

Sources of Nickel in Pontardawe

6th October 2016

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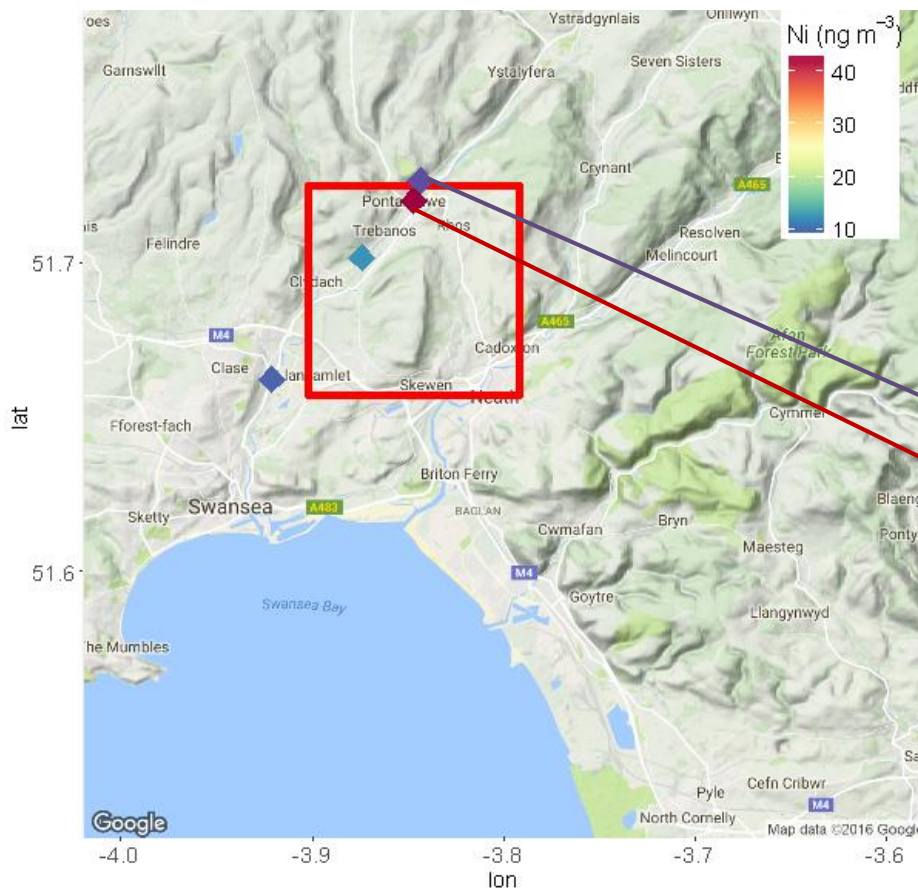
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³ University of York

