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A bottom-up perspective of the net land methanol flux: synthesis of global eddy covariance flux measurements

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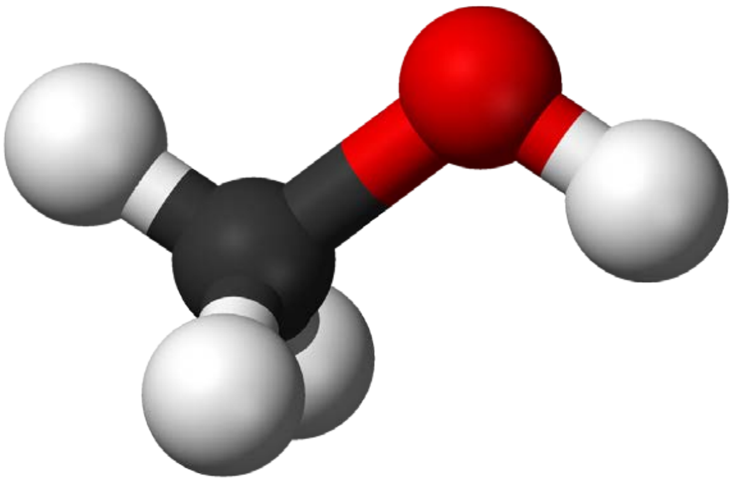
Motivation

- Methanol (CH_3OH) is the second most abundant volatile organic compound (VOC) in the troposphere after methane.



Motivation

- Methanol (CH_3OH) is the second most abundant volatile organic compound (VOC) in the troposphere after methane.
- Plays a significant role in controlling tropospheric oxidants.

Table 1. Methanol Chemical Reactions

(R-1)	$CH_3OH + OH + O_2 \rightarrow HO_2 + CH_2O + H_2O$
(R-2)	$CH_2O + hv + 2O_2 \rightarrow 2HO_2 + CO$
(R-3)	$HO_2 + NO \rightarrow NO_2 + OH$
(R-4)	$NO_2 + hv \rightarrow NO + O$
(R-5)	$O + O_2 \rightarrow O_3$
(R-6)	$CH_4 + OH \rightarrow \rightarrow CH_3OH + products$
(R-7)	$C_3H_6 + OH \rightarrow \rightarrow CH_3OH + products$
(R-8)	$CH_3O_2 + CH_3O_2 \rightarrow CH_3OH + CH_2O + O_2$

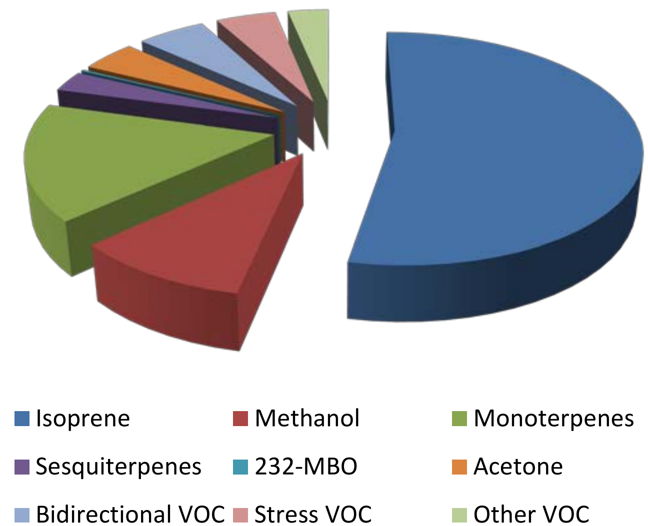
Where $\rightarrow \rightarrow$ indicates a multiple reaction pathway.

Tie et al. (2003)



Motivation

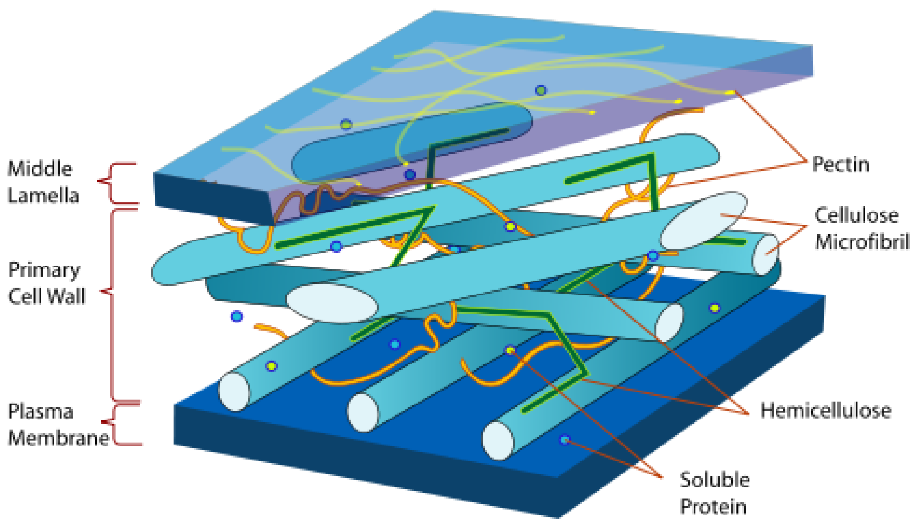
- Methanol (CH_3OH) is the second most abundant volatile organic compound (VOC) in the troposphere after methane.
- Plays a significant role in controlling tropospheric oxidants.
- Methanol emission comprise 10% of total global VOC emissions, being thus the second most important single contributor after isoprene.

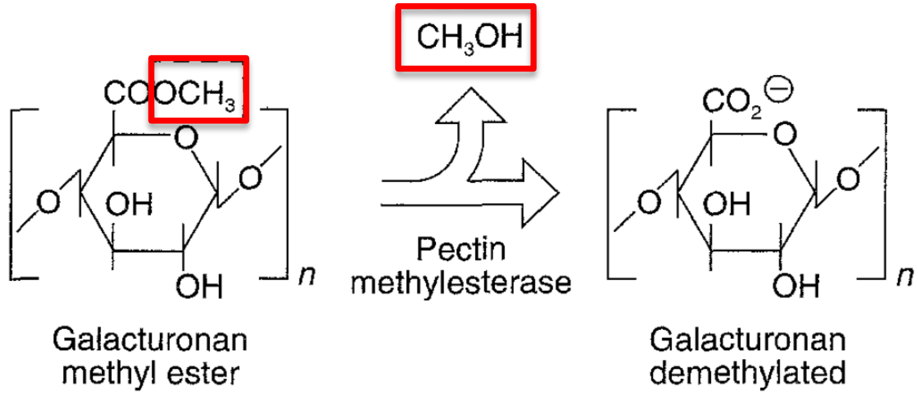


After Guenther et al. (2012)

Motivation

- Methanol is produced as a by-product of pectin metabolism during cell wall synthesis.





Fall & Benson (1996)

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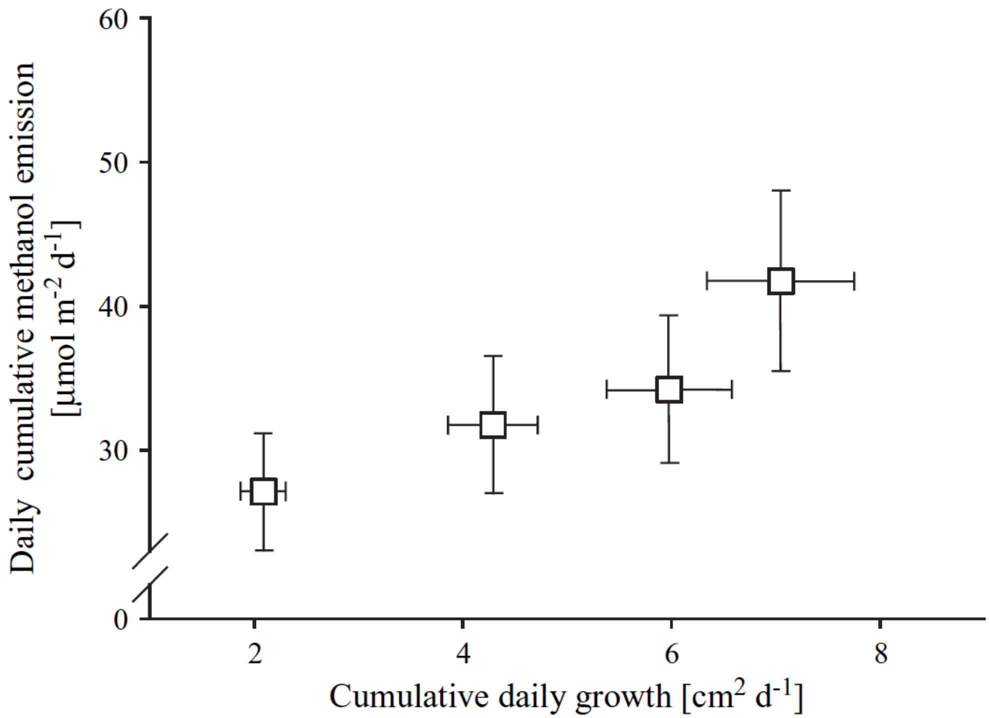
Motivation

