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Sources of Nickel in Pontardawe

6th October 2016

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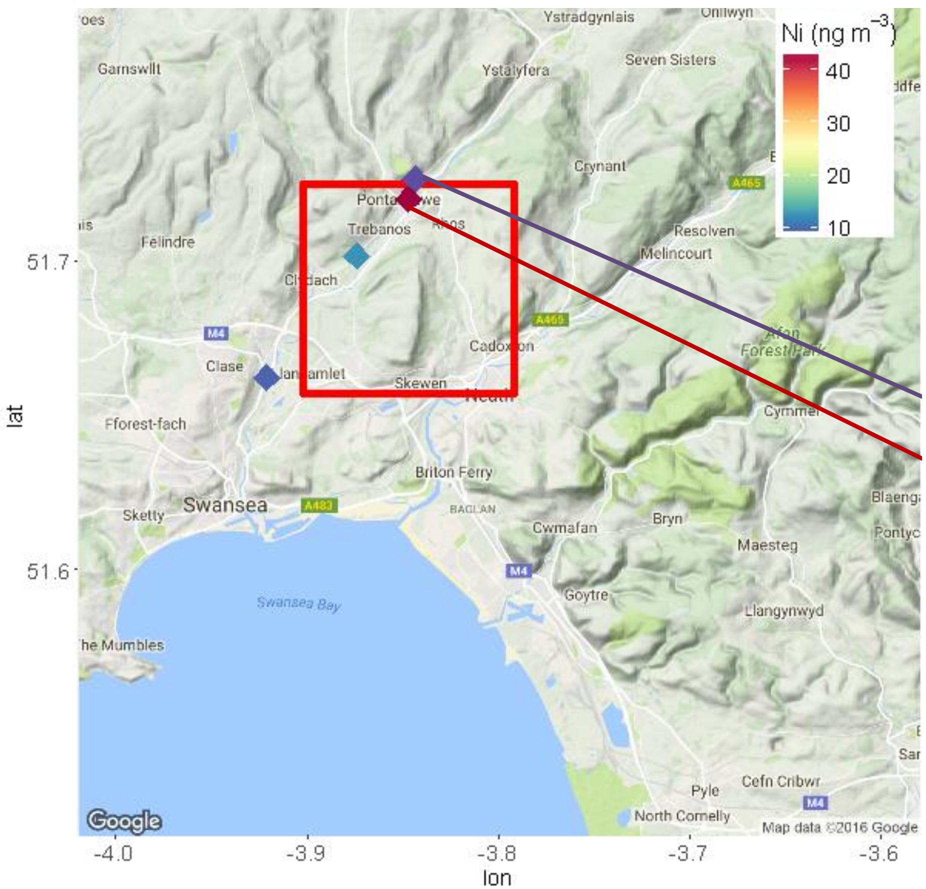
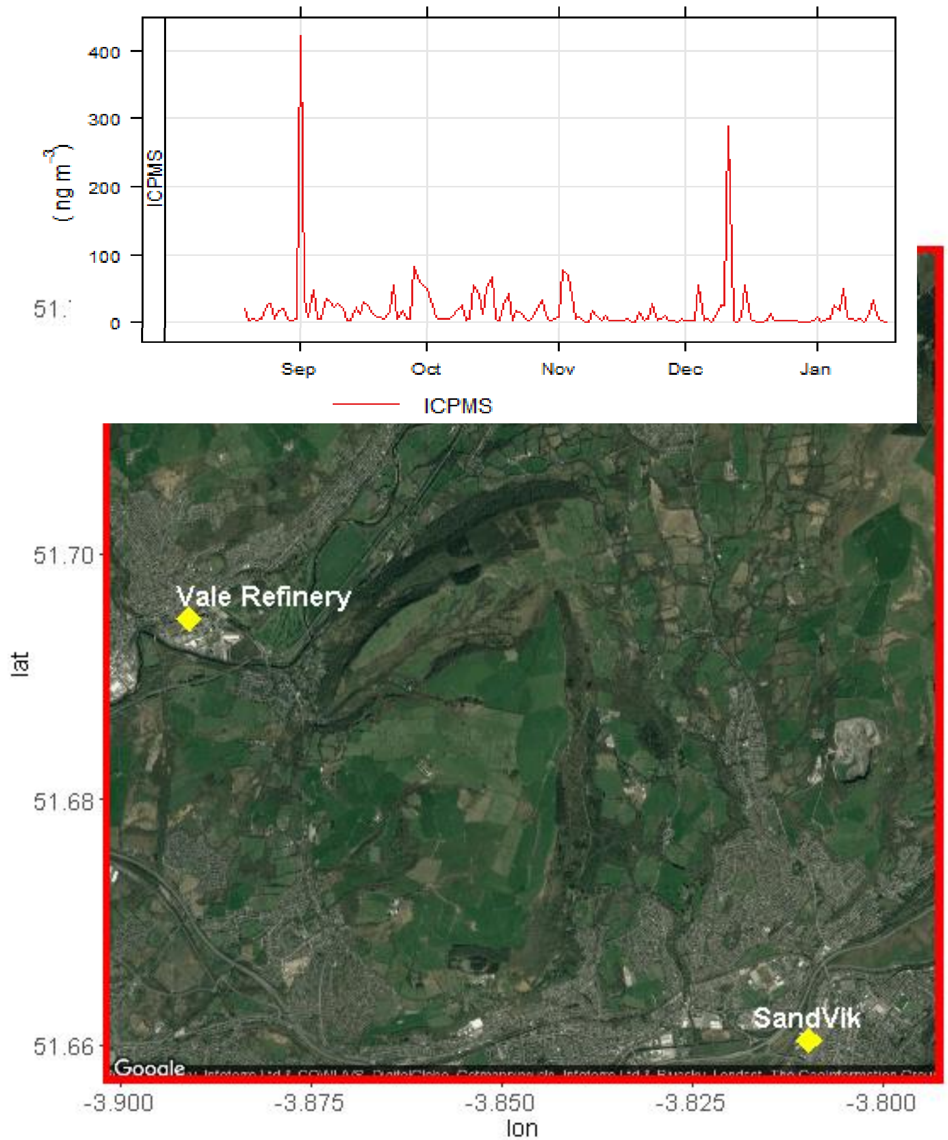
Background

EU Target Value: **20 ng m^{-3}**

2014 annual Ni concentrations



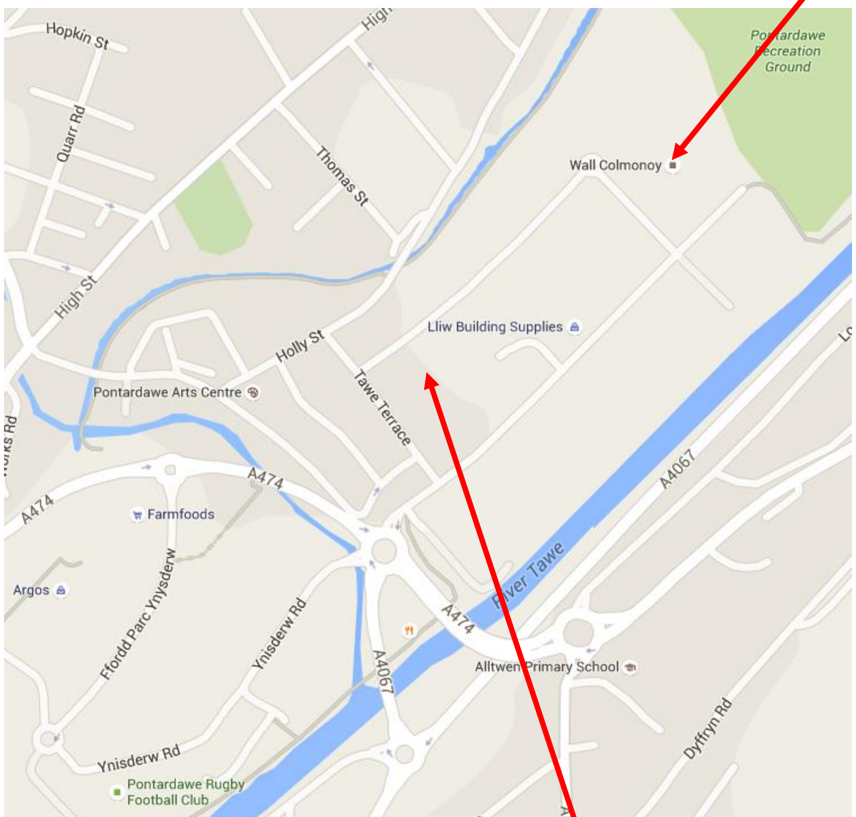
NPL measuring daily filters since August 2015

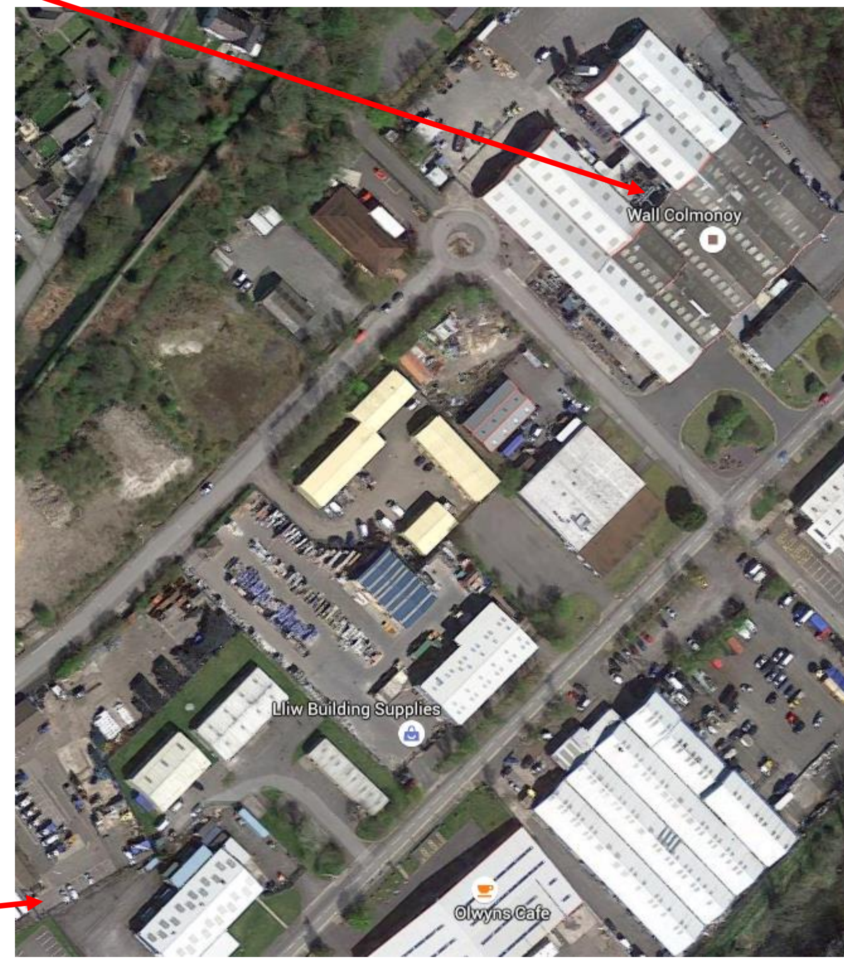


Goddard et al., 2014

Background

Wall Colmonoy





Tawe Terrace

Aims

- 6-week campaign
  (25th November – 24th December 2015)
- Identify and quantify the emissions from key sources in and around Pontardawe
- Provide information to both the regulatory bodies and to the process operators