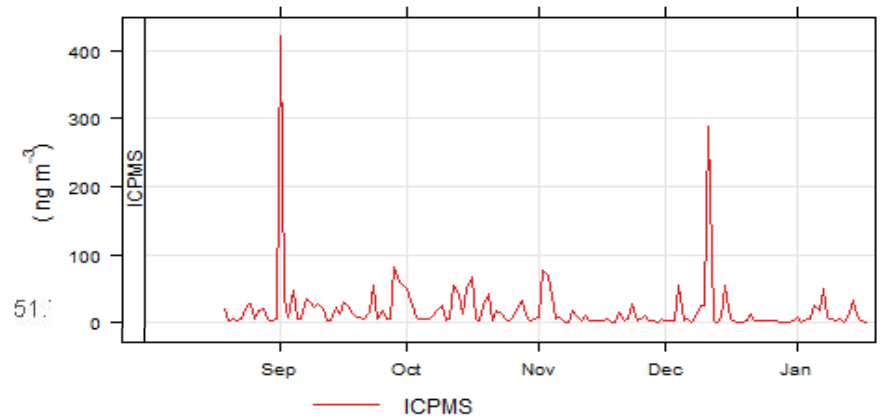
Background

EU Target Value: **20 ng m⁻³**

2014 annual Ni concentrations

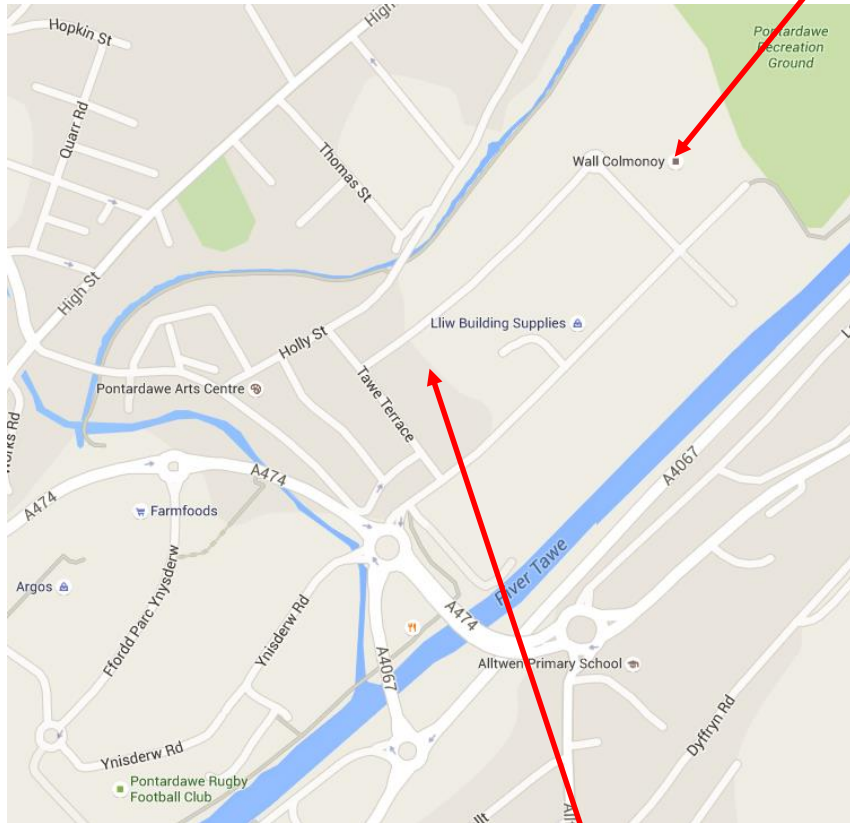


NPL measuring daily filters since August 2015

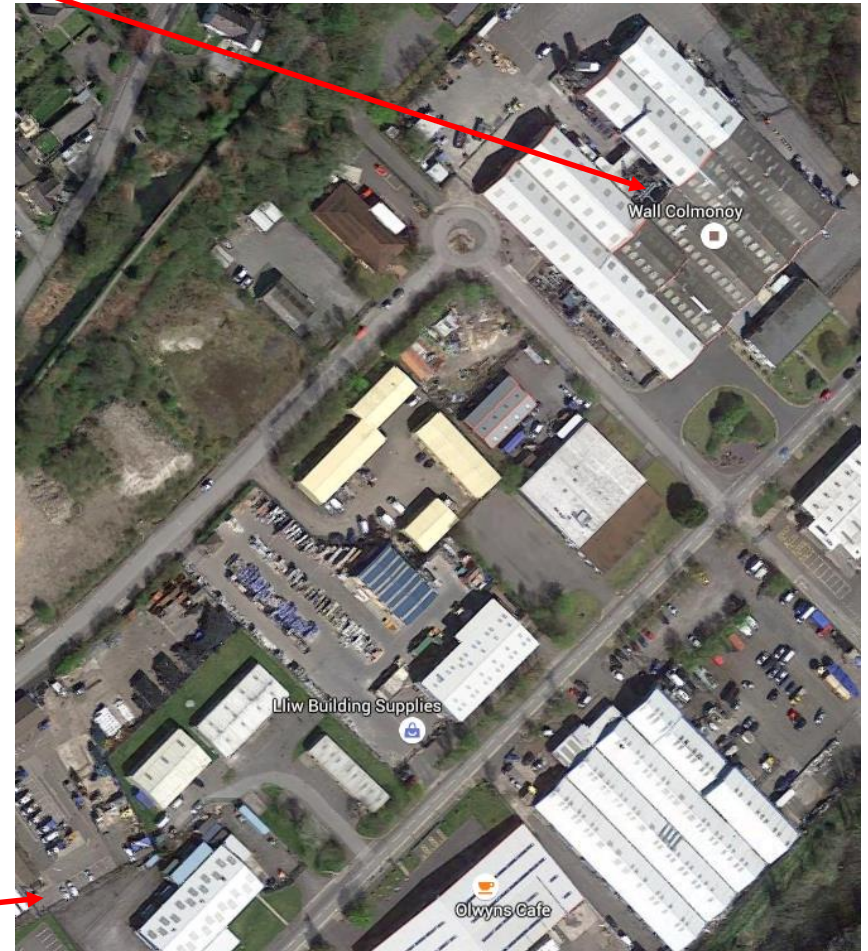


Background

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)

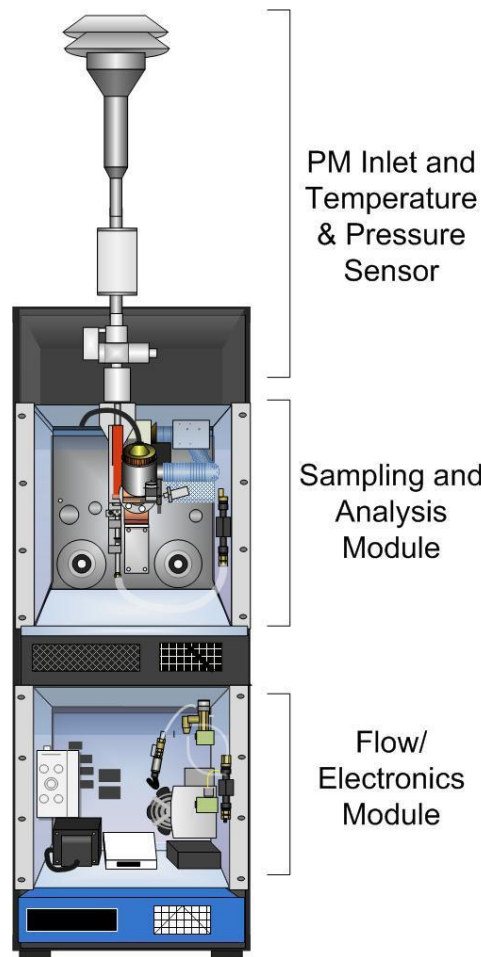
INSTRUMENTATION AT MARPL

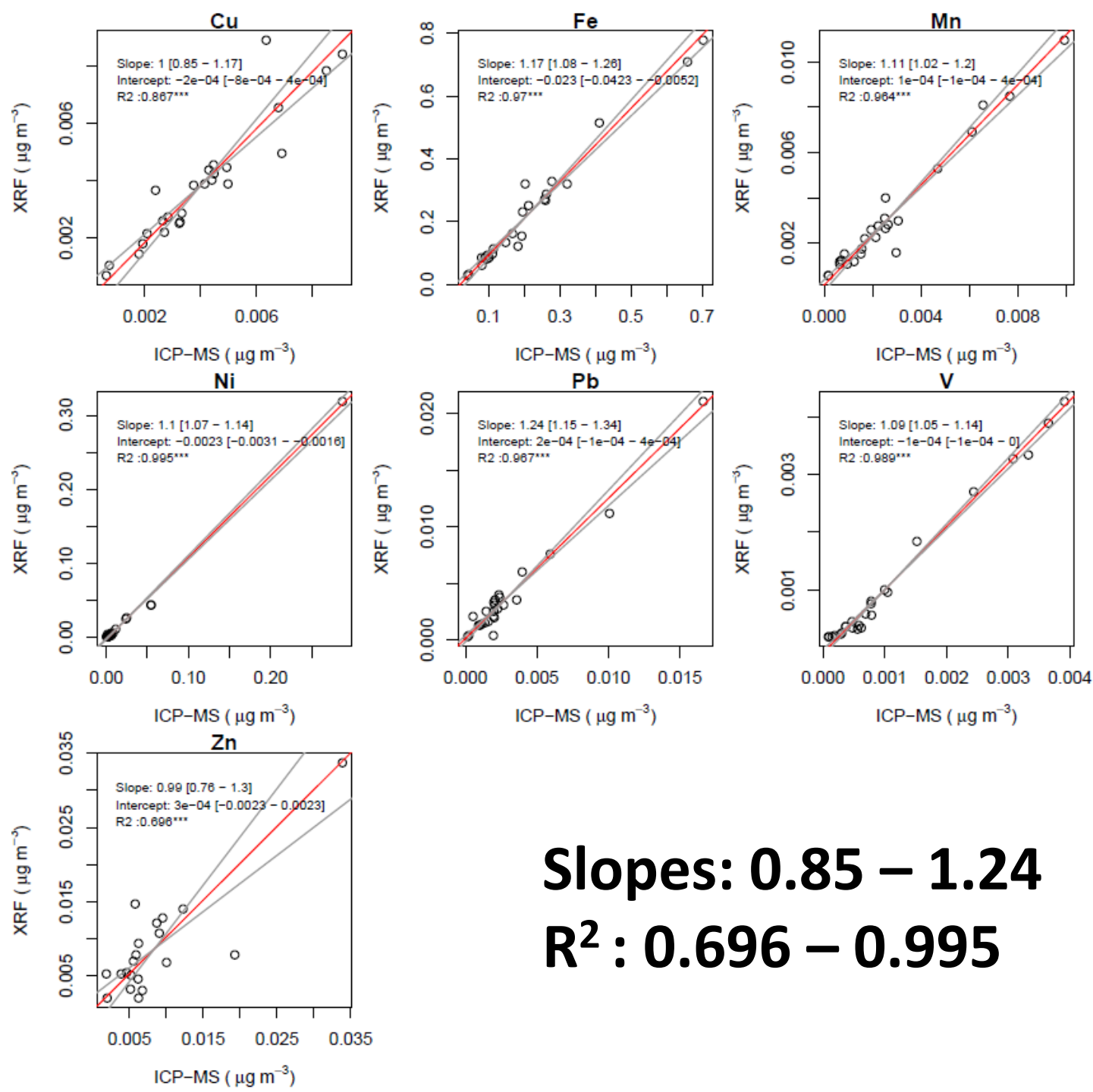
- 23 metals at hourly resolution (XRF)
- Black Carbon (Aethalometer)
- NO_x (NO + NO₂) (Blue Light Converter)
- Met data: wind, RH, TEMP (10 m mast)