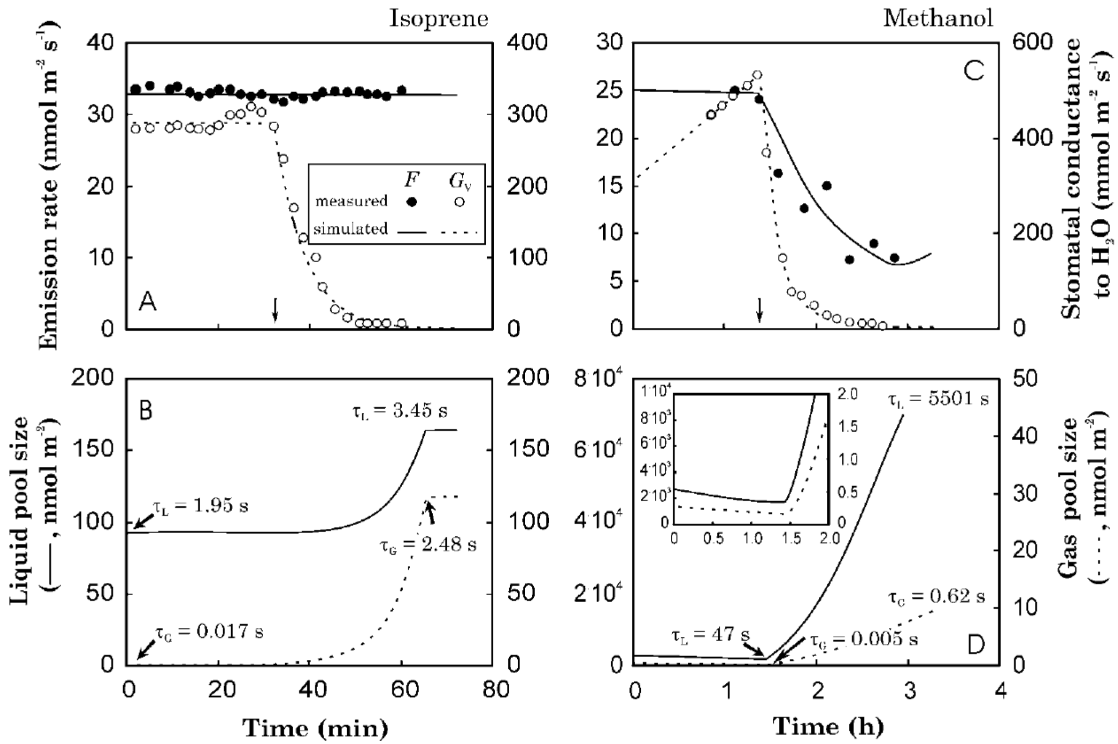
- Methanol production thus generally scales with plant growth.



Hüve et al. (2007)

Motivation

- Due to the low Henry constant of methanol, methanol emissions are under strong stomatal control.



Niinemets & Reichstein (2003)

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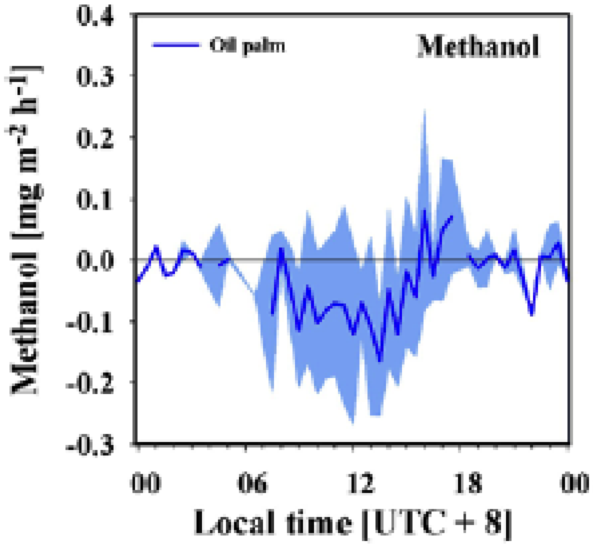
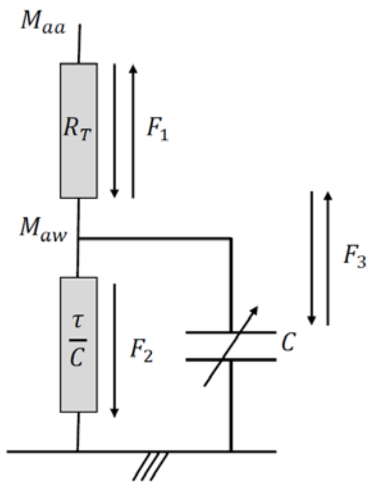
Motivation

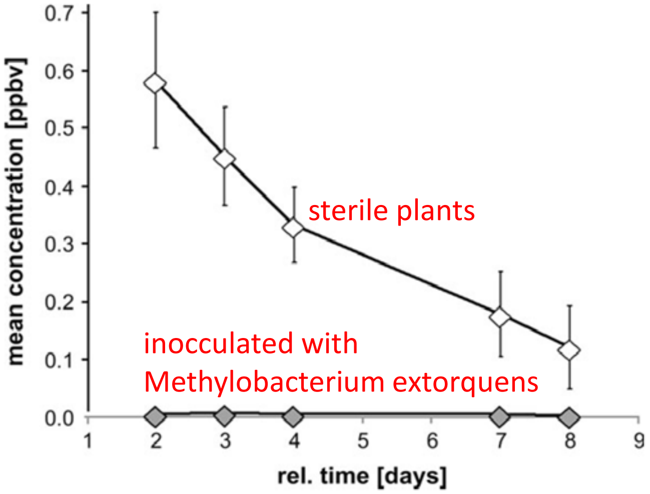
- At ecosystem scale, deposition of methanol is increasingly reported and has been linked to the presence of surface water, methylotrophic bacteria and chemical transformations.