Methods

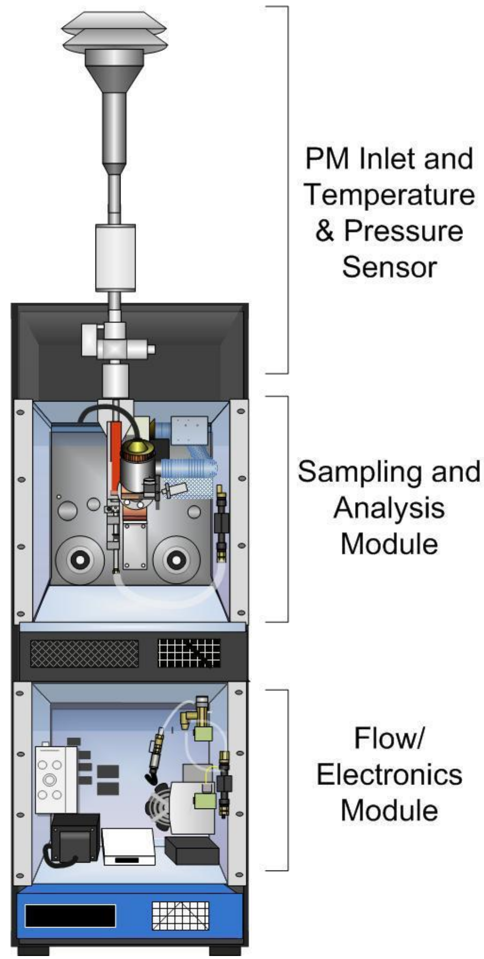
Mobile Atmospheric Research Platform (MARPL)

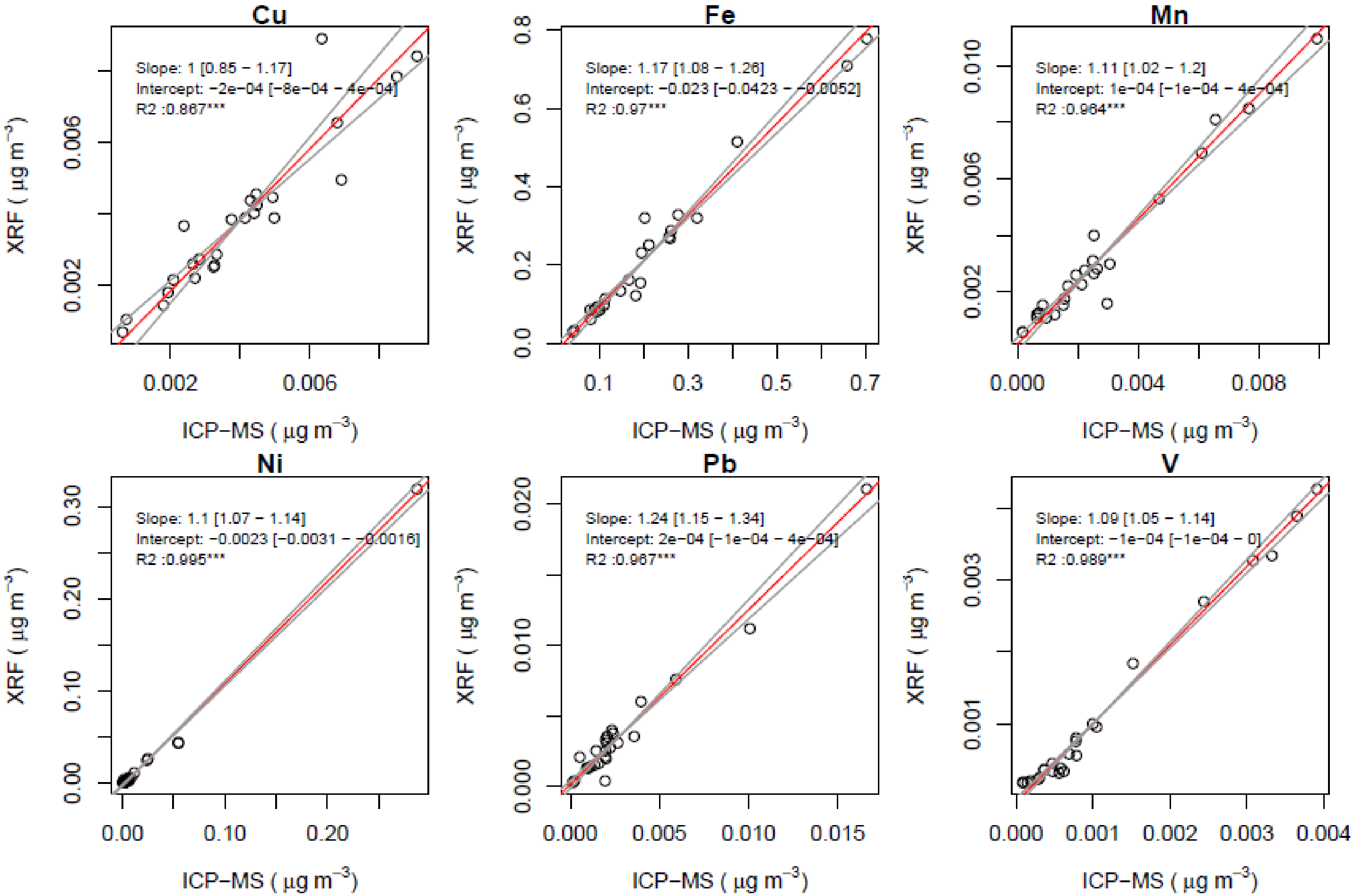
INSTRUMENTATION AT MARPL

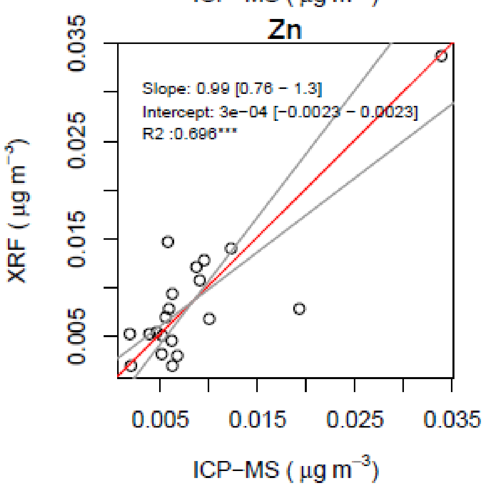
- 23 metals at hourly resolution (XRF)
- Black Carbon (Aethalometer)
- NOx (NO + NO_2) (Blue Light Converter)
- Met data: wind, RH, TEMP (10 m mast)

Methods - XRF Measurements

- Elements
  - Regulatory (Ni, As, Cd, Pb),
  - Abrasion (Ba, Cu, Sb, Zn),
  - Mineral (Ca, Fe, Mn, Mo, Si, Ti)
  - Traffic (Ce, Pt, Se, V)
  - Marine (Cl, K)
  - Industrial (Cr)
  - Fireworks (Sr)
  - Secondary Aerosol (S)
- Method
  - Hourly samples
  - Daily QA/QC checks at midnight
- Quality Assurance / Quality Control
  - Leak, flow & checks thin film standard tested before and after deployment
  - Filter blank run for >24 sample hours
  - Data blank corrected
- Limits of detection (LOD)
  - 3 x standard deviation of blank
  - Replaced data below LOD with LOD/2





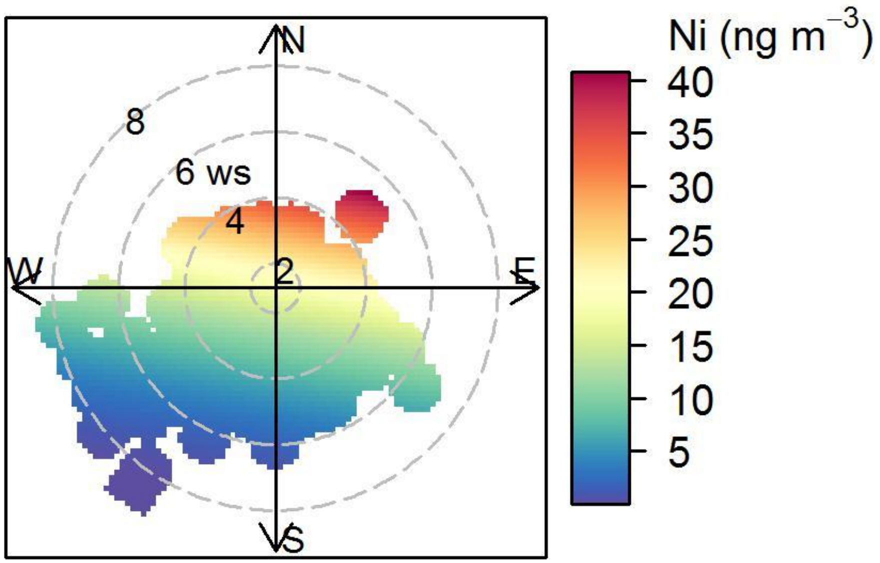


Slopes: 0.85 – 1.24

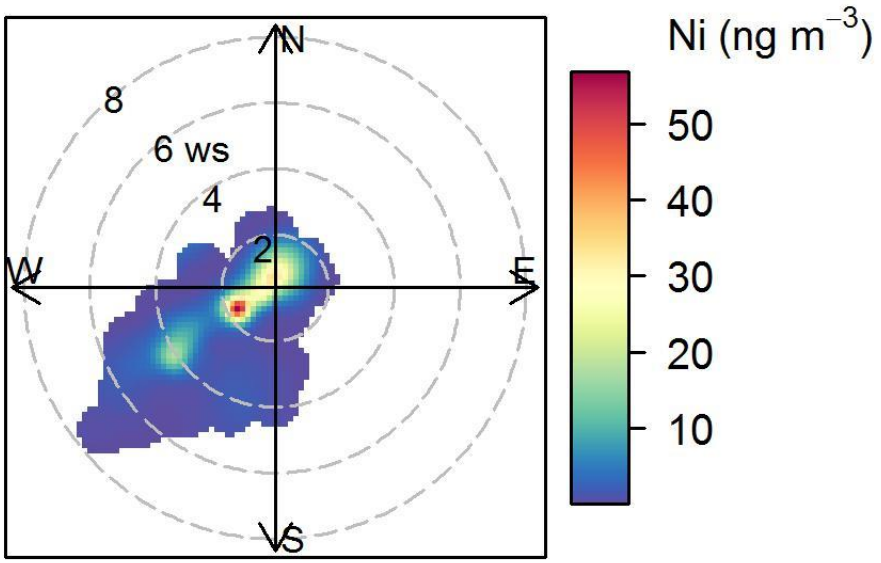
R^2 : 0.696 – 0.995

Impact of increased time resolution on understanding sources

Daily Means



Hourly Means



Methods – How do we extract source information of Ni from this data?

- Atmospheric information
  - Ni variation in over time of day, day of week
  - Ni variation in relation to meteorological conditions
  - Measurements and relationship between Ni and other tracers
- Source activity information
  - What is likely to be released alongside Ni, from where and when?
  - What are the likely ratio between Ni and different elements?
- Combine this information….