Methods - XRF Measurements

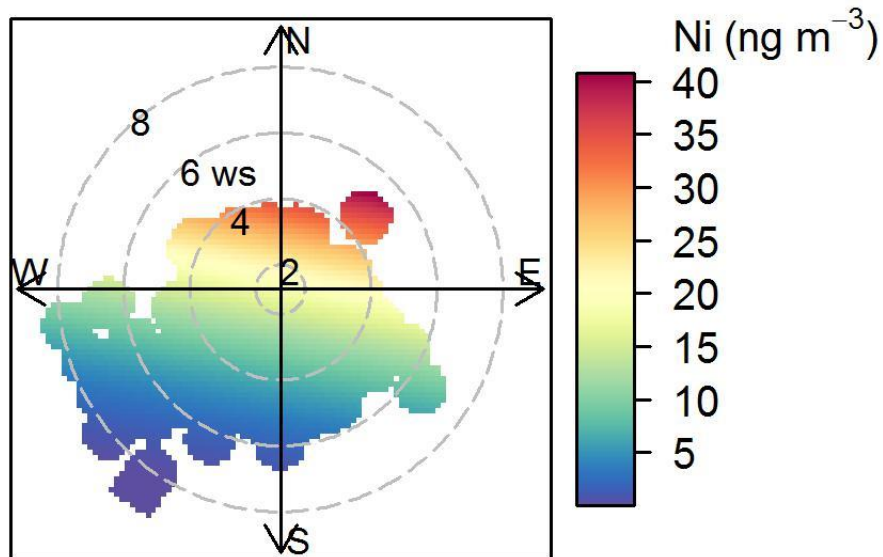
- Elements
 - Regulatory (Ni, As, Cd, Pb),
 - Abrasion (Ba, Cu, Sb, Zn),
 - Mineral (Ca, Fe, Mn, Mo, Si, Ti)
 - Traffic (Ce, Pt, Se, V)
 - Marine (Cl, K)
 - Industrial (Cr)
 - Fireworks (Sr)
 - Secondary Aerosol (S)
- Method
 - Hourly samples
 - Daily QA/QC checks at midnight
- Quality Assurance / Quality 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



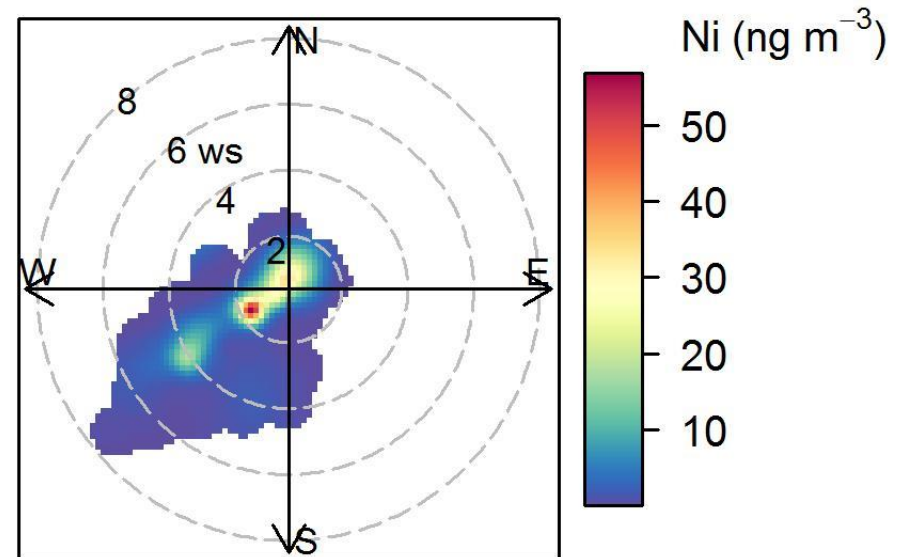


Impact of increased time resolution on understanding sources

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

CoWCrFeMnMoSi

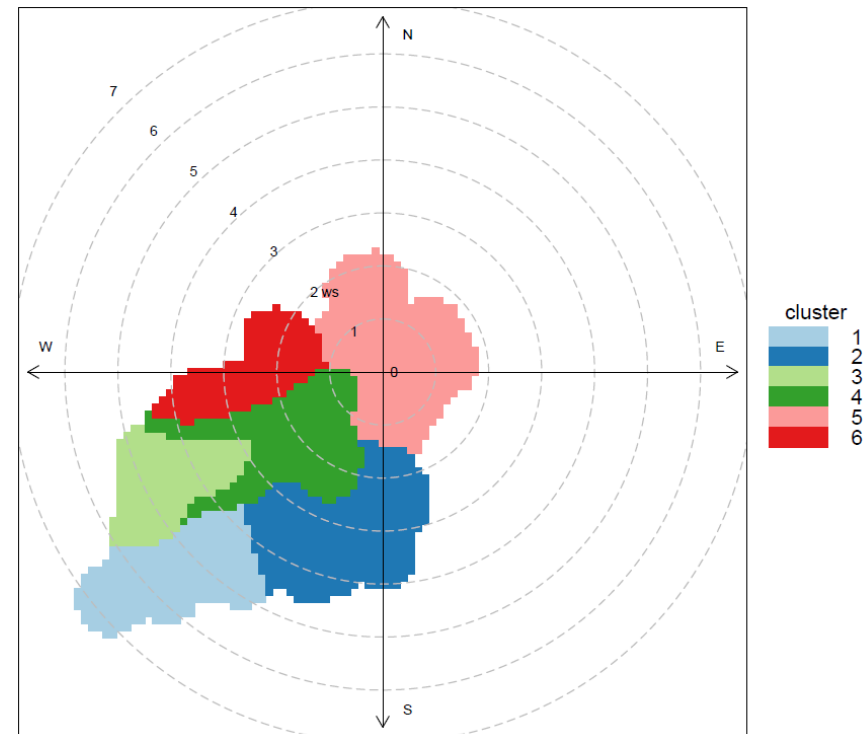
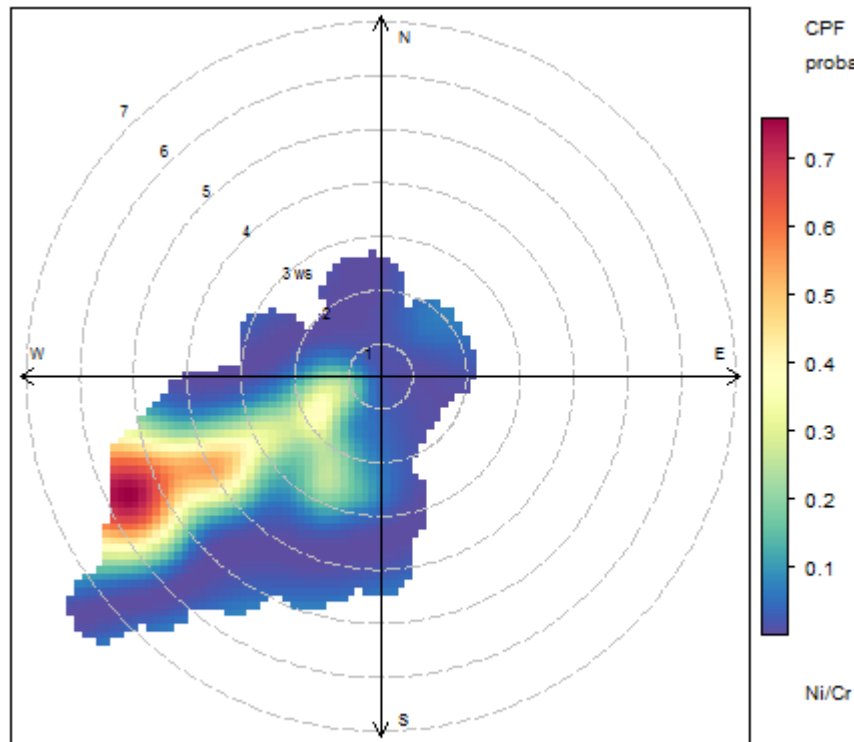
Most of alloys contain **Ni** and **Cr**