Misztal et al. (2011)



Laffineur et al. (2012)



Abanda-Nkpwatt et al. (2006)



Motivation

	Singh et al. (2000)	Heikes et al. (2002)	Galbally & Kirstine (2002)	Tie et al. (2003)	Von Kuhlmann et al. (2003)	Jacob et al. (2005)	Millet et al. (2008)	Stavrakou et al. (2011)
Primary biogenic	75	280	100	287	77	128	80	100
Plant decay	20	20	13			23	23	
Biomass burning	6	12	13	25	15	13	12	4
Primary anthropogenic	3	8	4		2	4	5	9
Ocean source	n.a.	n.a.	6	n.a.	n.a.	n.a.	85	43
Atmospheric production	18	30	19	31	28	38	37	31
Total sources	**122**	**350**	**155**	**343**	**122**	**206**	**242**	**188**
Dry deposition land	n.a.	-70	-24	-85	-37	-55	-40	-28
Dry deposition ocean	n.a.	-80	n.a.	n.a.	n.a.	-10	-101	-48
Wet deposition land	n.a.	-5	-11	-50	-9	-5	-5	-1
Wet deposition ocean	n.a.	-5	-6	n.a.	n.a.	-7	-8	-2
Gas phase chemistry	n.a.	-110	-113	-149	-77	-129	-88	-108
Total sink	**-45**	**-270**	**-154**	**-284**	**-123**	**-206**	**-242**	**-187**
Net land flux	**104**	**245**	**95**	**177**	**48**	**108**	**75**	**85**
Land emission model	MEGAN	MEGAN	NPP	MEGAN	MEGAN	NPP	NPP	MEGAN

Motivation

- Methanol (CH_3OH) is the second most abundant volatile organic compound (VOC) in the troposphere after methane.
- Plays a significant role in controlling tropospheric oxidants.
- Methanol emission comprise 10% of total global VOC emissions, being thus the second most important contributor after isoprene.
- Consensus that methanol is primarily of biogenic origin, but terrestrial source estimates vary widely (48-245 Tg y^{-1}).
- The data underlying the land budget calculations largely stem from small-scale leaf gas exchange measurements.
- **The main objective of this study is to use micrometeorological ecosystem-scale methanol flux measurements, which have increasingly become available during the past decade, to provide a bottom-up perspective of the net land methanol flux.**

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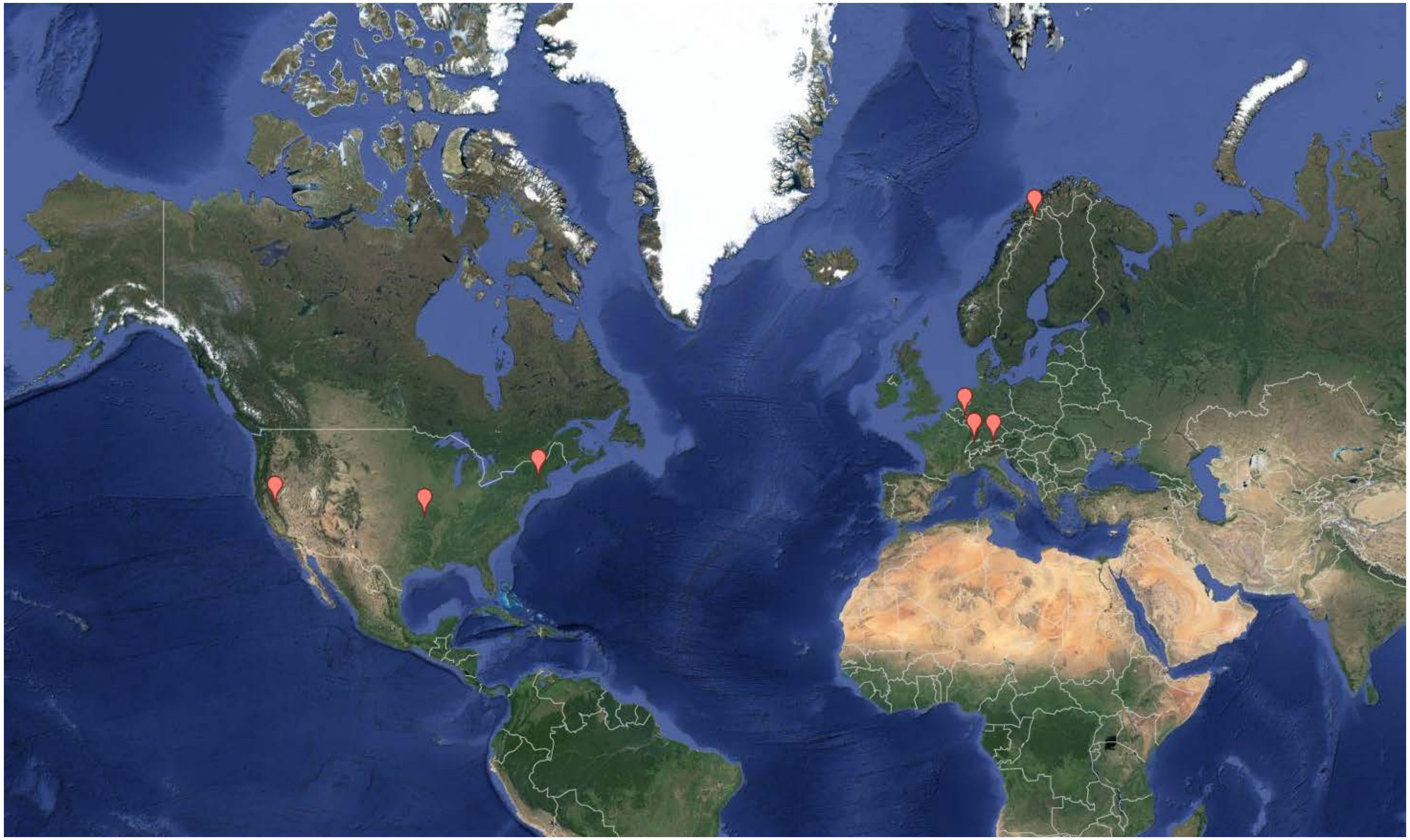
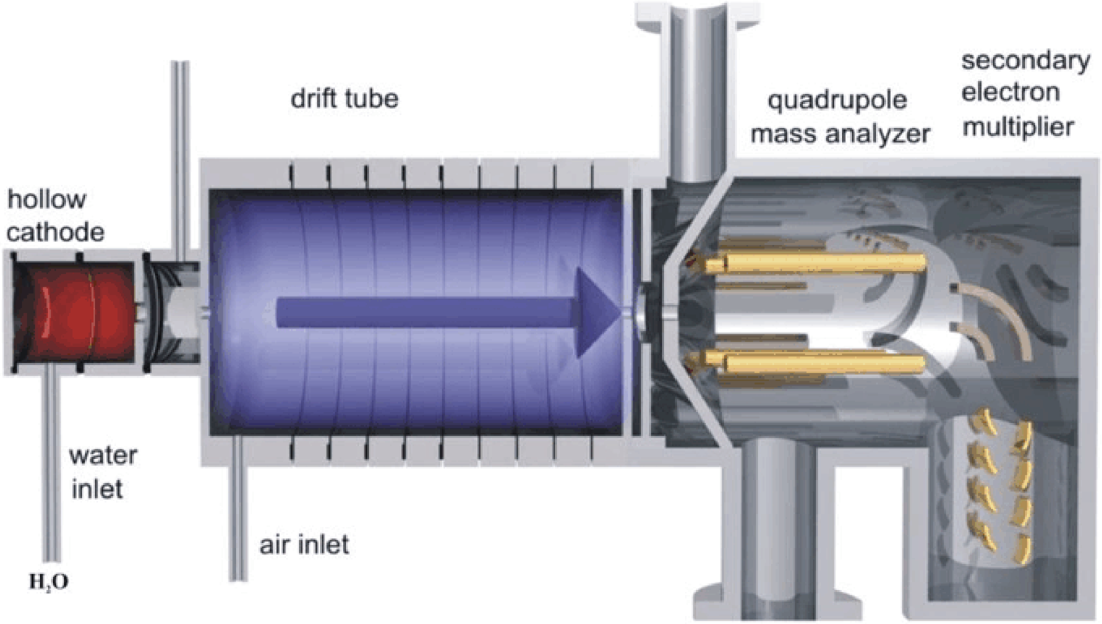
Study sites