Methods - Wall Colmonoy source information

Composition alloys

NiCrBSiFe
NiPSiB
NiPSiCMoC
NiCrBSiFeC
NiSiB
NiCrBSiPFe
NiCrBSiFeW
FeCrNiSiMnMoB
NiCrP
NiCrPSi
CoWCCrFeMnMoSi

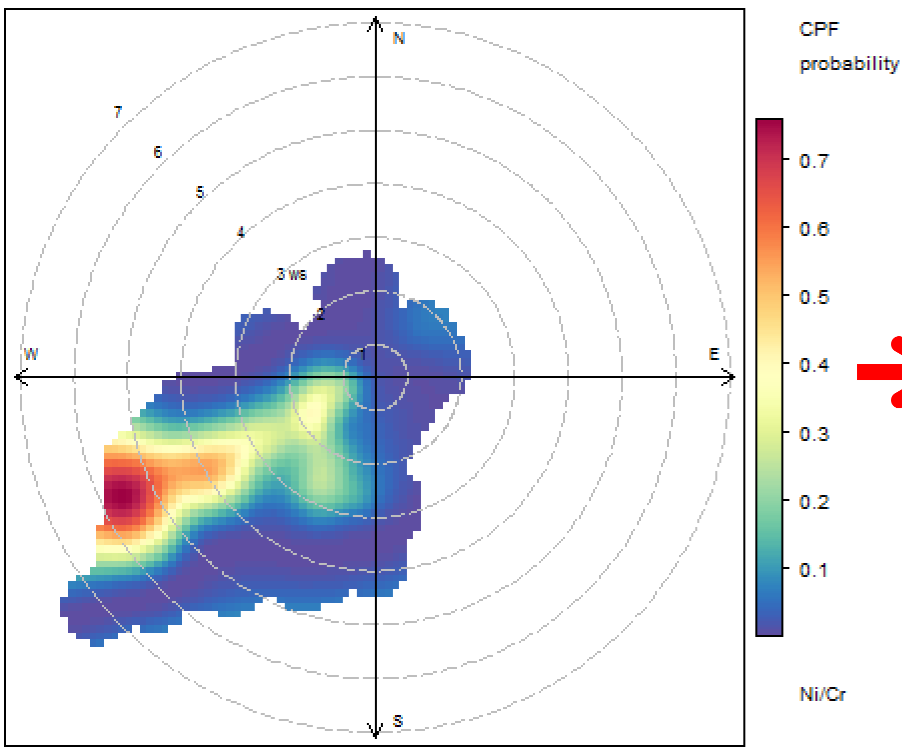
Most of alloys contain **Ni** and **Cr**

Ni/Cr ratio: **8:1 [4:1 - 21:1]**

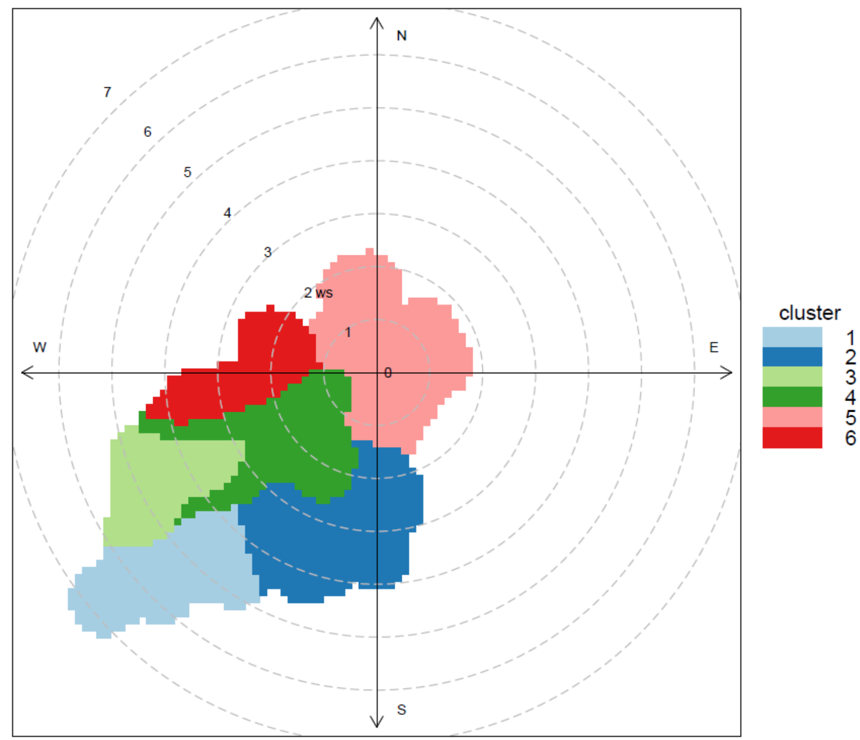
Melting 10 pm – 2 pm

Methods - Cluster analysis

- Assign each hourly measurement to a source of Ni
- **k-means** applied to bivariate polar plots (BPP). Cluster analysis **identify areas** in the BPP that have **similar features** in terms of **wind conditions and pollutant concentrations**



CPF at the 75th percentile (=14)



Methods – Cluster analysis

- Disadvantage: (subjective) choice of # clusters
- Criteria to chose the # clusters:
  - Ni/Cr ratios from WC cluster ~ emission ratios
  - Minimize the no. hours in the WC cluster with wind speed > 1.6 m s^{-1}

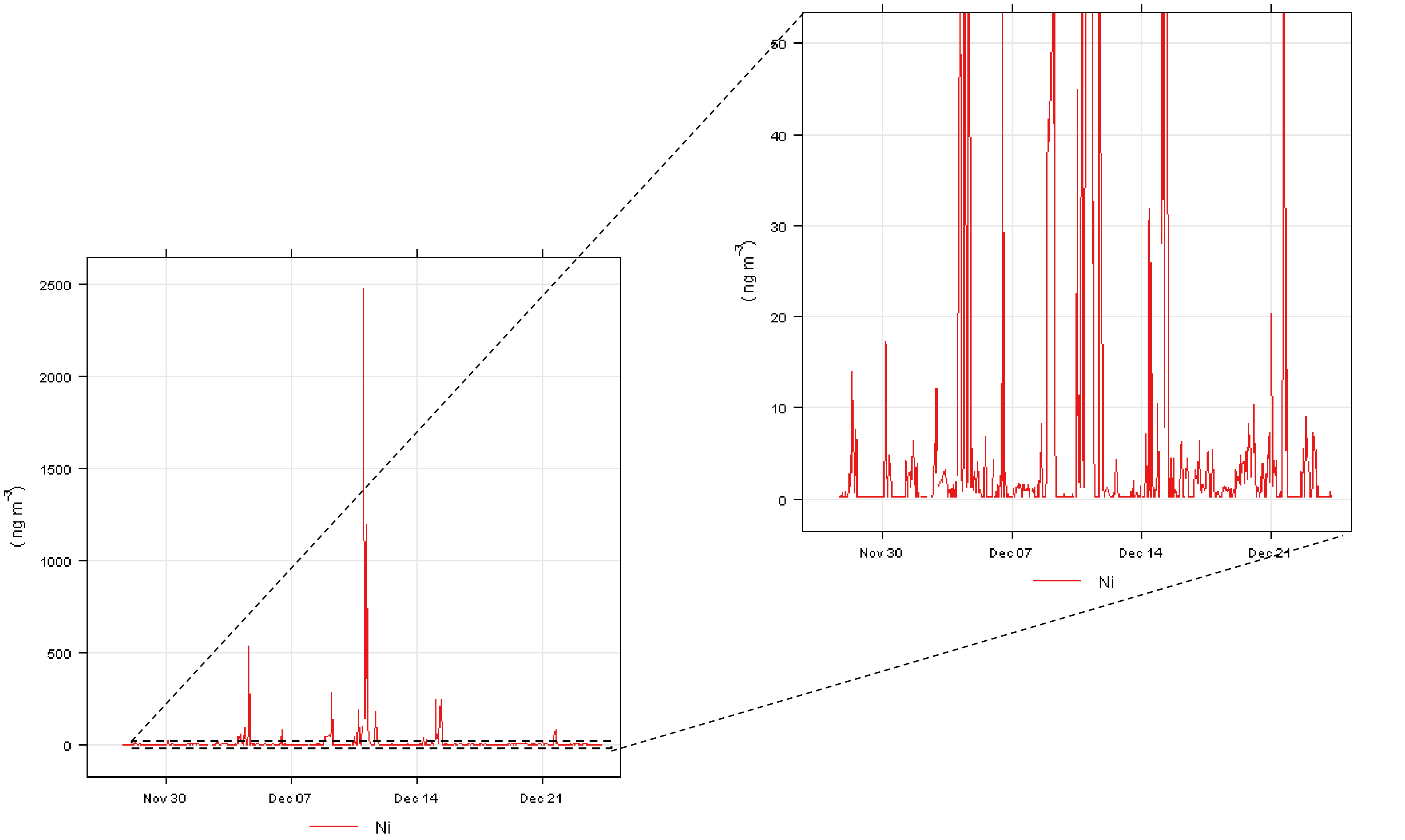
    (to exclude distal sources)
  - Minimize the no. of clusters with large Ni/Cr ratios

Results - Data Summary

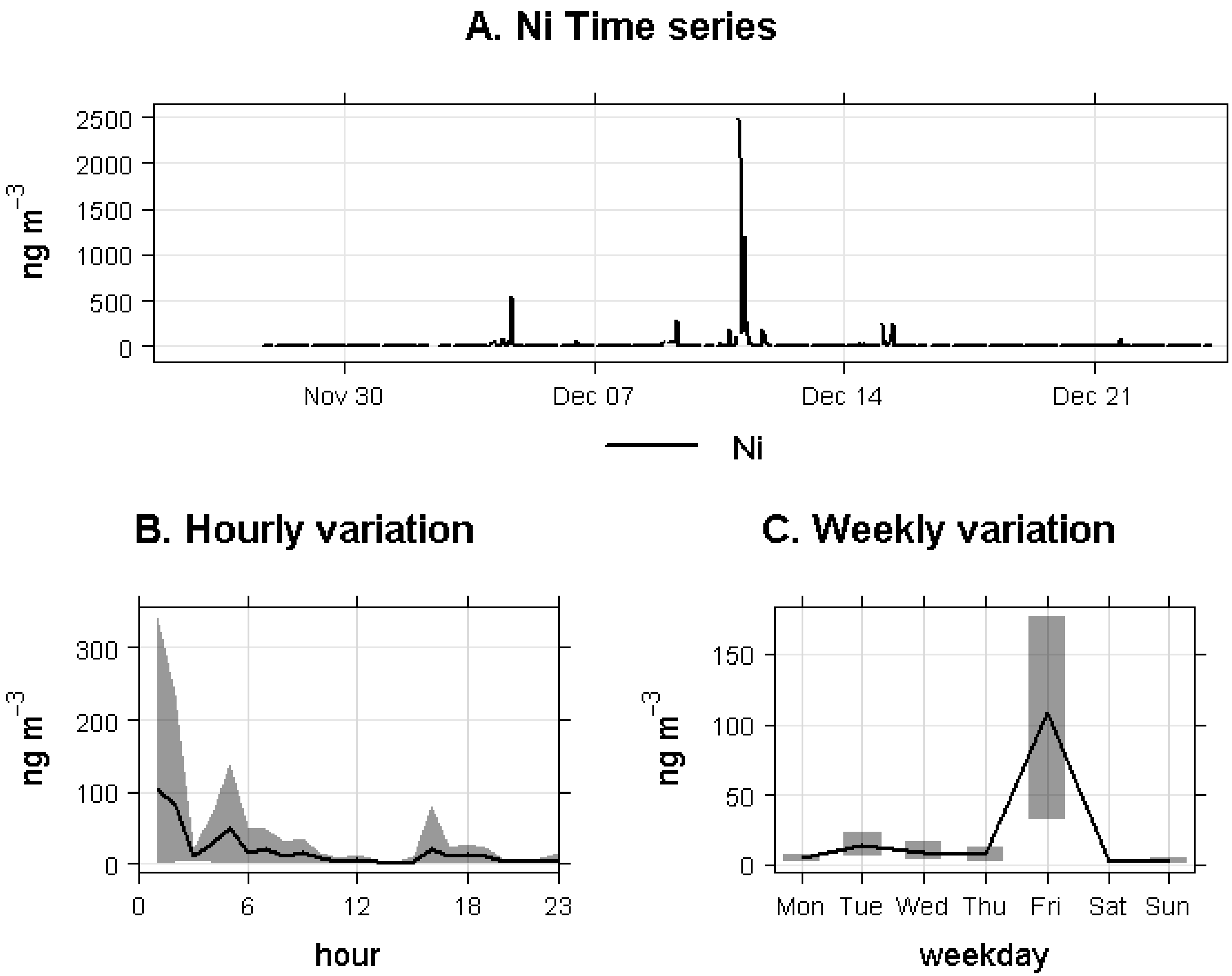
(ng m^{-3})