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

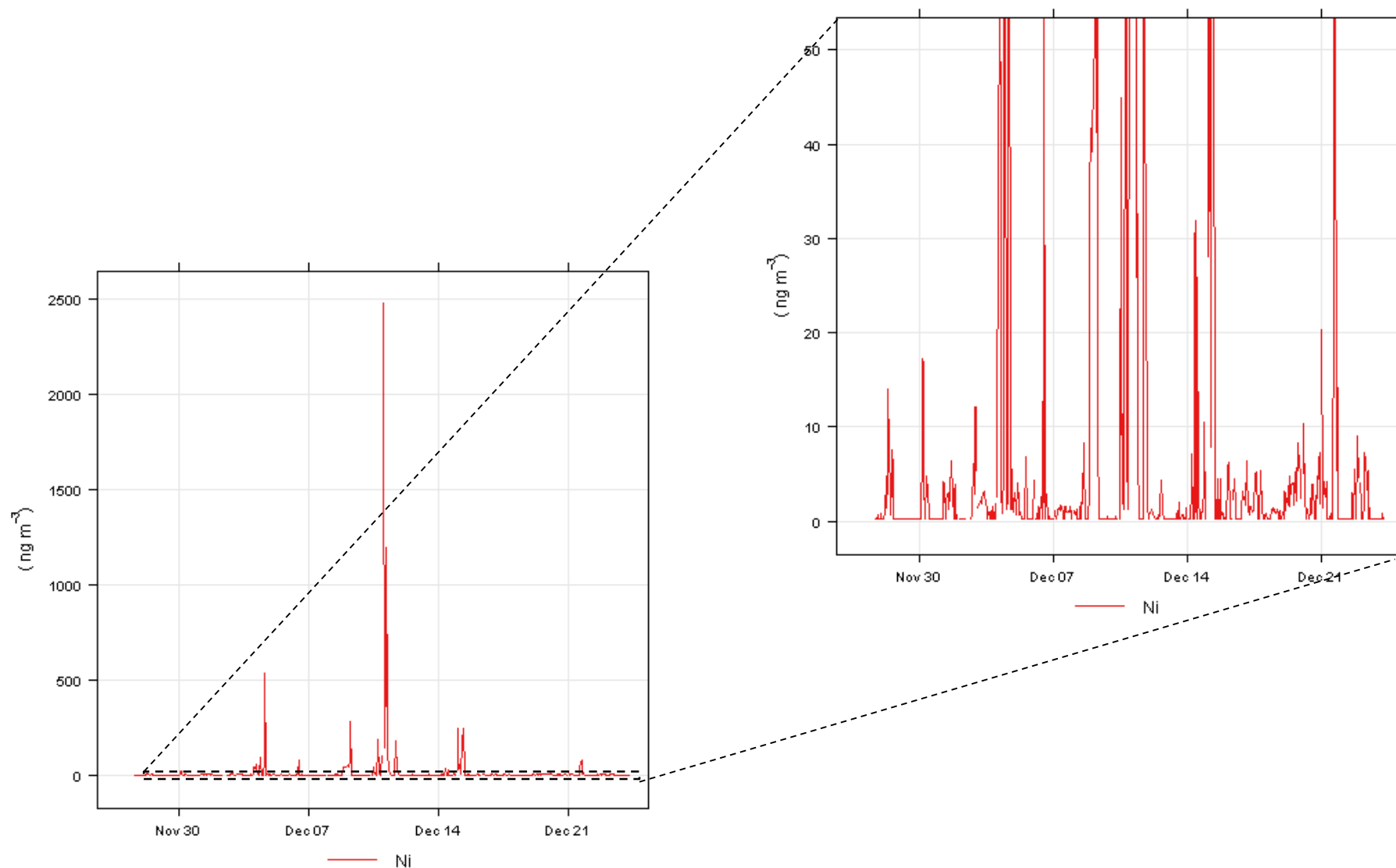
- Disadvantage: (subjective) choice of # clusters
- Criteria to choose the # clusters:
 - Ni/Cr ratios from WC cluster $\sim$ emission ratios
 - Minimize the no. hours in the WC cluster with wind speed $> 1.6 \text{ m s}^{-1}$
(to exclude distal sources)
 - Minimize the no. of clusters with large Ni/Cr ratios

Results - Data Summary

(ng m⁻³)

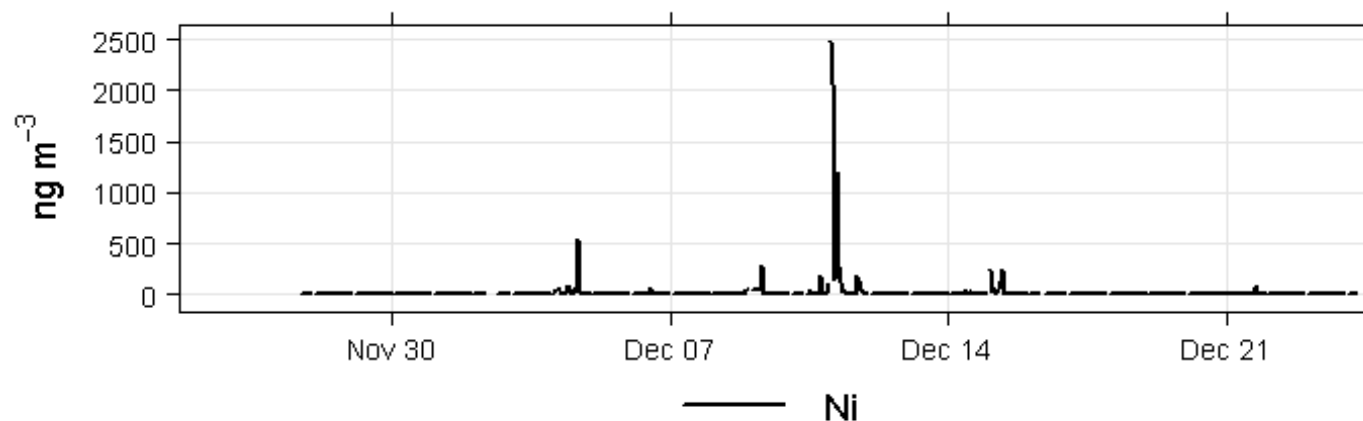
	XRF Hourly (Nov-Dec 2015)				XRF Daily (Nov-Dec 2015)				ICP MS Daily (Aug 15 – Jan 16)				2015
Element	Mean	Median	Min	Max	Mean	Median	Min	Max	Mean	Median	Min	Max	Mean
As	0.4	0.0	0.0	12.1	0.4	0.2	0.0	2.2	0.6	0.5	0.0	2.8	0.5
Ba	1.4	1.1	1.1	22.2	1.4	1.1	1.1	3.1					
Ca	186.1	144.9	3.6	4059.6	191.2	154.7	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