Study sites

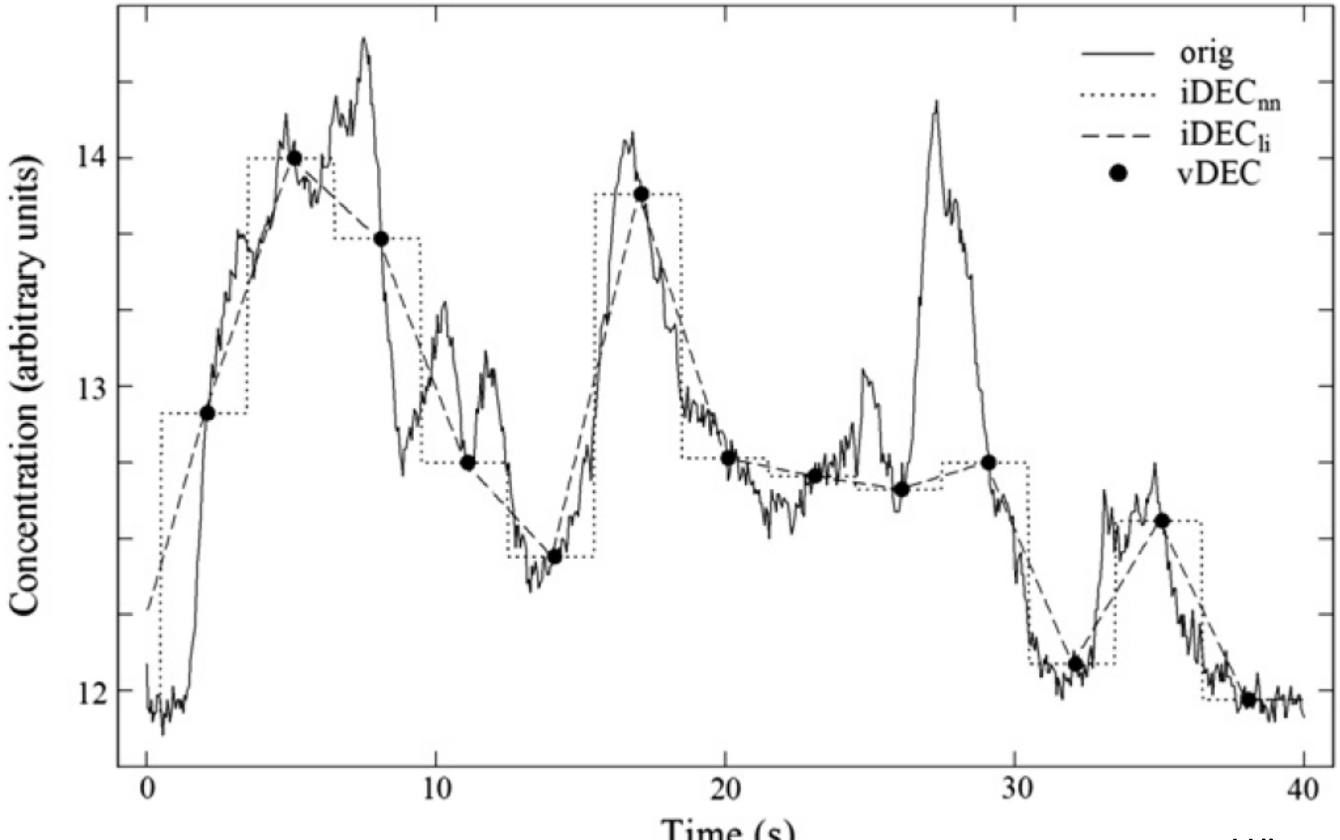
	Blodgett forest	Stordalen	Vielsalm	Neustift	Oensingen-INT	Oensingen-EXT	Harvard forest	Missouri Ozark
Country	USA	Sweden	Belgium	Austria	Switzerland	Switzerland	USA	USA
Latitude	38.89 N	68.33 N	50.30 N	47.12 N	47.28 N	47.28 N	42.54 N	38.76 N
Longitude	120.63 W	19.05 E	5.98 E	11.32 E	7.73 E	7.73 E	72.17 W	92.16 W
Elevation	1315	351	450	970	450	450	340	219
MAP (mm)	1290	304	1000	852	1100	1100	1066	1110
MAT (degC)	9.0	-0.7	7.5	6.5	9.0	9.0	7.8	13.6
Climate	Mediterranean	Boreal	Temperate maritime	Temperate alpine	Temperate continental	Temperate continental	Temperate	Temperate continental
Biome	Coniferous evergreen forest	Wetland	Mixed forest	Grassland	Grassland	Grassland	Mixed forest	Deciduous broadleaf forest
Flux method	REA	EC	EC	EC	EC	EC	EC	EC
MeOH analysis	GC-FID	PTR-MS	PTR-MS	PTR-MS	PTR-MS	PTR-MS	PTR-MS	PTR-TOF

MeOH quantification



Virtual disjunct eddy covariance

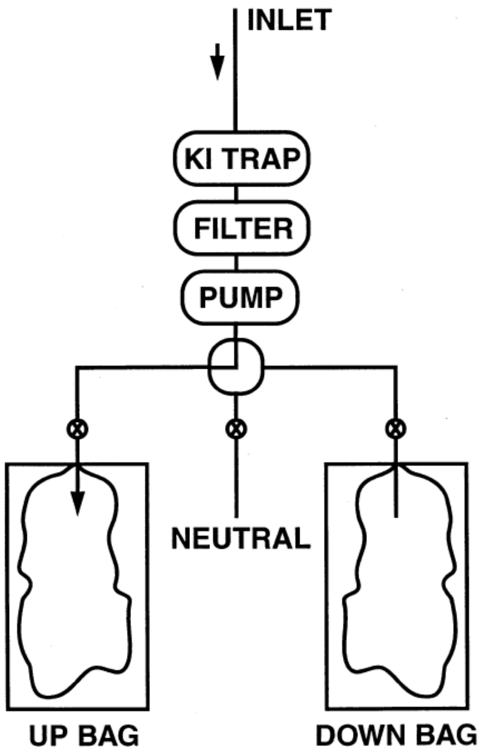
$$F = \overline{w'c'}$$

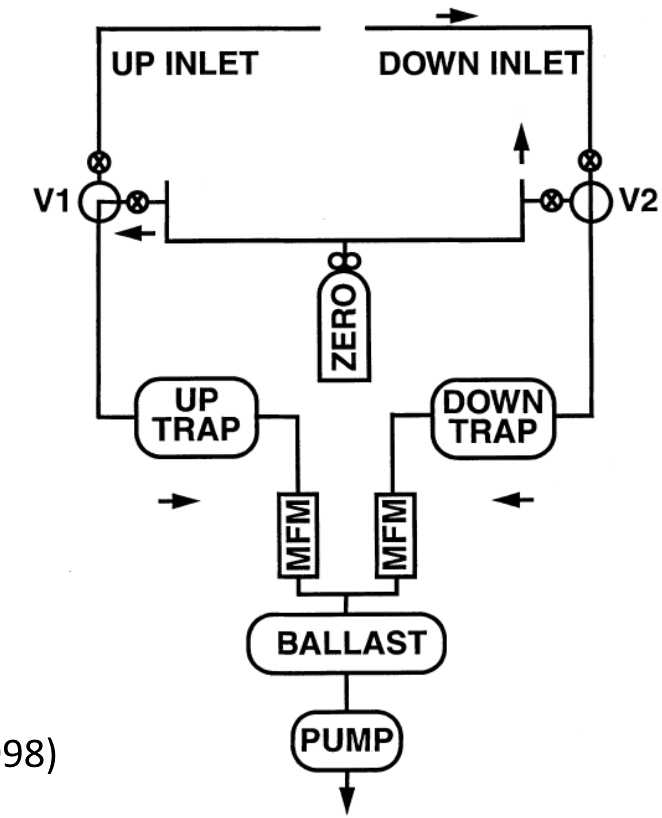


Hörtnagl et al. (2010)