	XRF Hourly (Nov-Dec 2015)				XRF Daily (Nov-Dec 2015)				ICP MS Daily (Aug 15 – Jan 16)				2015
Element	**Mean**	**Median**	**Min**	**Max**	**Mean**	**Median**	**Min**	**Max**	**Mean**	**Median**	**Min**	**Max**	**Mean**
As	0.4	0.0	0.0	12.1	0.4	0.2	0.0	2.2	0.6	0.5	0.0	2.8	0.5
Ba	1.4	1.1	1.1	22.2	1.4	1.1	1.1	3.1					
Ca	186.1	144.9	3.6	4059.6	191.2	154.7	50.3	505.8					
Ce	0.8	0.4	0.4	4.9	0.9	0.8	0.5	1.9					
Cl	5082.2	4626.3	19.6	18419.3	5176.2	4962.9	333.4	12682.9					
Cr	1.6	0.1	0.1	84.8	1.6	0.4	0.1	9.8	5.1	2.4	0.2	23.5	5.6
Cu	3.8	2.3	0.4	53.3	3.8	3.9	0.7	8.9	5.4	4.4	0.2	29.1	5.2
Fe	220.0	98.3	8.1	3572.1	225.2	153.7	27.6	778.7	185.2	142.8	6.8	2210.0	186.4
K	151.2	132.1	3.4	694.1	154.1	138.2	82.5	340.7					
Mn	3.1	1.4	0.1	78.3	3.1	2.3	0.5	11.0	4.1	2.4	0.2	99.5	4.2
Mo	1.2	0.6	0.6	198.8	1.2	0.6	0.6	10.3					
Ni	**19.7**	**0.8**	**0.3**	**2475.6**	**20.4**	**2.5**	**0.3**	**319.2**	**18.9**	**6.3**	**0.0**	**420.6**	**23.6**
Pb	3.7	1.0	0.3	124.0	3.7	2.6	0.3	21.1	5.8	3.6	0.1	100.5	6.0
Pt	0.3	0.2	0.2	20.8	0.3	0.2	0.2	2.5					
S	518.6	443.6	5.3	1783.7	527.6	449.5	195.9	1125.9					
Se	0.2	0.1	0.1	10.1	0.2	0.2	0.1	0.9	0.7	0.7	0.0	1.9	0.7
Si	275.1	102.3	102.3	7304.9	283.9	102.3	102.3	1822.2					
Sr	2.5	1.9	0.4	13.0	2.5	2.2	0.5	6.3					
Ti	8.4	1.5	0.5	168.9	8.7	2.8	0.6	65.5					
V	1.1	0.2	0.2	11.3	1.1	0.5	0.2	4.3	0.6	0.3	0.0	7.0	0.6
Zn	7.2	2.9	0.3	147.3	7.3	5.3	0.6	33.8	9.3	6.6	0.1	58.9	10.0

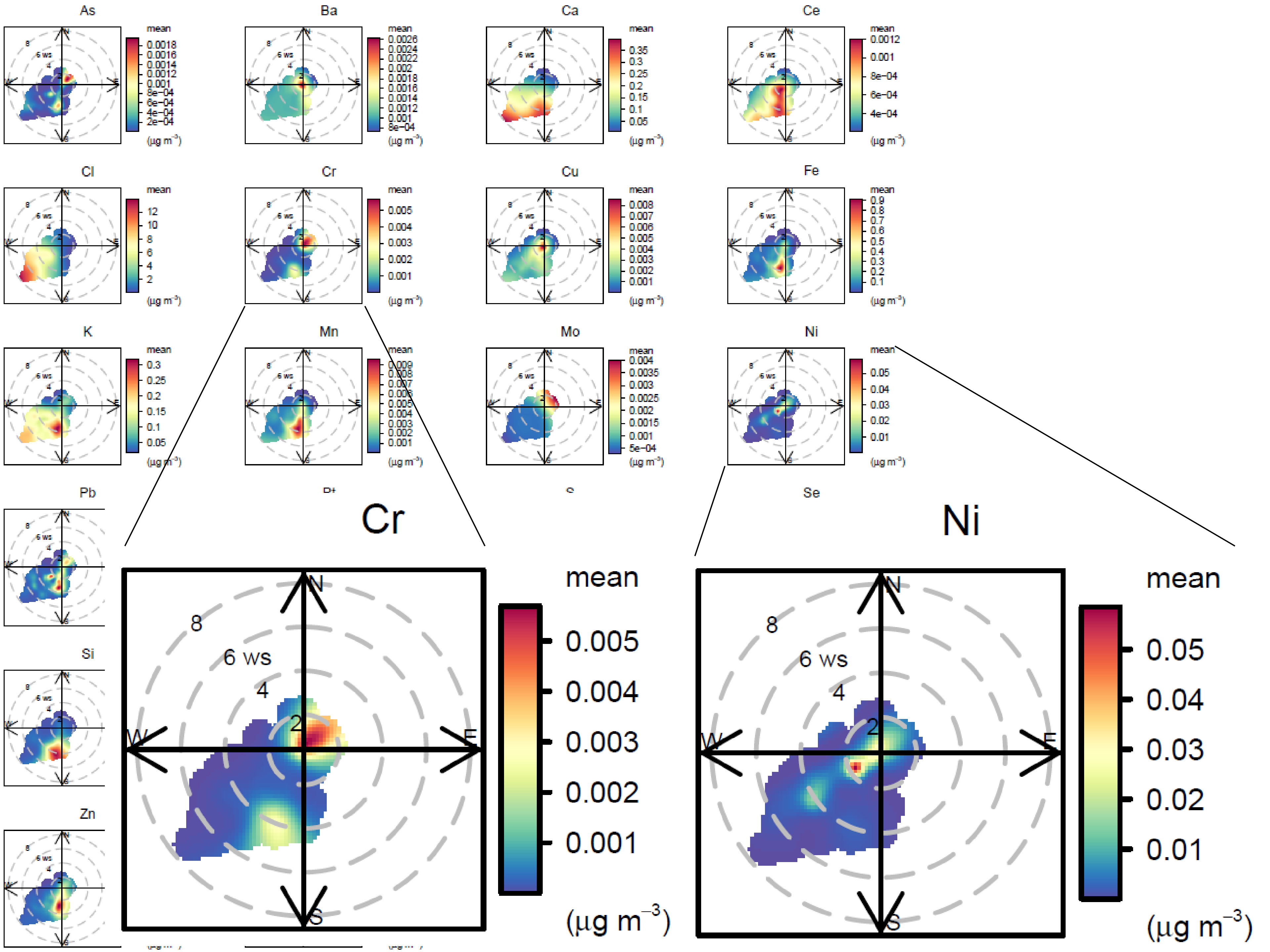
Results - Ni hourly time series



Results – Hourly and weekly variation

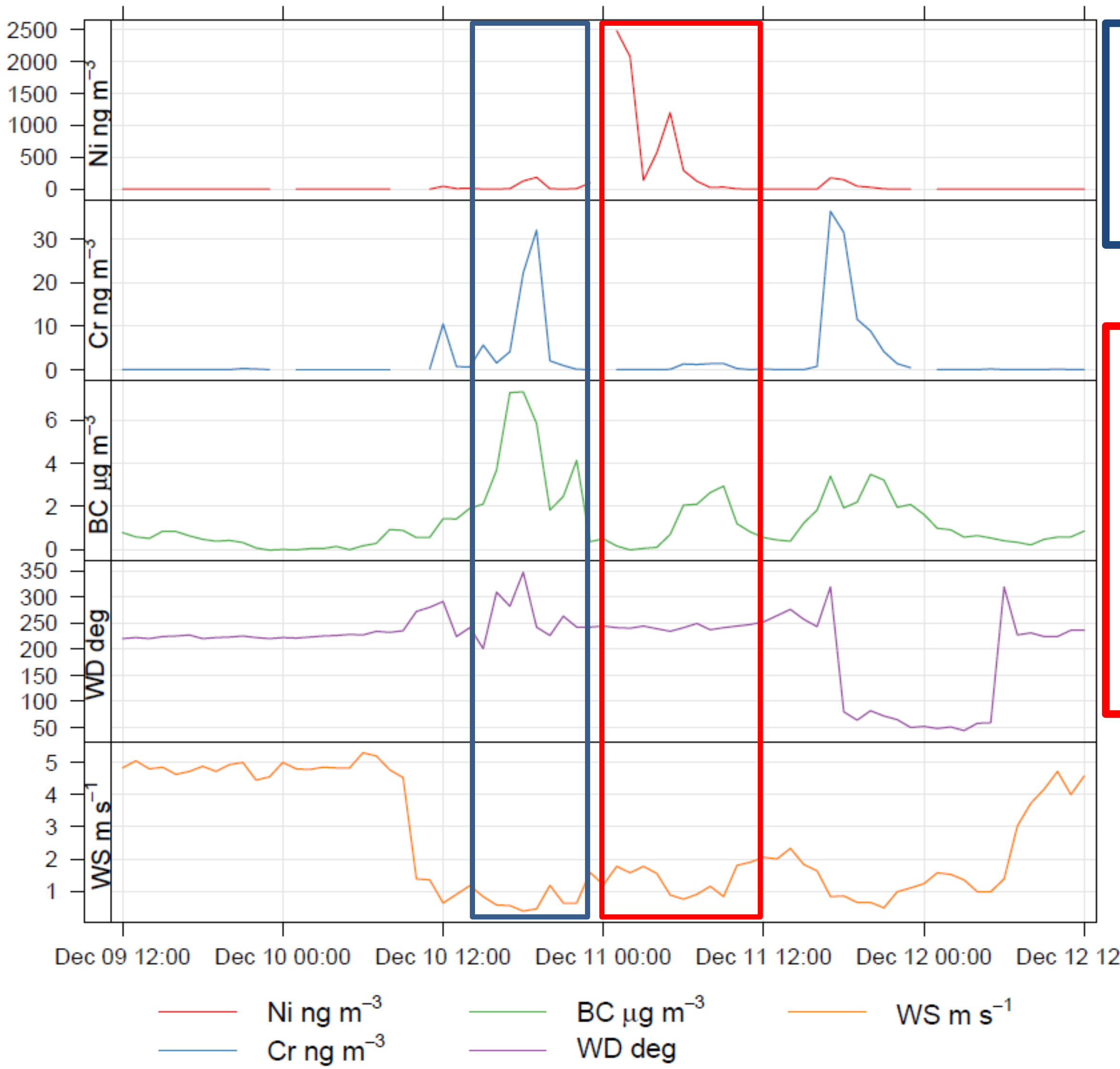


- The **diurnal** and **weekly variation** strongly **influenced** by the **single peak** in the early hours on Friday Dec 11th.
- Concentrations on **weekends lower** than **weekdays**.