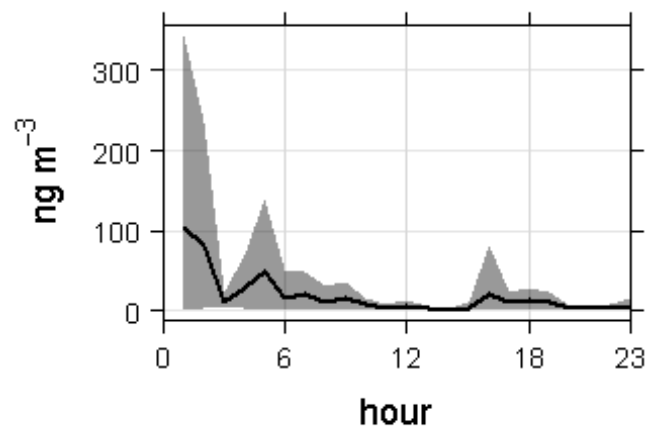
Results – Hourly and weekly variation

A. Ni Time series

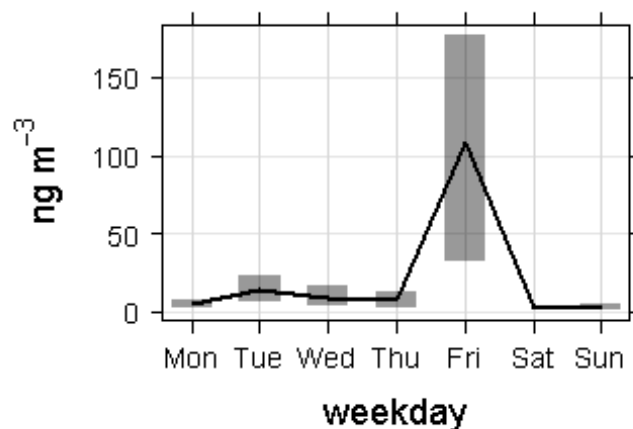


- The **diurnal** and **weekly variation** strongly **influenced** by the **single peak** in the early hours on Friday Dec 11th.