Relaxed eddy accumulation

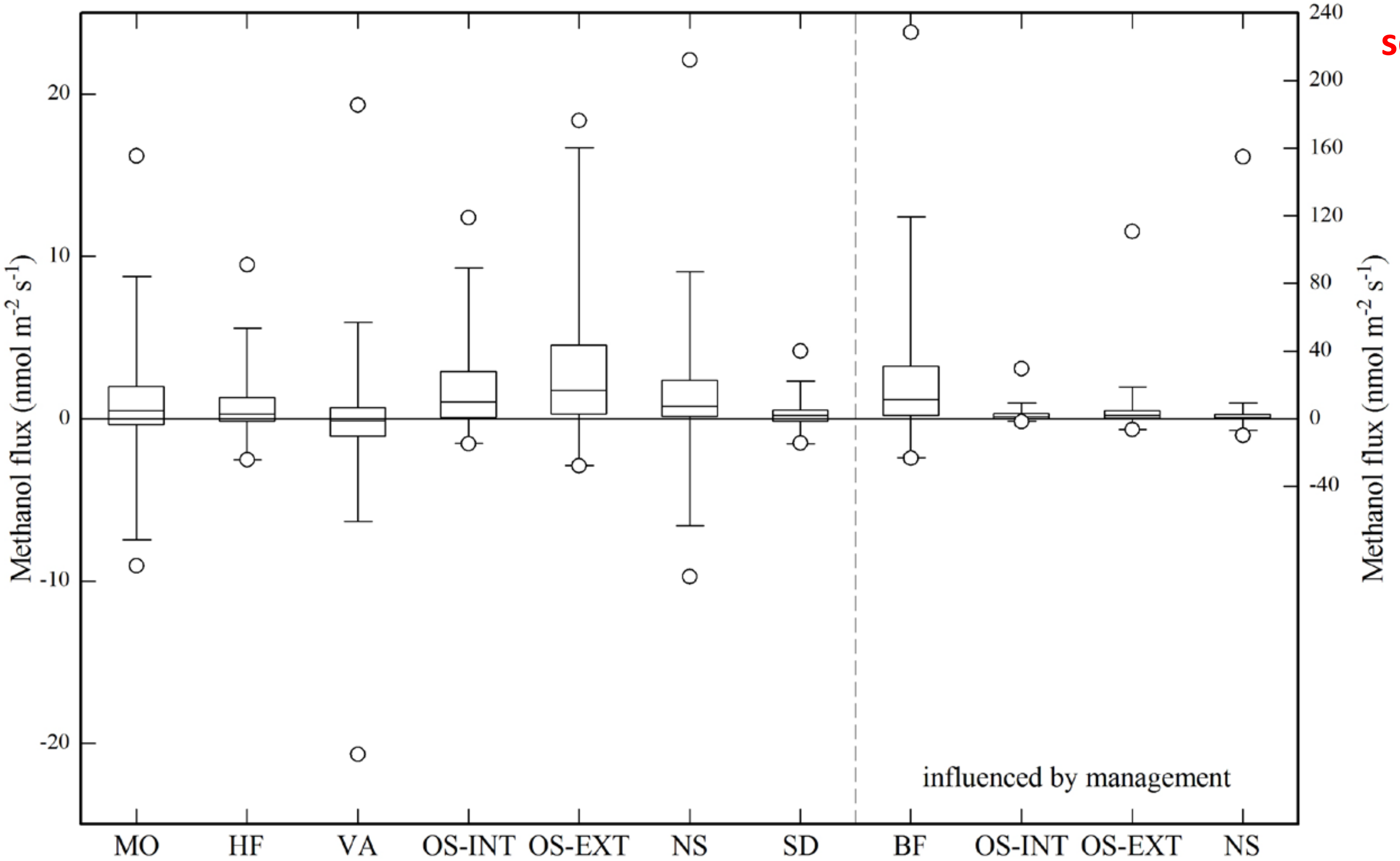
$$F = b\sigma_w\left(\overline{c_{up}} - \overline{c_{dn}}\right)$$





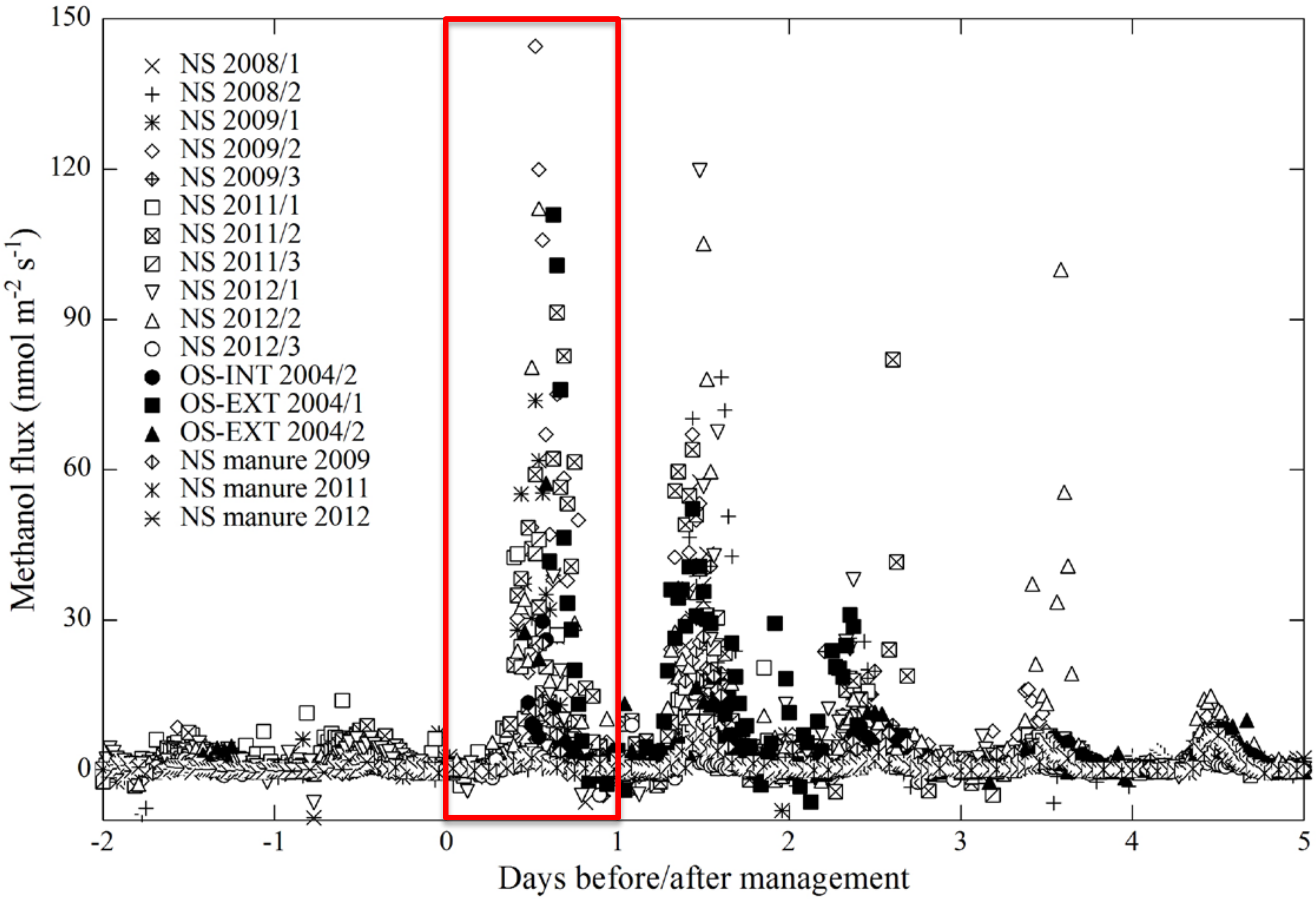
Bowling et al. (1998)