As
Ba
Ca
Ce
Cl
Cr
Cu
Fe
K
Mn
Mo
Ni
Pb
Si
Se
Zn
Cr
mean
0.005
0.004
0.003
0.002
0.001
(μg m⁻³)
Ni
mean
0.05
0.04
0.03
0.02
0.01
(μg m⁻³)

Results - Peak event on 11th Dec 2015



Ni ~ 180 ng m^{-3} & Cr ~ 30 ng m^{-3}; wind was blowing from 360 degrees at wind speeds < 1.0 m s^{-1}

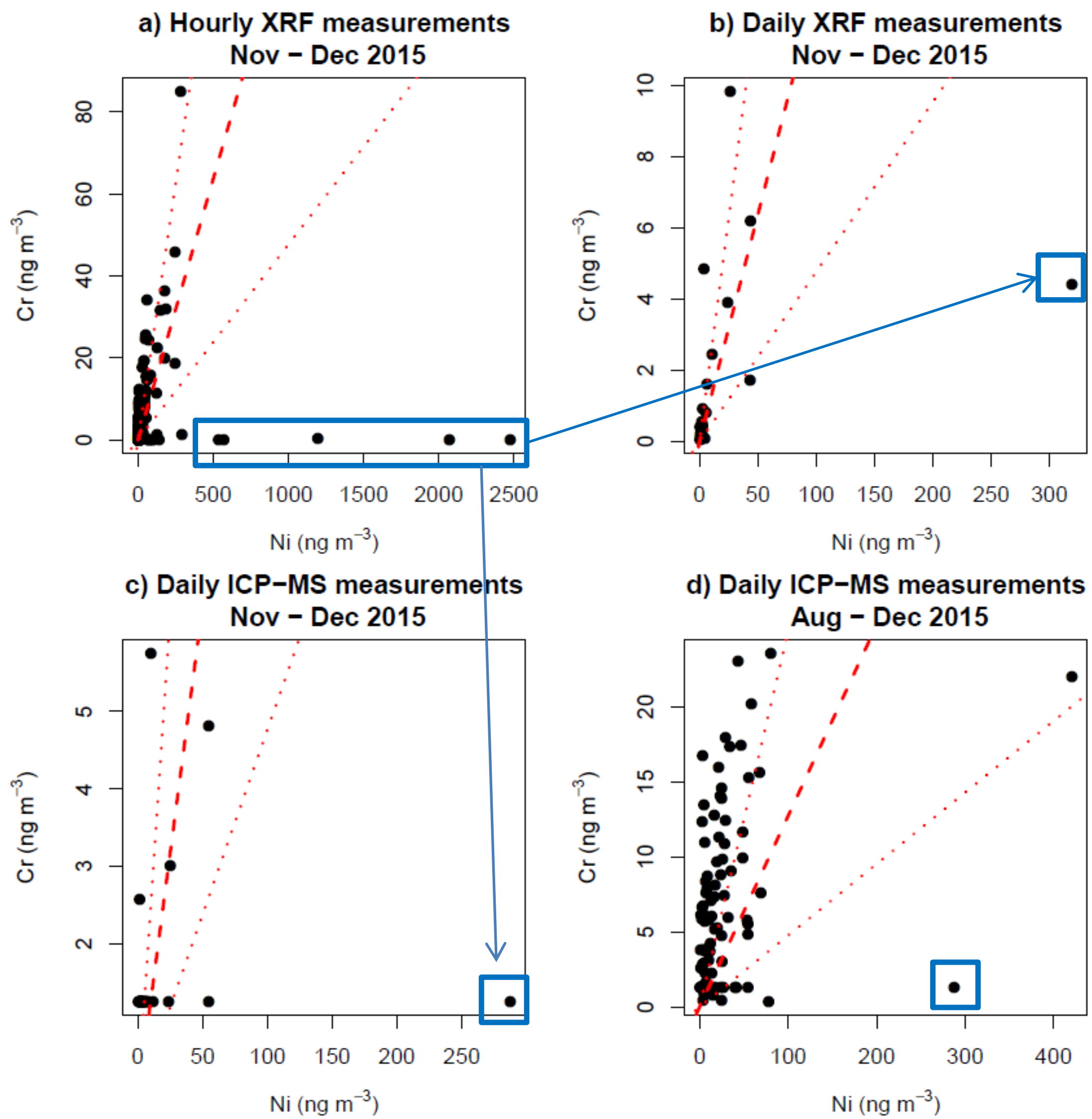
Ni peaked at 2500 ng m^{-3} at 1:00 am while Cr concentrations ~ 0 ng m^{-3}; wind was blowing from 240 degrees at wind speeds > 1.5 m s^{-1}

Air was clean (no BC or NO_X)