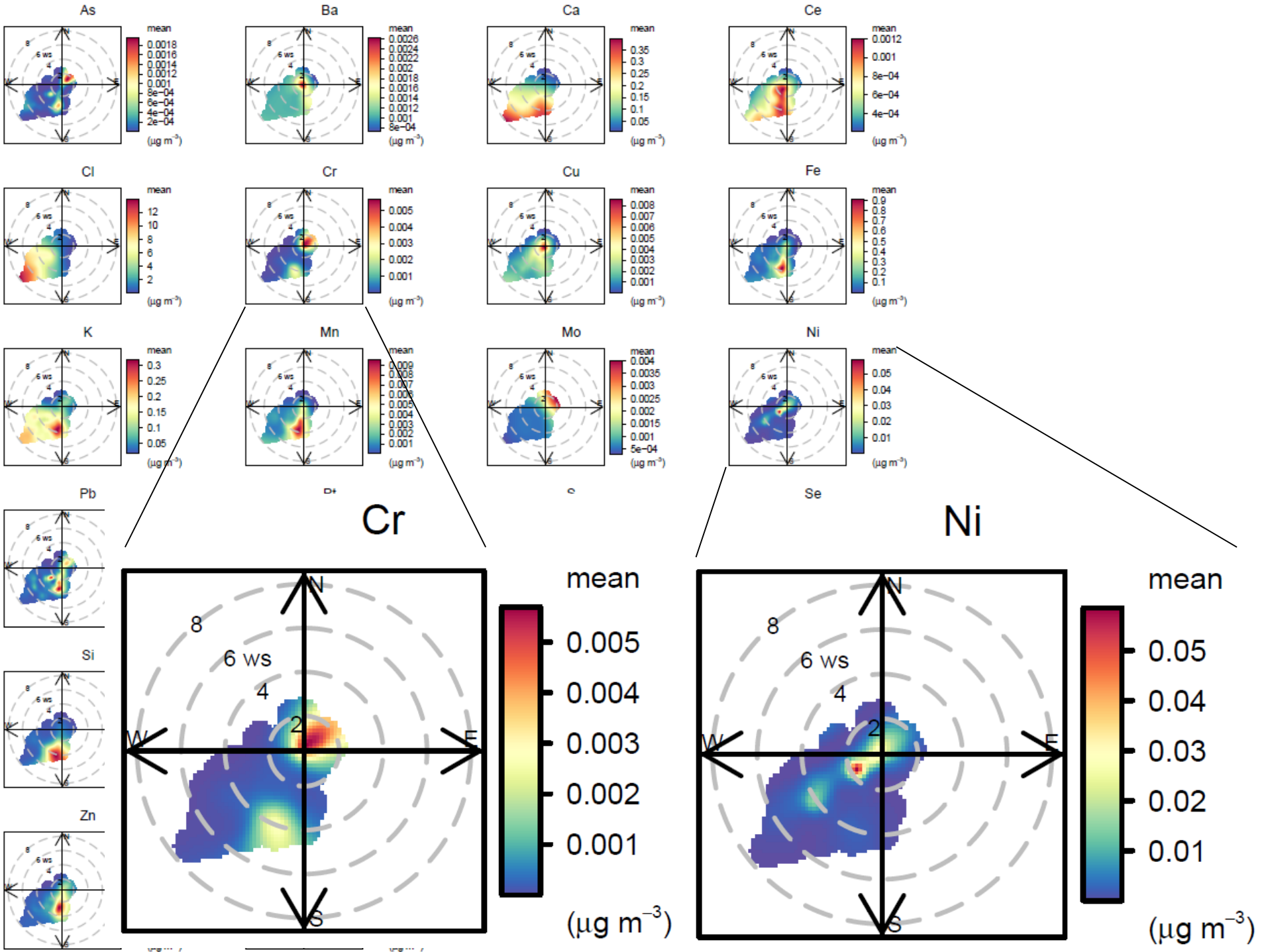
B. Hourly variation



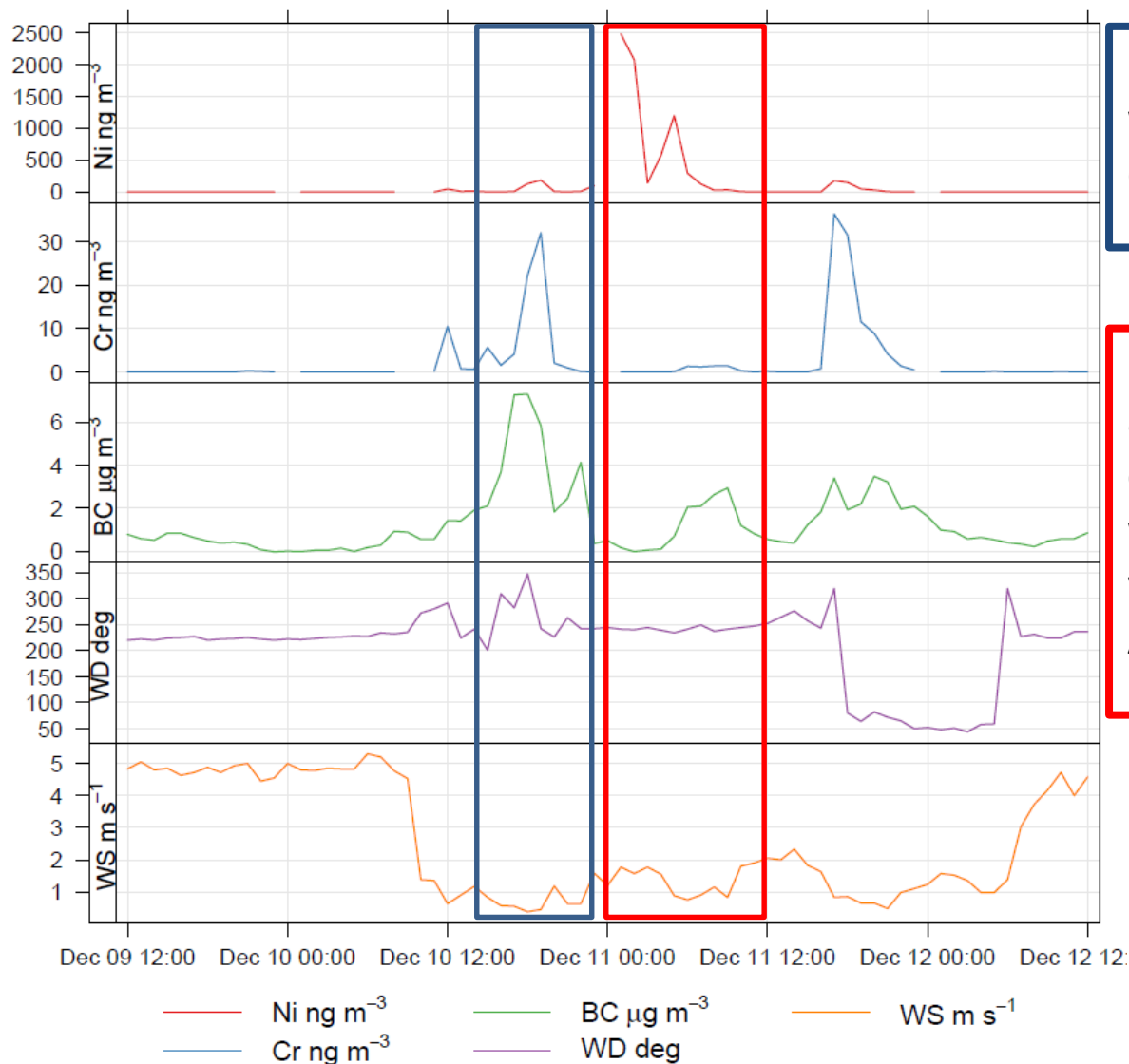
C. Weekly variation



- Concentrations on **weekends** **lower** than **weekdays**.



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

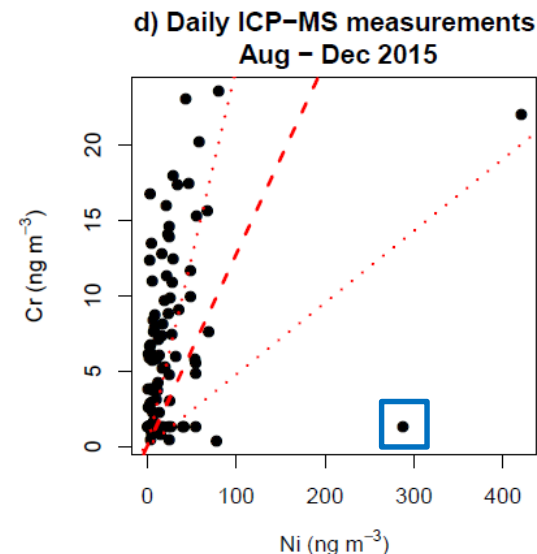
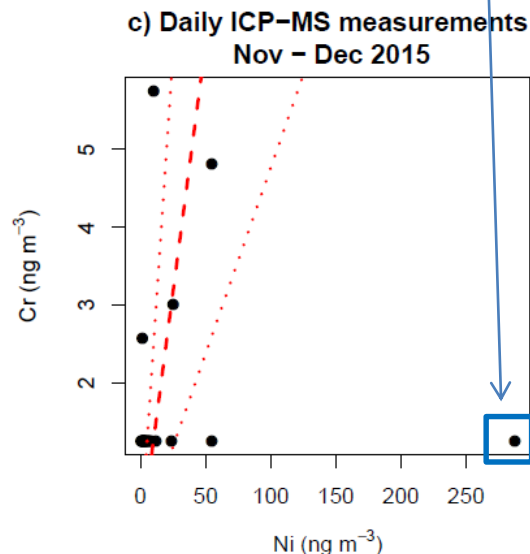
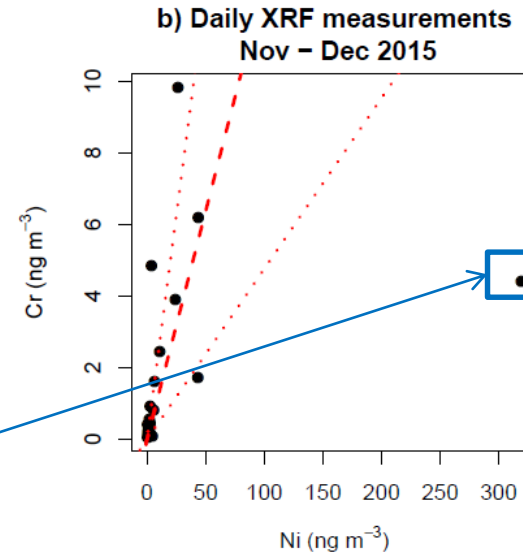
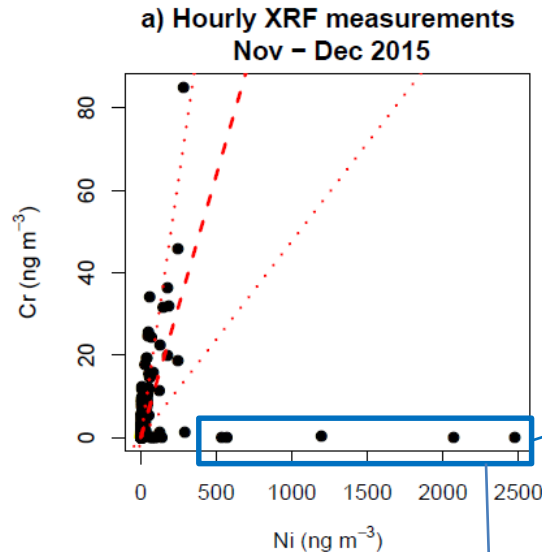
Ni peaked at 2500 ng m⁻³
at 1:00 am while Cr
concentrations ~ 0 ng m⁻³; wind
was blowing from 240 degrees at
wind speeds > 1.5 m s⁻¹
Air was clean (no BC or NO_x)