Exploratory analysis

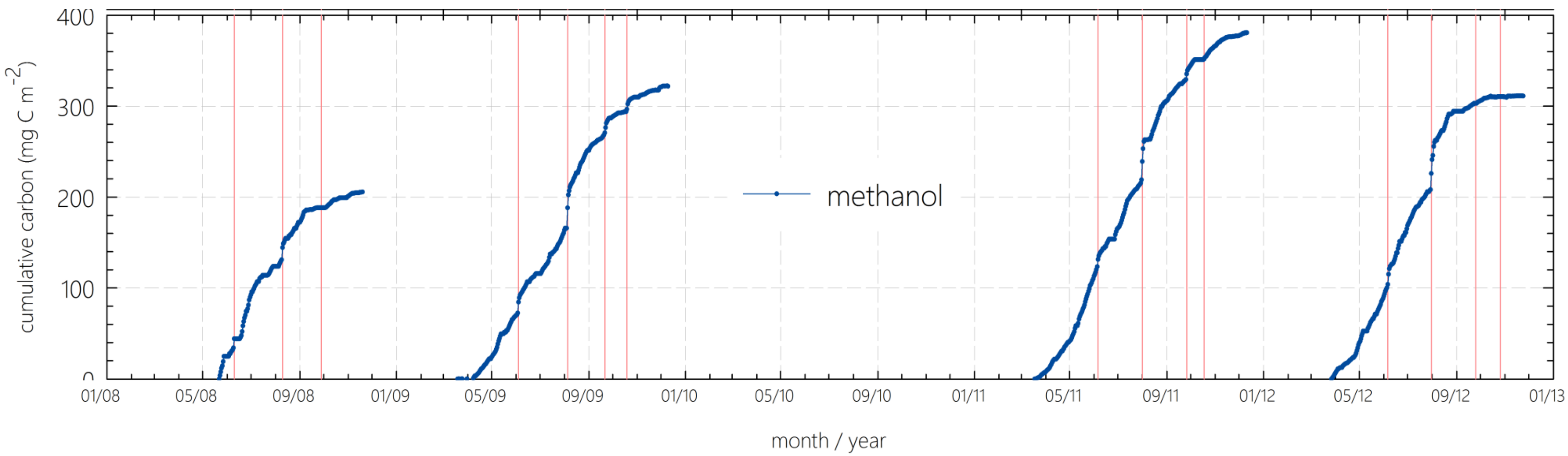


scale!