Results - Peak event as observed hourly/daily data

Ni / Cr
Wall
Colmonoy
alloys

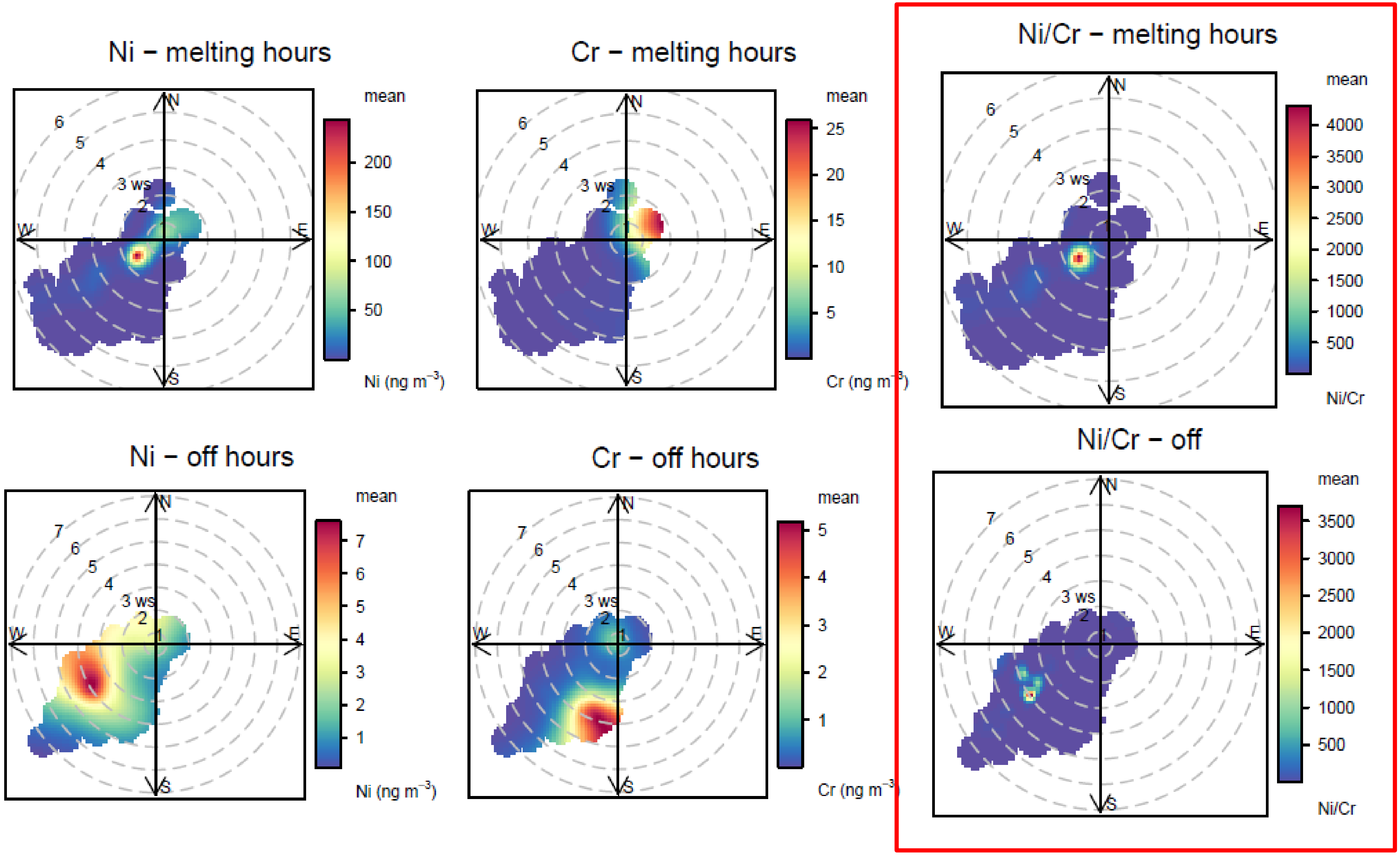
11th Dec 2015



ICP-MS LOD
(2.52 ng m^{-3}) for Cr

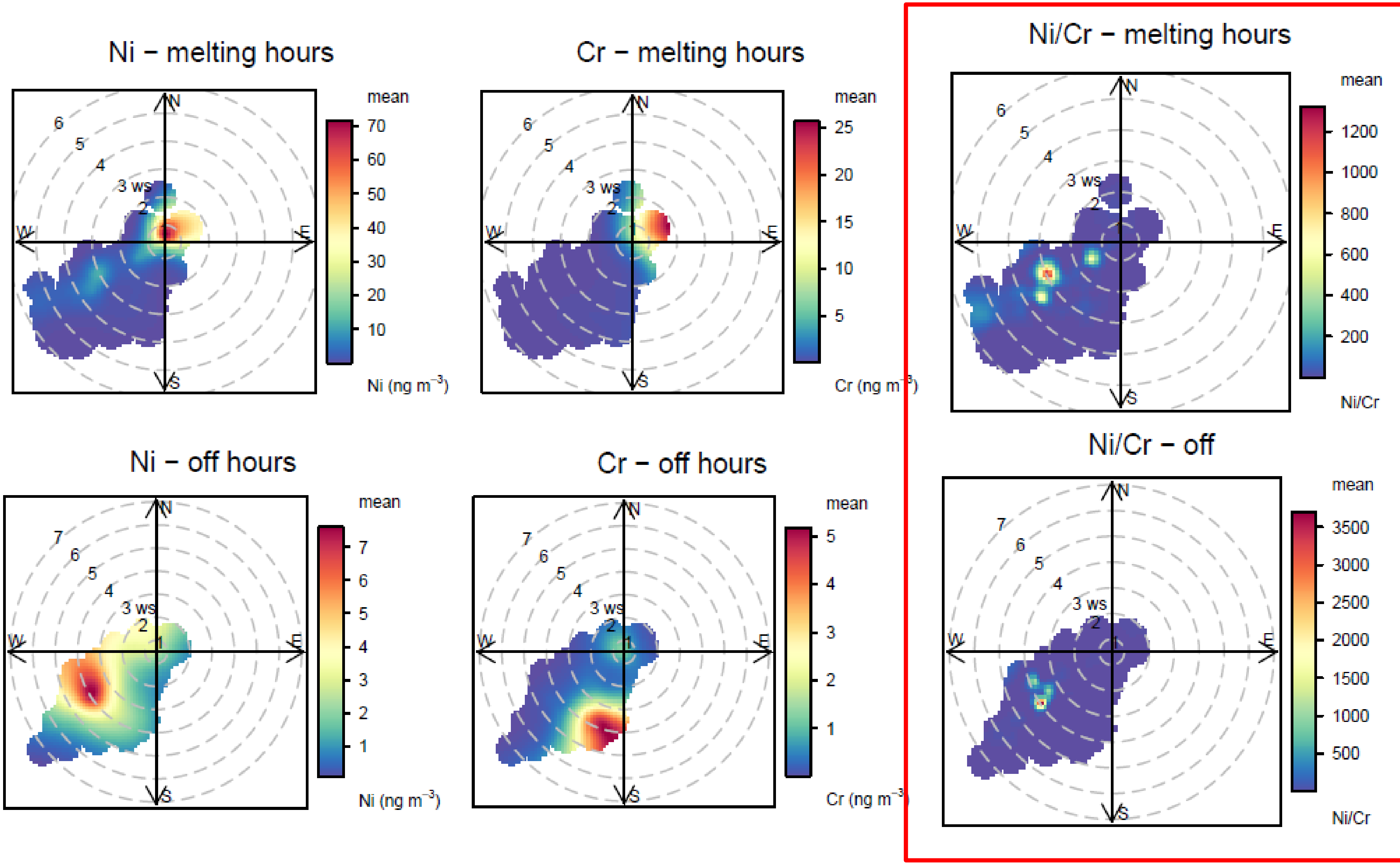
Results - Polar Plots Ni/Cr ratios

Plume Grounding

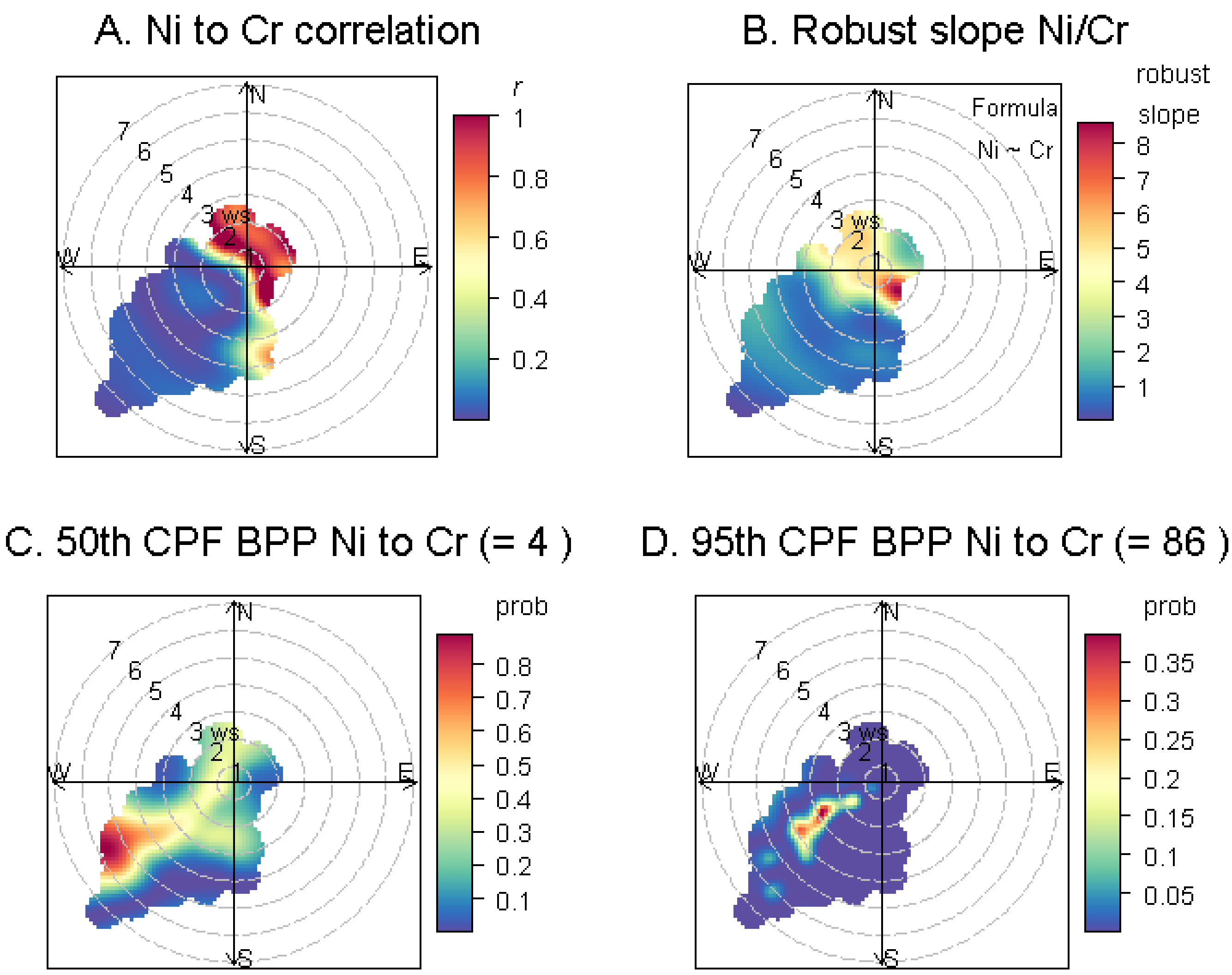


Results - Polar Plots Ni/Cr ratios peak event removed

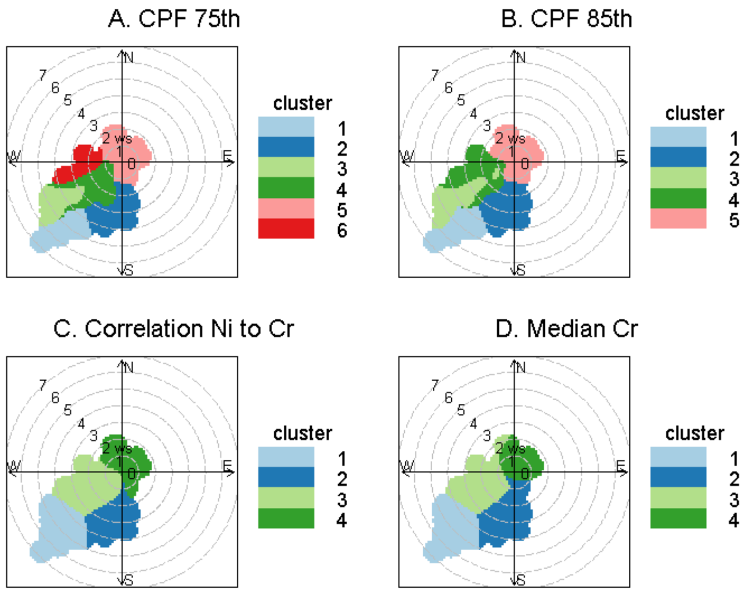
Plume Grounding



Results – Ni and Cr sources

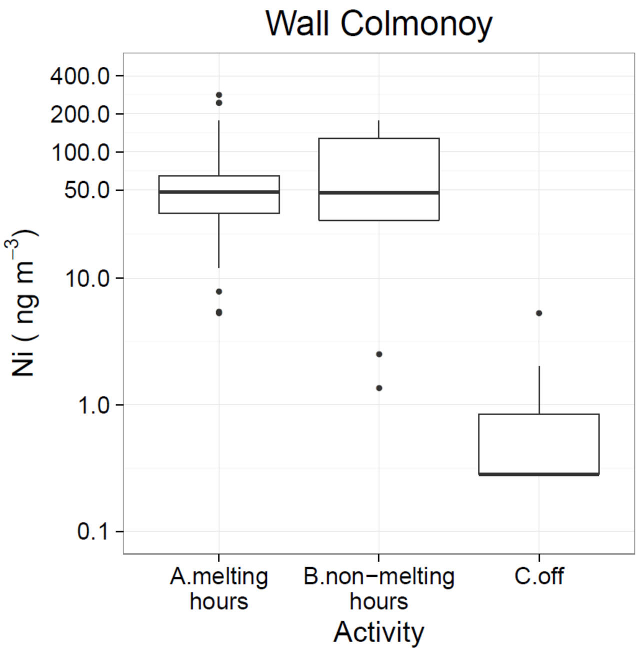


Results – Cluster analysis

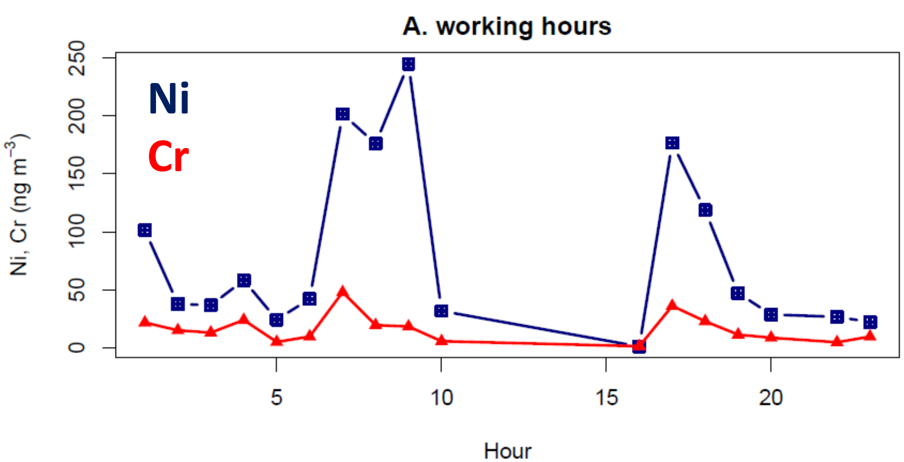


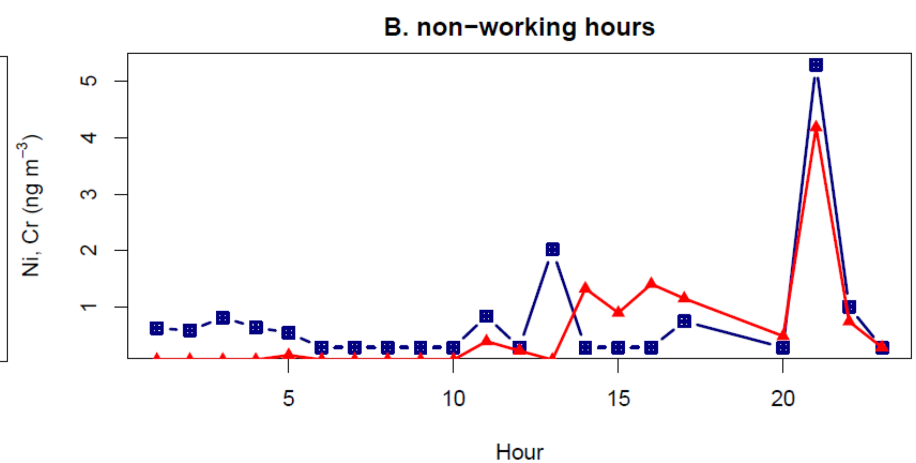
Cluster analysis	BPP 75th CPF Ni/Cr	BPP 85th CPF Ni/Cr	R Ni to Cr	Median Cr
# hours WC	86	86	70	64
Contribution WC (%)	23.8	23.8	21.4	21.9
# hours SW-background	207	169	282	265
Contribution SW-background (%)	7.5	7	0.3	16
# hours SW-peaks	16	16	16	16
Contribution SW-peaks (%)	66.7	66.7	66.7	66.7
# hours S	98	131	133	64
Contribution S (%)	1.2	1.6	1.6	4

