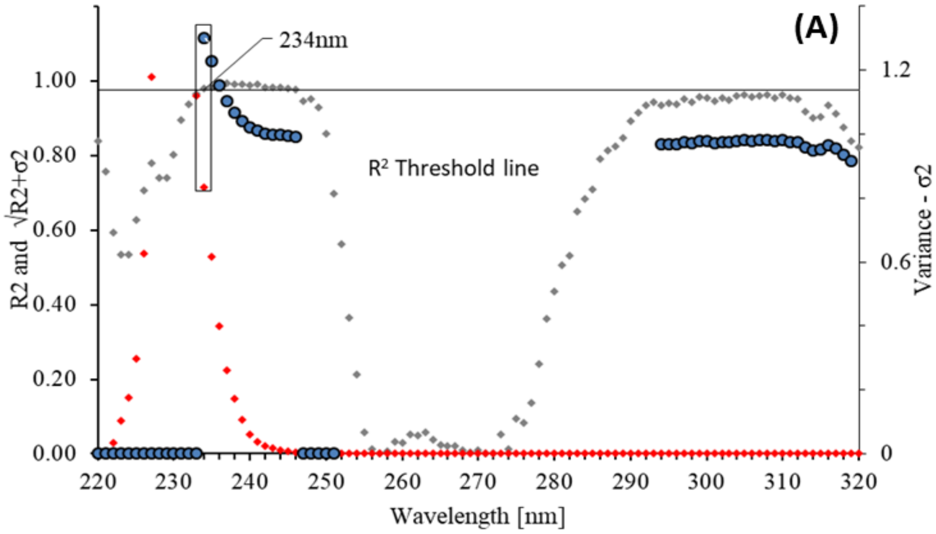


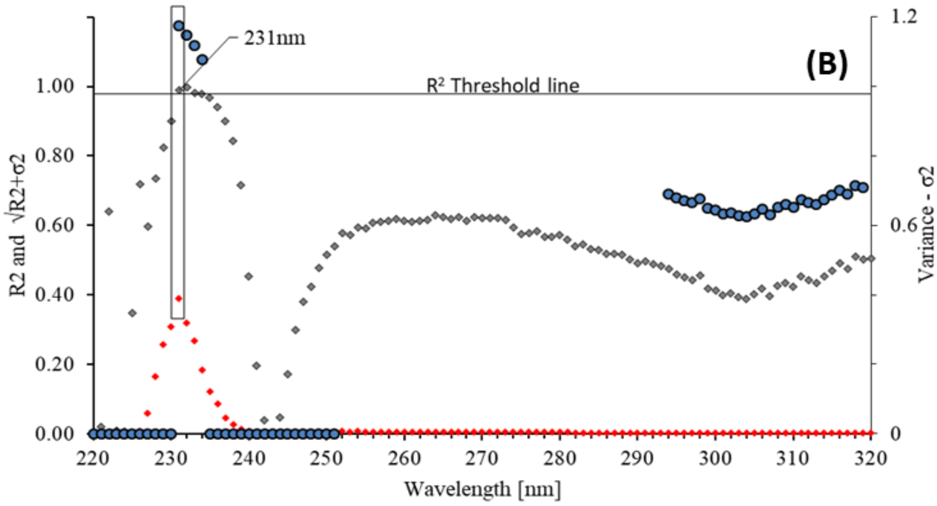
Figure S7 - Organic and conventional greenhouses R^2 vs. wavelength: Note how nitrate concentration in the organic greenhouse can be measured at a narrow range around 230nm, while at the conventional greenhouse nitrate can be measured between 230-240nm and around the 300nm area.

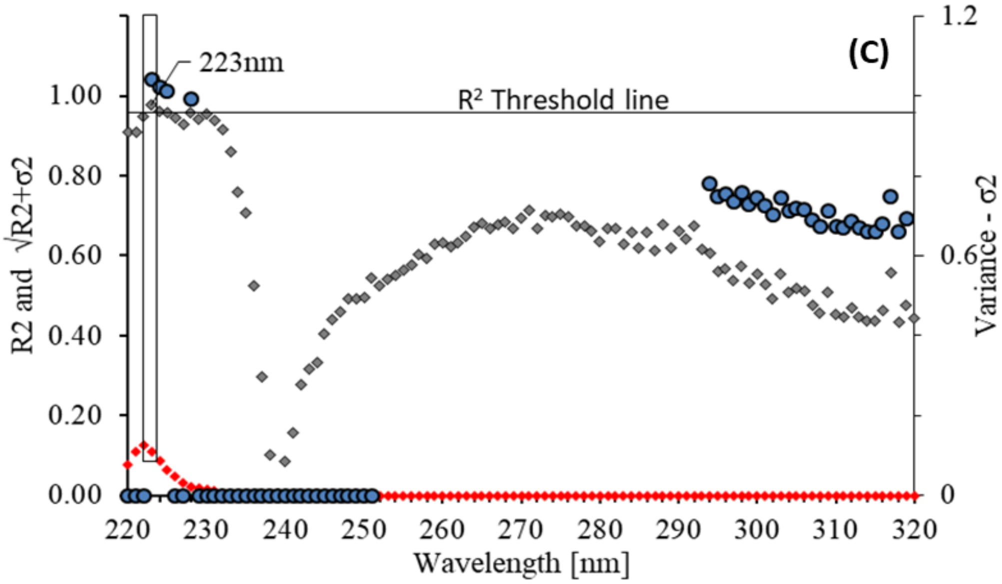
Table - S8 - DOC concentration as measured for porewater samples taken from VMS ports at the different fields:

VMS port	DOC concentration [ppm]			
	Open crop field	Citrus orchard	Conventional greenhouse	Organic greenhouse
1	5.7	6.8	3.5	9.8
2	3.2	4.5	2.6	8.9
3	1.6	6.8	2.7	6.0
4	4.0	2.9	3.9	5.5
5	2.1	4.8	2.8	5.9
6	1.9	4.7	1.6	5.6

Section S9 – The two-step analytical procedure, graphically demonstrated for: (A) conventional greenhouse (B) Organic greenhouse and (C) Citrus orchard.







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