Effects of disturbance

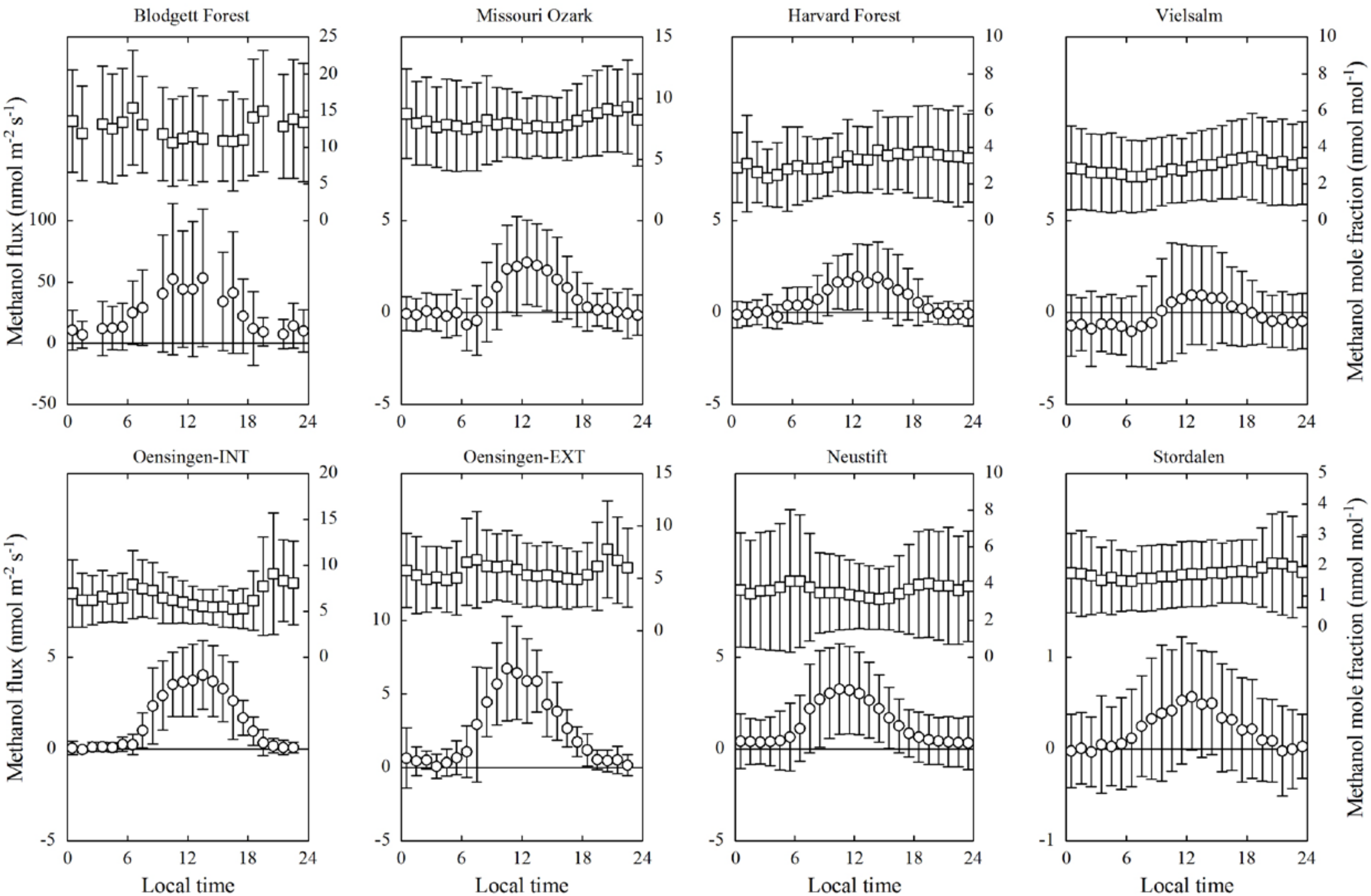


Effects of disturbance

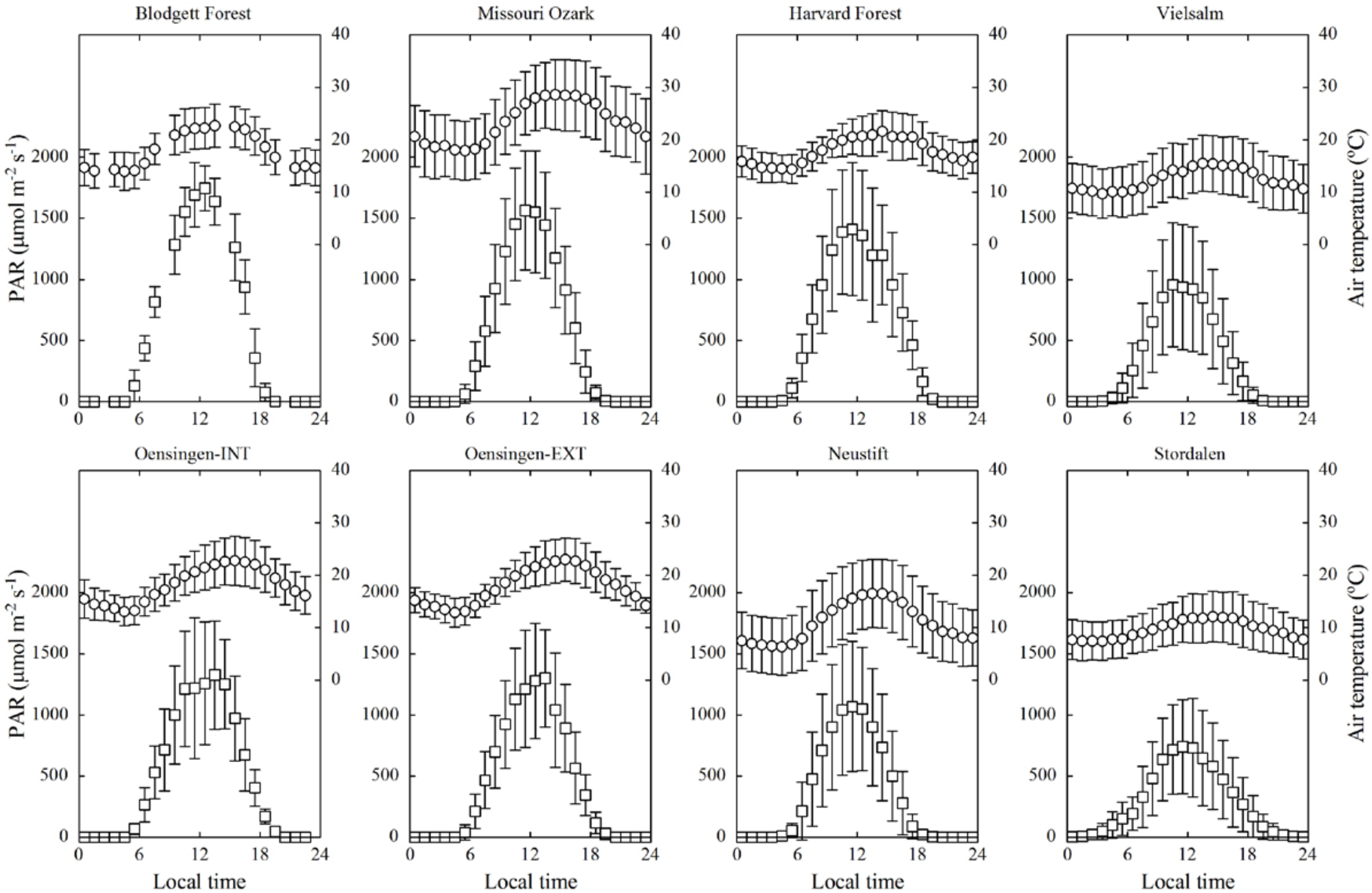


Hörtnagl et al. (2011 & unpublished)

Exploratory analysis



Exploratory analysis



Exploratory analysis

	BF	MO	HF	VA	OS-INT[a]	OS-EXT[a]	NS[a]	SD
PAR	0.38 ***	0.54 ***	0.71 ***	0.41 ***	0.82 ***	0.80 ***	0.70 ***	0.52 ***
RH	-0.10 *	-0.51 ***	-0.65 ***	-0.57 ***	-0.56 ***	-0.28 ***	-0.46 ***	-0.43 ***
TA	0.23 ***	0.49 ***	0.68 ***	0.26 ***	0.50 ***	0.37 ***	0.61 ***	0.18 ***
SWC	-0.25 ***	-0.15 ***	0.05 ns	0.01 ns	-0.03 ns	-0.03 ns	-0.31 ***	na
u_*	0.43 ***	0.34 ***	0.55 ***	0.04 ***	0.54 ***	0.30 ***	0.32 ***	0.00 ns
ET	0.37 ***	0.40 ***	0.67 ***	0.37 ***	0.82 ***	0.76 ***	0.71 ***	0.41 ***
GPP	0.42 ***	0.21 ***	0.60 ***	0.27 ***	0.63 ***	0.65 ***	0.63 ***	0.27 ***
TSEOP	-0.17 ***	0.18 ***	0.14 *	0.28 ***	-0.08 *	0.04 ns	-0.08 ***	0.04 *
n	469	2497	220	8853	490	492	17627	1853

[a] ... exclusive of data influenced by management

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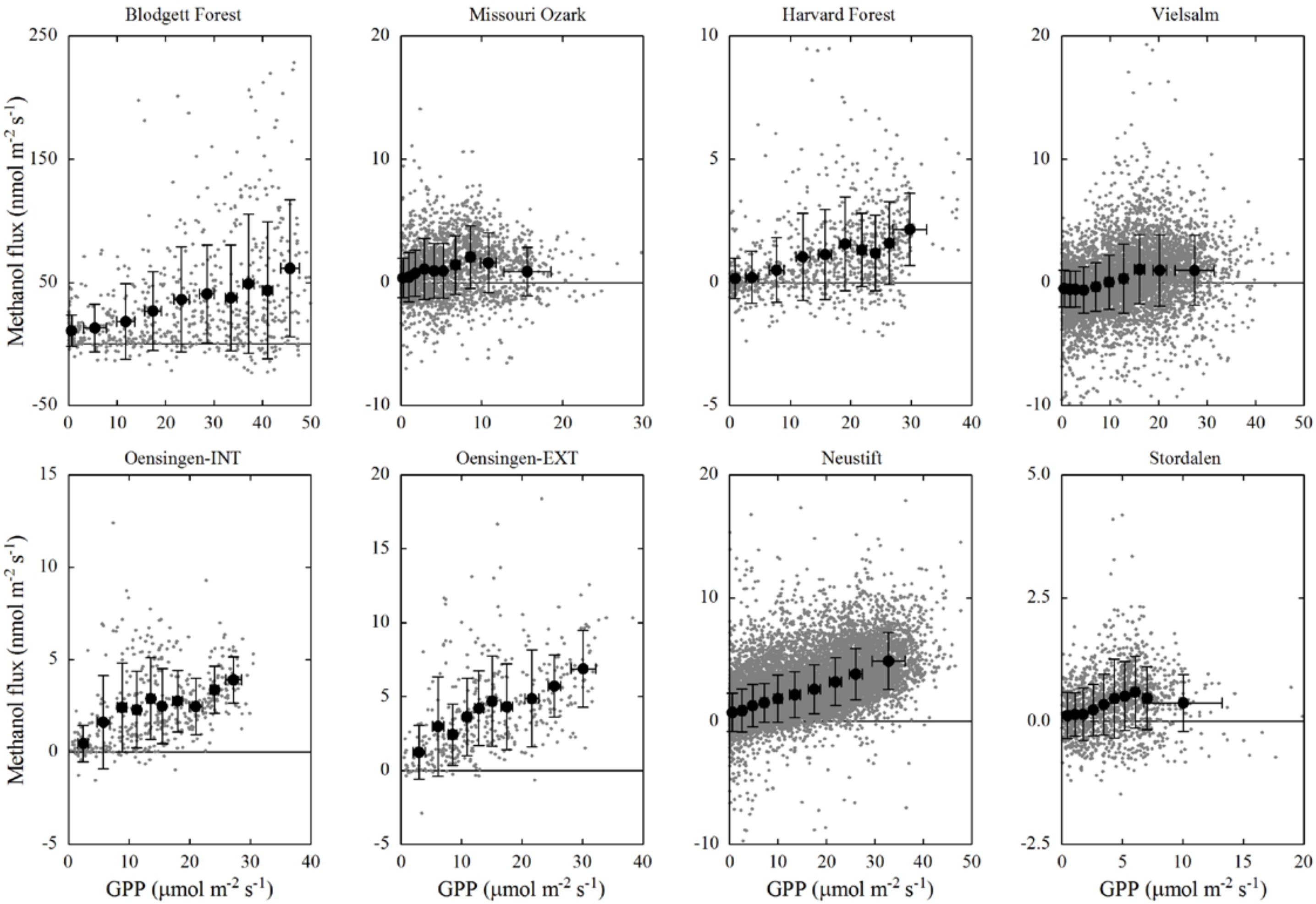
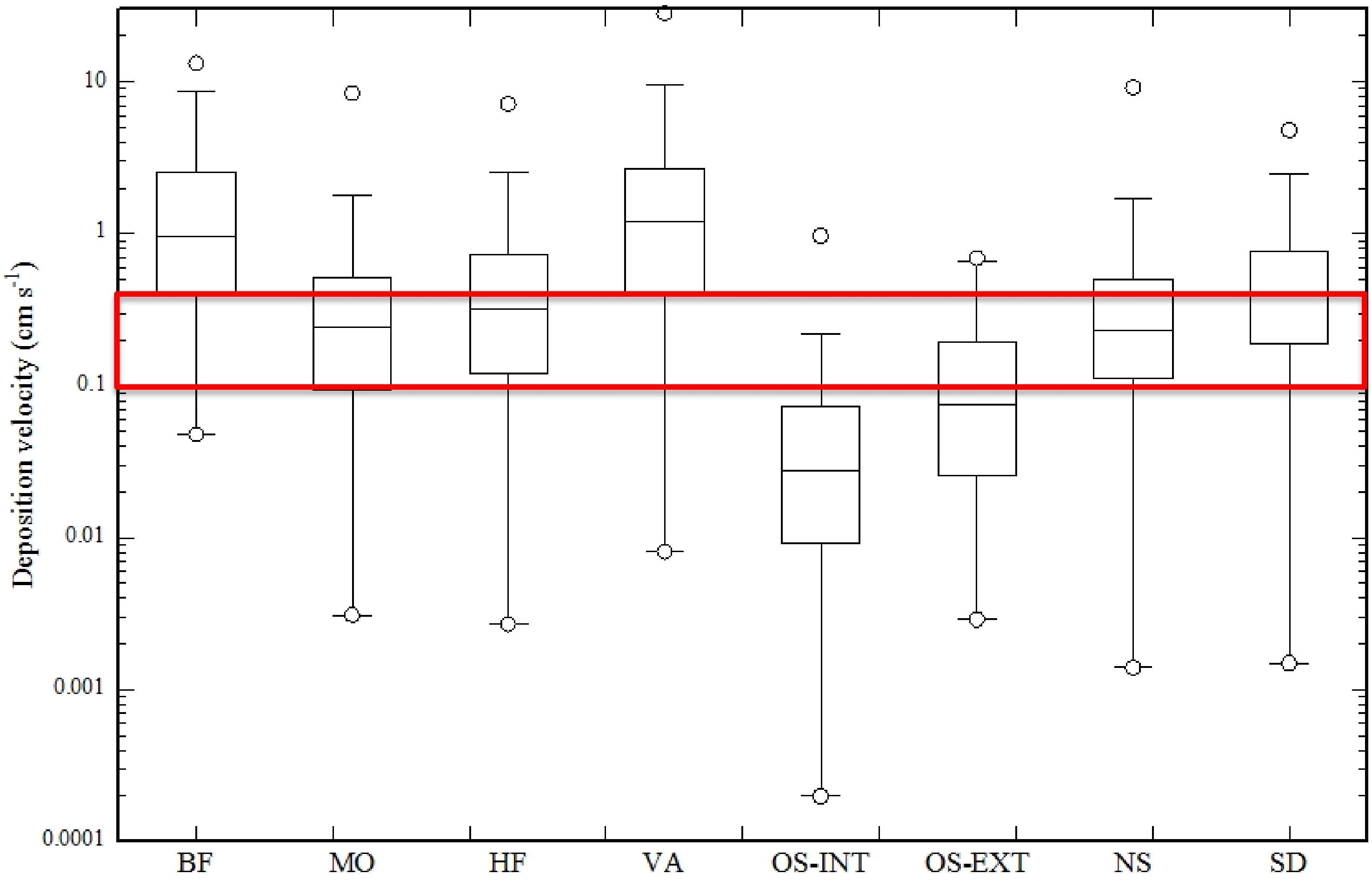
Relation to productivity