Results - Identification of WC activities



	Melting hours	Non-melting hours	Off
Mean Ni (ng m^{-3})	75.7	71.6	0.74
Median Ni (ng m^{-3})	47.9	47.3	0.28
Max Ni (ng m^{-3})	281.9	176.6	5.3
No. hours	23	9	28
Contribution (%)	72.3	26.8	0.9



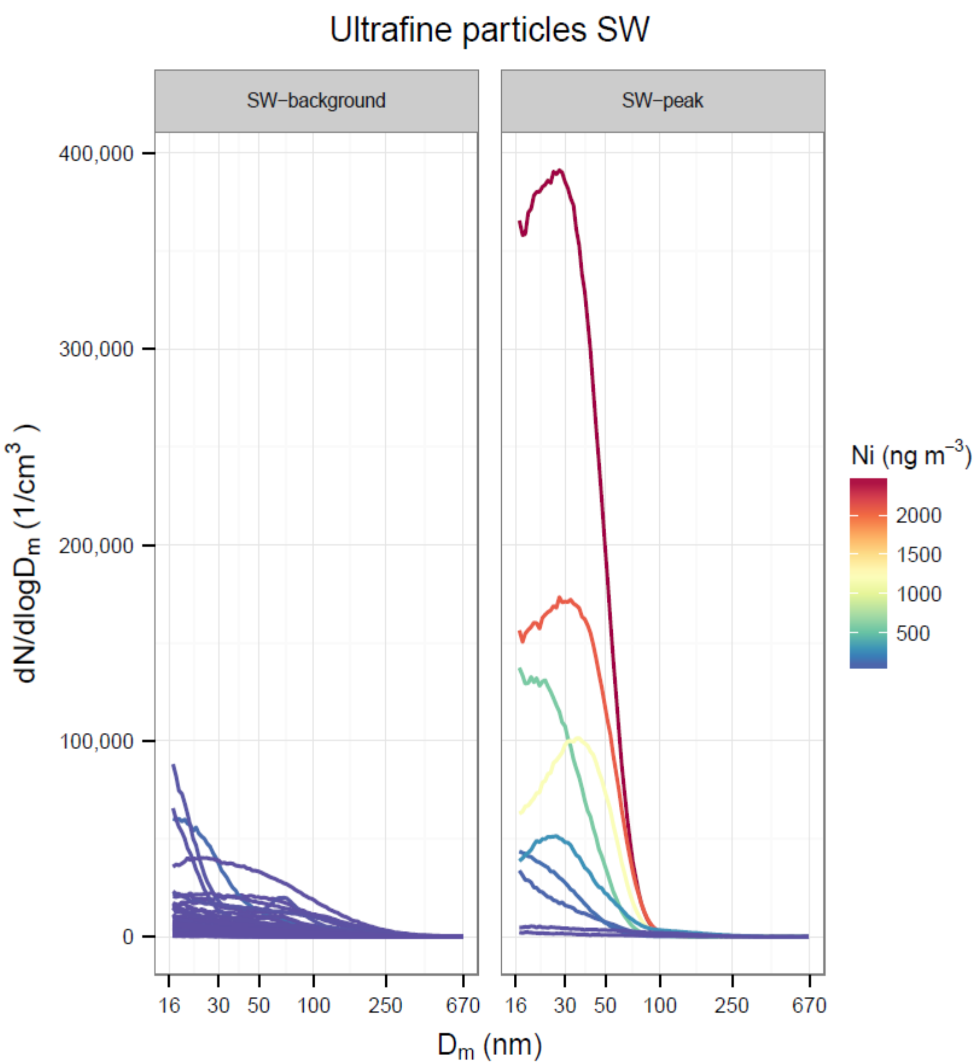


Results - Transient plumes from the SW

Date	Wind speed ($m\ s^{-1}$)	Wind dir (deg N)	Ni ($ng\ m^{-3}$)	Cr ($ng\ m^{-3}$)
04-Dec 10:00	3.0	238	95.47	0.06
04-Dec 11:00	3.5	230	65.28	0.06
04-Dec 15:00	3.5	234	72.97	0.06
04-Dec 16:00	4.0	229	534.13	0.06
06-Dec 10:00	3.8	235	12.66	0.06
06-Dec 12:00	3.6	243	76.72	0.06
08-Dec 13:00	5.2	233	8.29	0.06
10-Dec 23:00	1.6	237	97.92	0.06
11-Dec 01:00	1.8	236	2475.55	0.06
11-Dec 02:00	1.6	235	2069.55	0.06
11-Dec 03:00	1.8	239	139.97	0.06
11-Dec 04:00	1.6	234	569.54	0.06
11-Dec 05:00	0.9	229	1195.55	0.13
11-Dec 06:00	0.8	236	291.89	1.35
21-Dec 21:00	2.0	237	14.21	0.06
22-Dec 22:00	3.2	237	9.06	0.06

Peaks of Ni from the **SW** were characterized by **large Ni** signal but **depleted in Cr**

Results - Particle size distribution



- **Peaks of Ni** from the **SW** were associated with very **high particle counts** (>100,000 as dN/dlogD_m) with diameters of D_m~ **20-30 nm**
- **Low number of particle counts** from the **SW** under **background conditions** (<100,000 with the majority < 2,000).

Summary

- **MARPL** deployed in **Pontardawe Tawe Terrace** Nov-Dec 2015
- Measurements of **metals at hourly resolution**
  - Good correlation with daily filters measured by ICP-MS by NPL
- **Extra information** is gained when sampling at higher time resolution.
  - **Identification of short peak events** with different metal composition
  - Short-term peaks were masked when analyzing daily means
  - Relate **ambient concentrations to process activity**

Summary

- **Winds from the N** were **rich in Ni and Cr** consistent with **Wall Colmonoy's** activities
- Identified **peaks of Ni** when the wind blew from the **SW** at very high wind speeds. These peaks were very **high in Ni but low in Cr**; and also had **very high concentrations of small particles** (20-30 nm in diameter)

Summary

- **Quantified the Ni source areas** in the Tawe Terrace Nov – Dec '15
  - **Wall Colmonoy**: contributed **~22-24%**
  - **SW-peaks: ~67%**
  - **SW-background: 0.3-16%**
  - **S: 1-4%**
- Only conditions experienced during the campaign can be assessed; **longer time series** with **high-time resolved metals data** needed to calculate contribution of sources to annual mean

Acknowledgements

- Funding bodies
  - Welsh Government - Identifying Key Sources of Emissions (C224/2015/2016)
  - Defra Contract AQ0643 Automatic London Network (2010-14) RMP 5442
  - UK Natural Environment Research Council grants - Clearflo (NE/H003231/1) and Traffic (NE/I008039/1)

Thank you for listening

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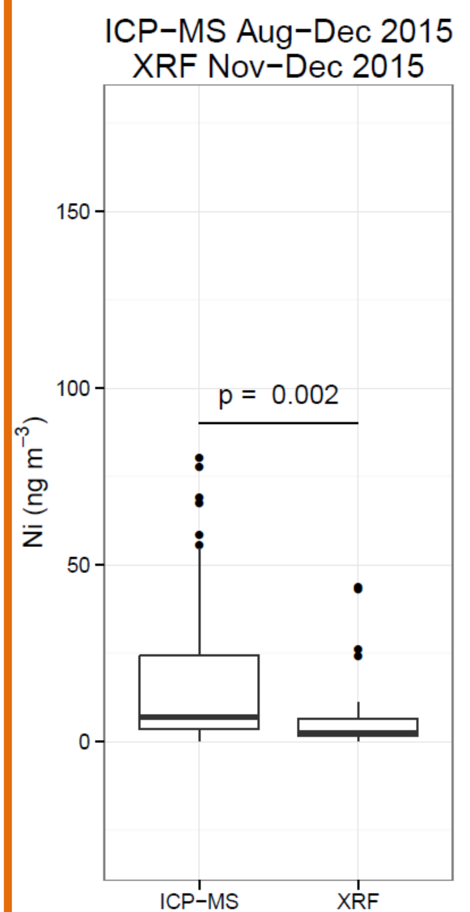
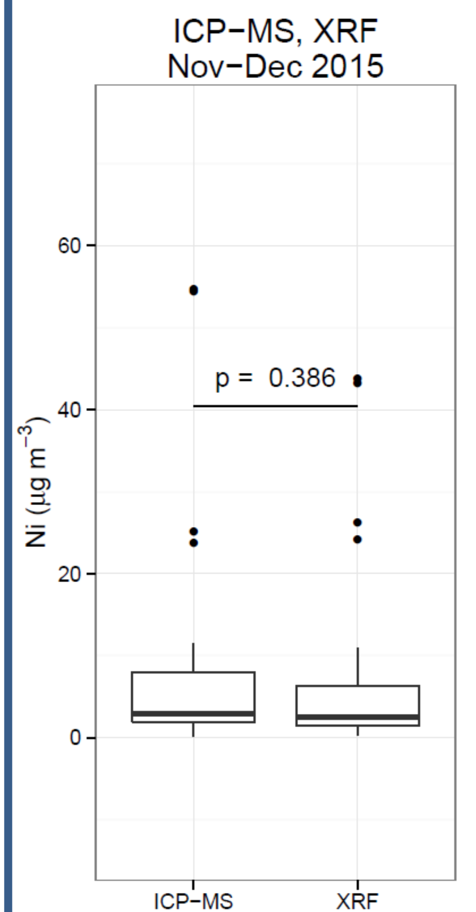
SUPPLEMENTARY SLIDES

Relationship between XRF and ICPMS

Daily measurements by ICP-MS between Aug-Dec and daily measurements by XRF between Nov – Dec' 15 were ***statically different***