Results - Peak event as observed hourly/daily data

--- Ni / Cr
Wall
Colmonoy
alloys

11th Dec 2015

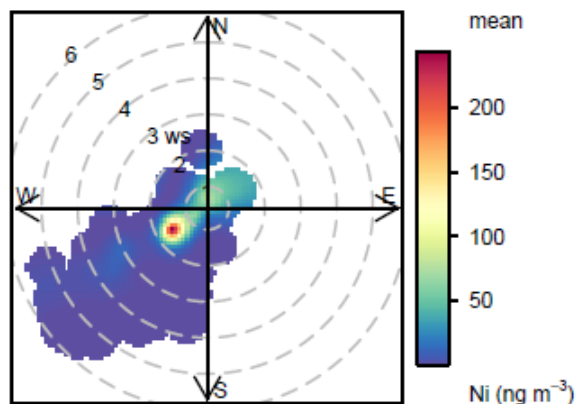
ICP-MS LOD
(2.52 ng m⁻³) for Cr



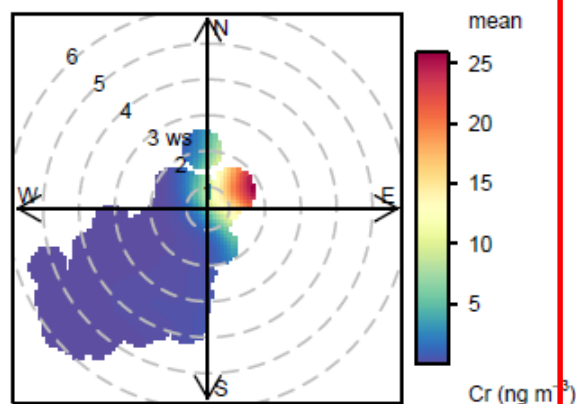
Results - Polar Plots Ni/Cr ratios

Plume Grounding

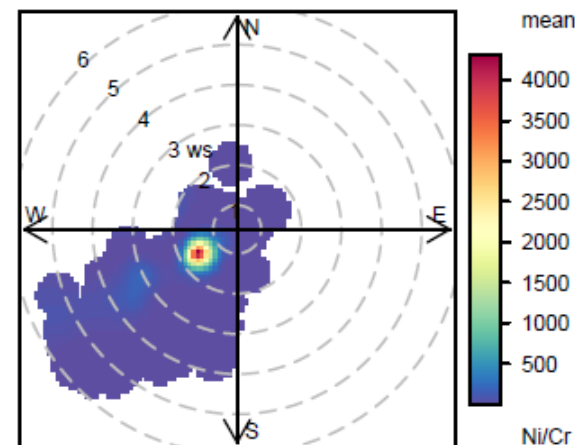
Ni - melting hours



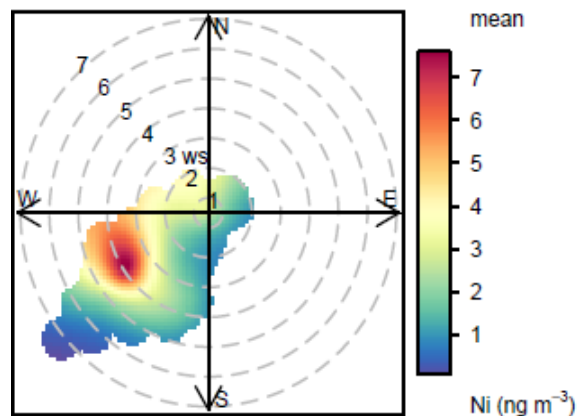
Cr - melting hours



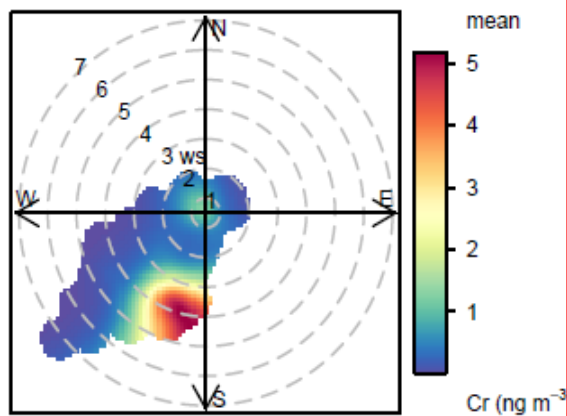
Ni/Cr - melting hours



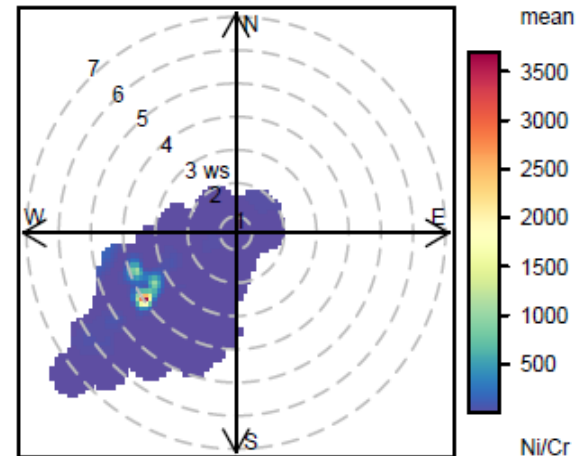
Ni - off hours



Cr - off hours

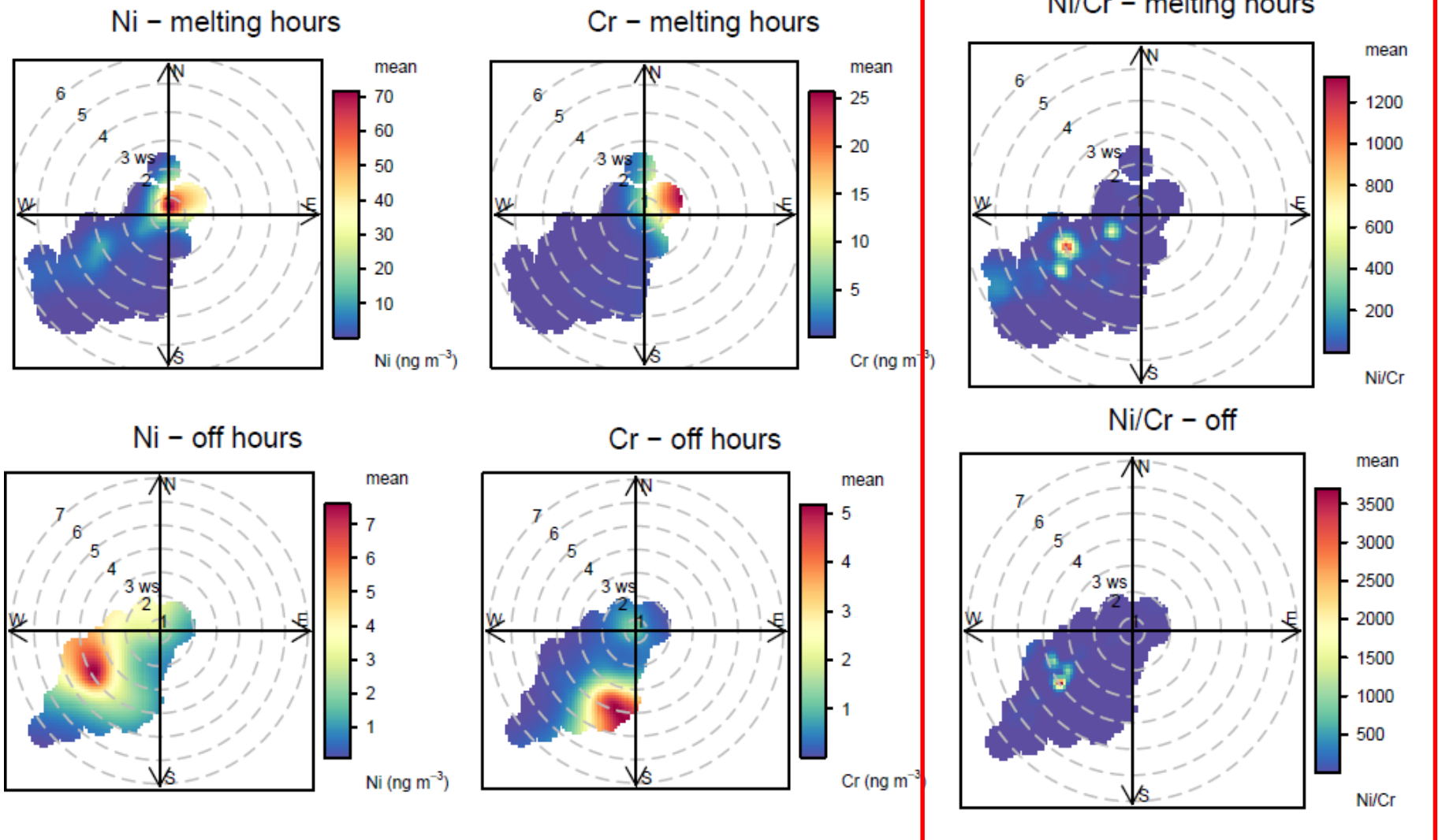


Ni/Cr - off



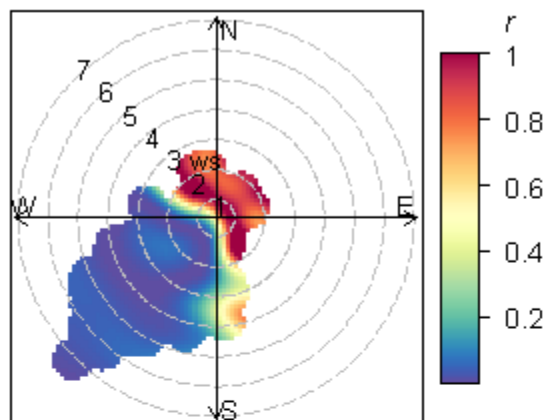
Results - Polar Plots Ni/Cr ratios peak event removed