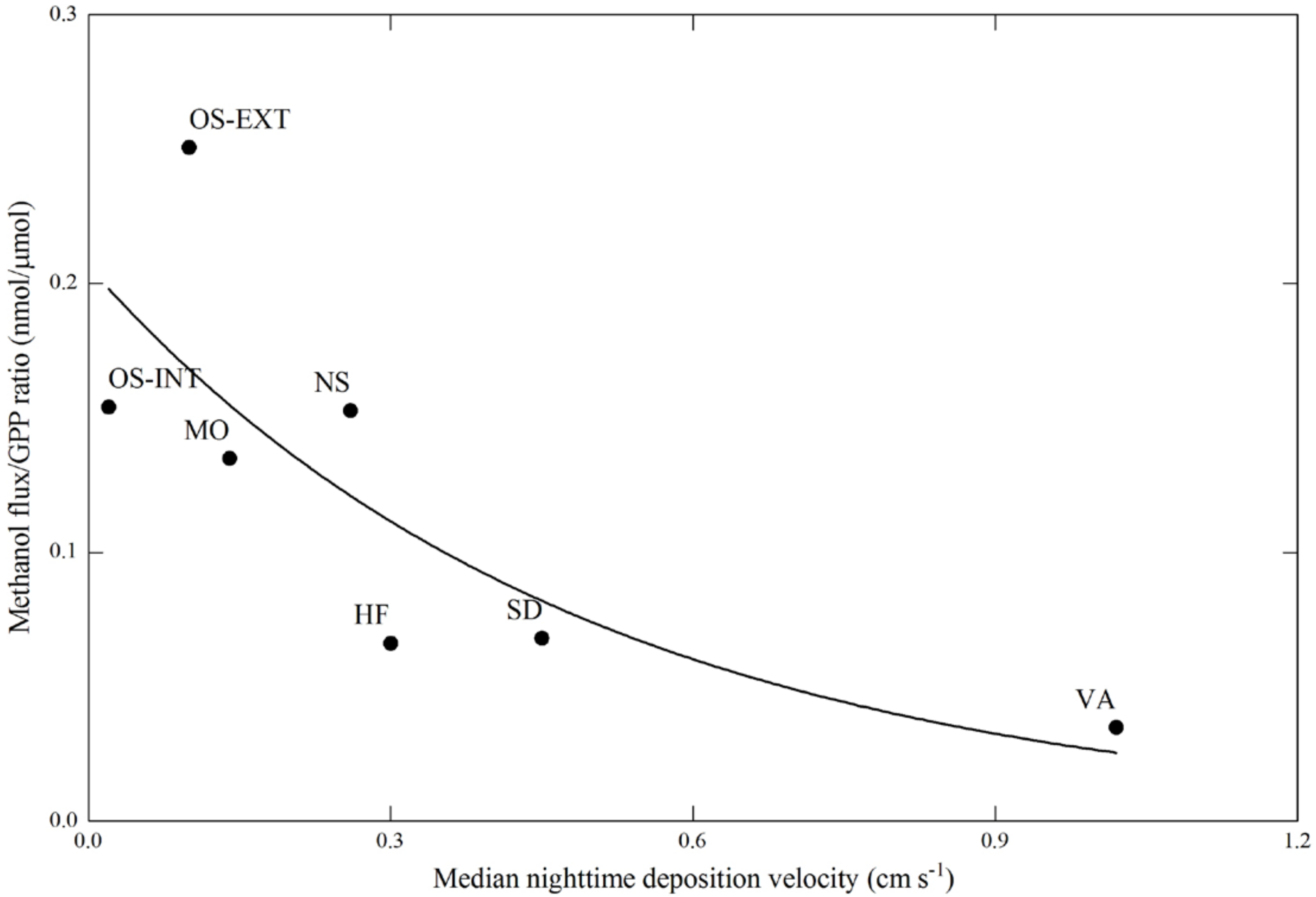
Exploratory analysis

	η^2 (%)
Corrected model	59.26 ***
Offset	0.00 ns
PAR	0.56 ***
TA	0.11 ***
RH	0.02 **
u_*	0.02 **
GPP	0.11 ***
TSEOP	0.00 ns
ET	0.06 ***
Site	5.01 ***
Site x PAR	0.34 ***
Site x TA	2.87 ***
Site x RH	7.08 ***
Site x u_*	0.63 ***
Site x GPP	1.02 ***
Site x TSEOP	0.35 ***
Site x ET	0.18 ***

Deposition


Deposition velocity (cm s-1)
10
1
0.1
0.01
0.001
0.0001
BF
MO
HF
VA
OS-INT
OS-EXT
NS
SD

Deposition


Methanol flux/GPP ratio (nmol/µmol)
Median nighttime deposition velocity (cm s-1)
0.0
0.1
0.2
0.3
0.0
0.3
0.6
0.9
1.2
OS-EXT
OS-INT
NS
MO
HF
SD
VA



Conclusions

- Unequivocal evidence that at ecosystem scale the methanol flux is bi-directional.

- Models generally treat emission and deposition separately, which makes it difficult to get the net flux right and makes it near impossible to make use of ecosystem flux measurements for calibration/validation.

- Plant productivity and surface wetness act in opposite ways on sign of methanol flux, on a sub-diurnal time scale stomatal conductance modulates methanol flux.

- Methanol emissions following disturbance need to be accounted for.