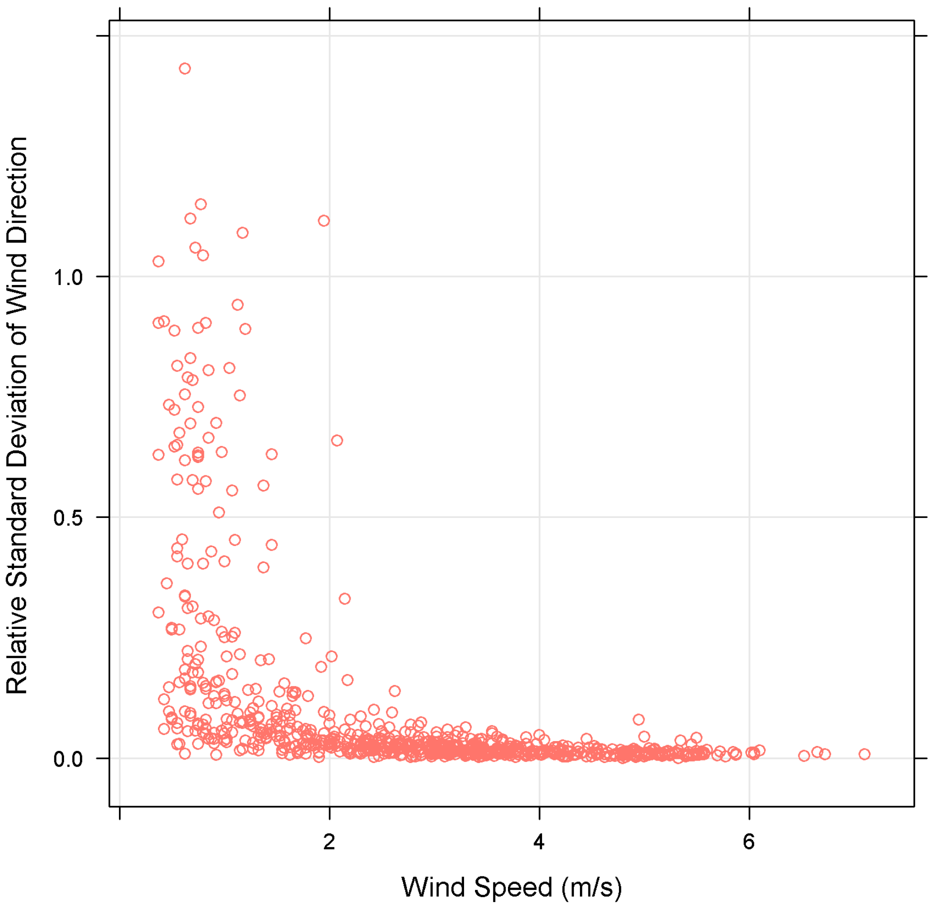


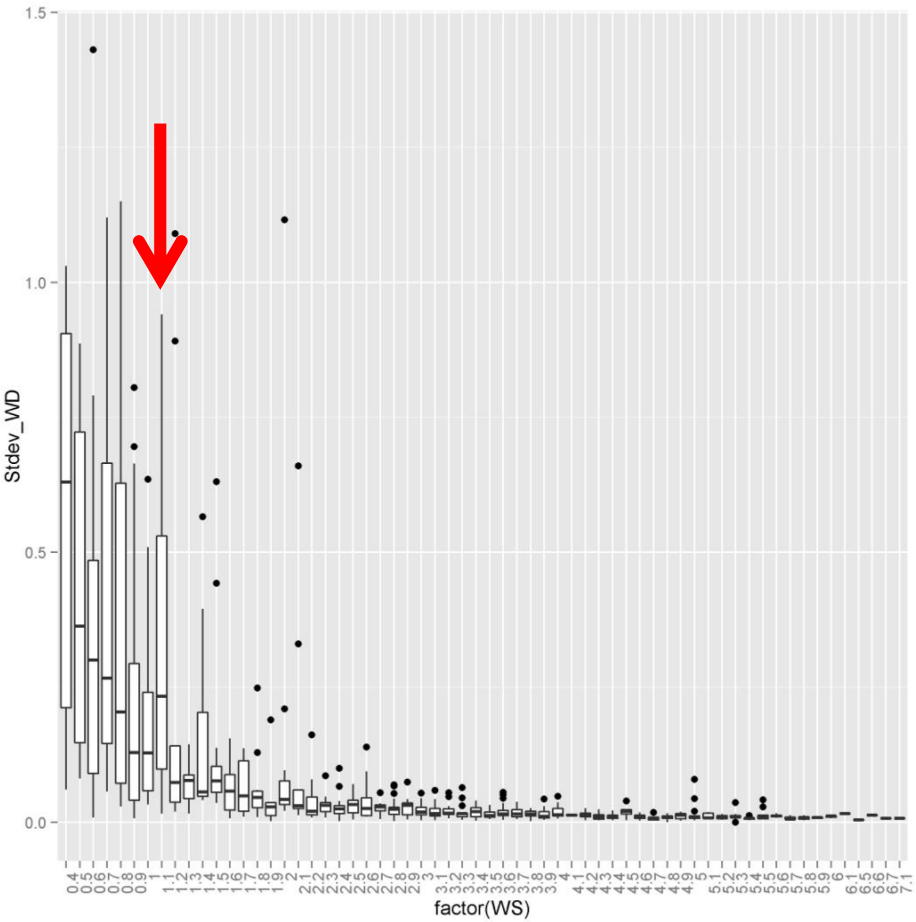


Daily measurements by both ICP-MS and XRF ***were statistically the same*** between Nov – Dec' 15

Ni (ng m^{-3})	Min	1st Q	Median	Mean	3rd Q	Max
ICP-MS (1st Aug – 23rd Dec)	0.19	3.39	6.82	20.92	24.26	420.60
XRF (28th Nov – 23rd Dec)	0.28	1.50	2.49	20.44	6.36	319.20

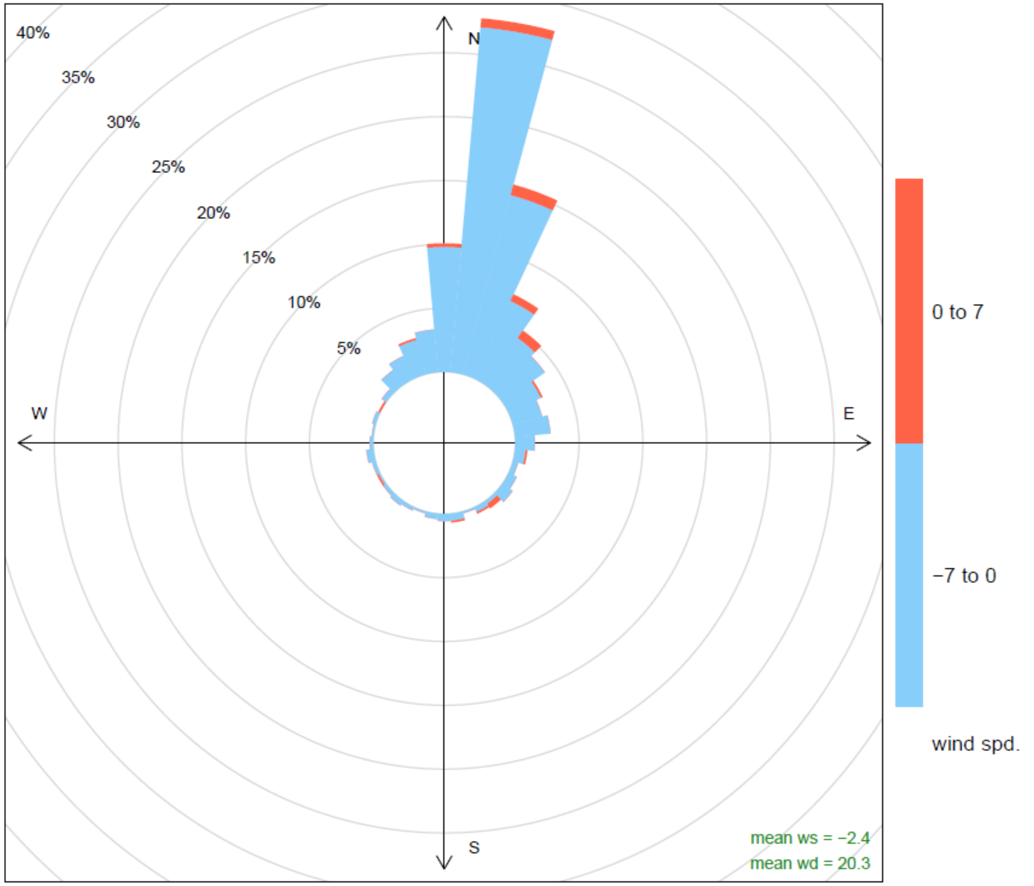
Sensitivity test wind data





Wind direction significant whenever wind speeds > 1m/s

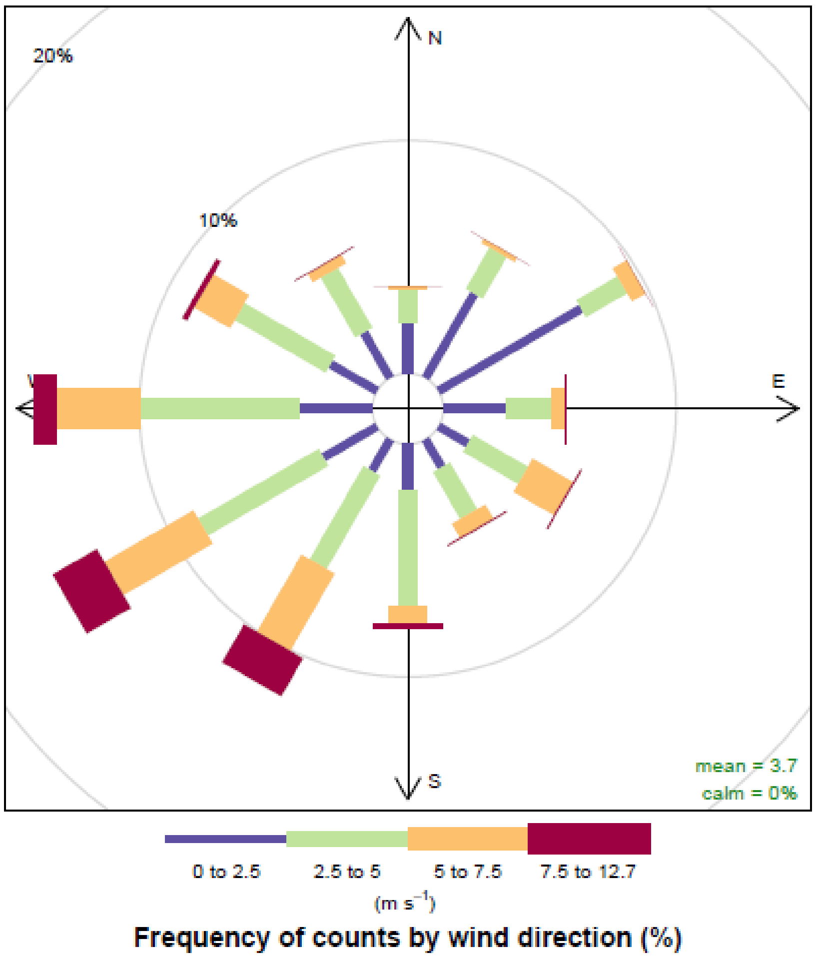
Meteorological Measurements



Frequency of counts by wind direction (%)

Meteorological Measurements

Swansea



Pontardawe