Plume Grounding

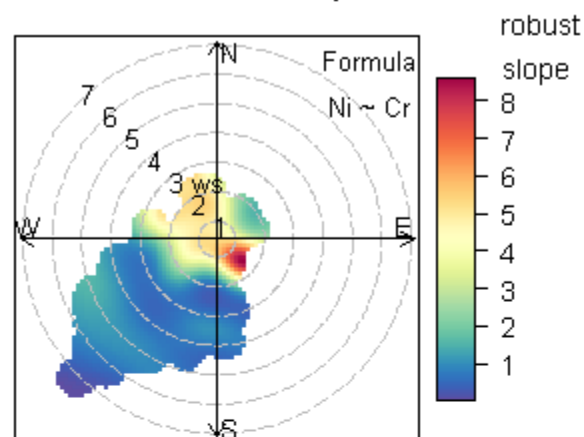


Results – Ni and Cr sources

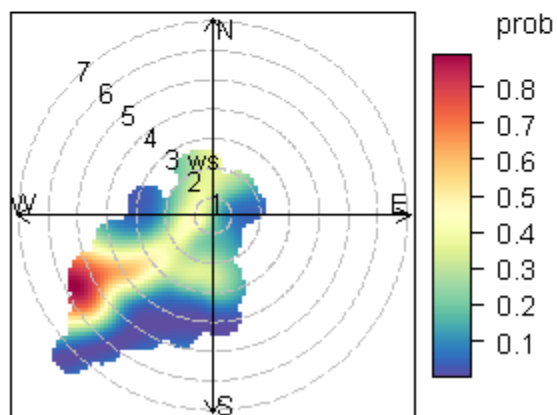
A. Ni to Cr correlation



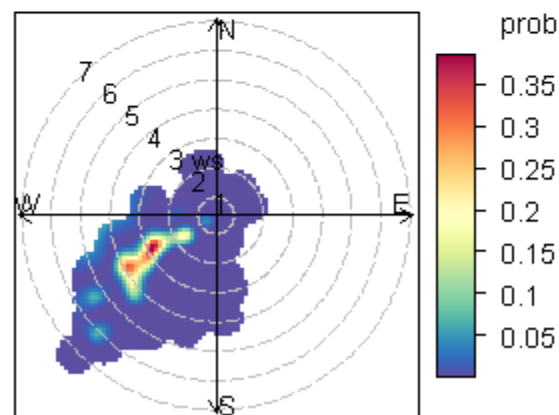
B. Robust slope Ni/Cr



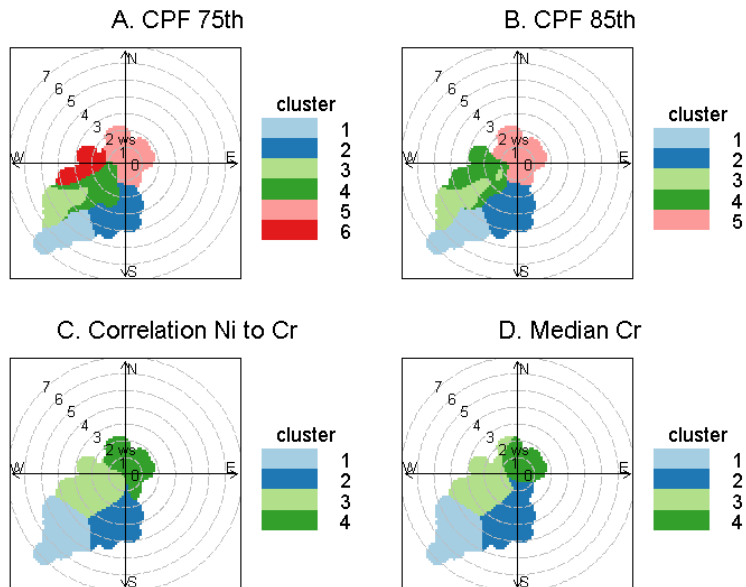
C. 50th CPF BPP Ni to Cr (= 4)



D. 95th CPF BPP Ni to Cr (= 86)



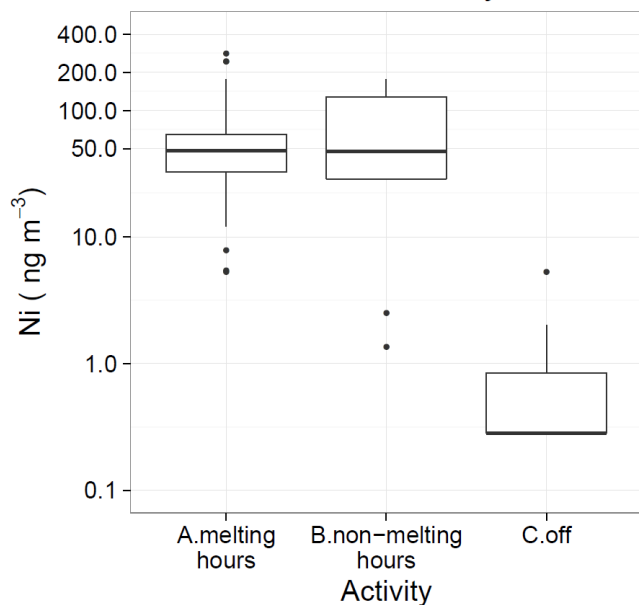
Results – Cluster analysis



Cluster analysis	BPP 75 th CPF Ni/Cr	BPP 85 th 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

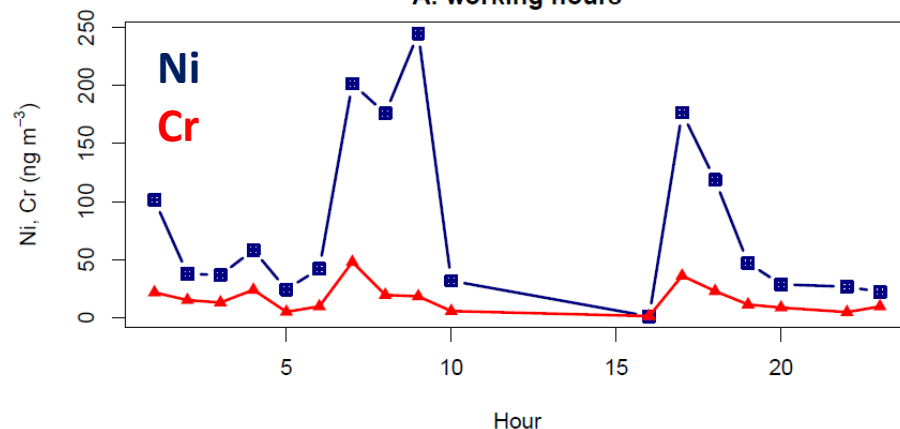
Results - Identification of WC activities

Wall Colmonoy

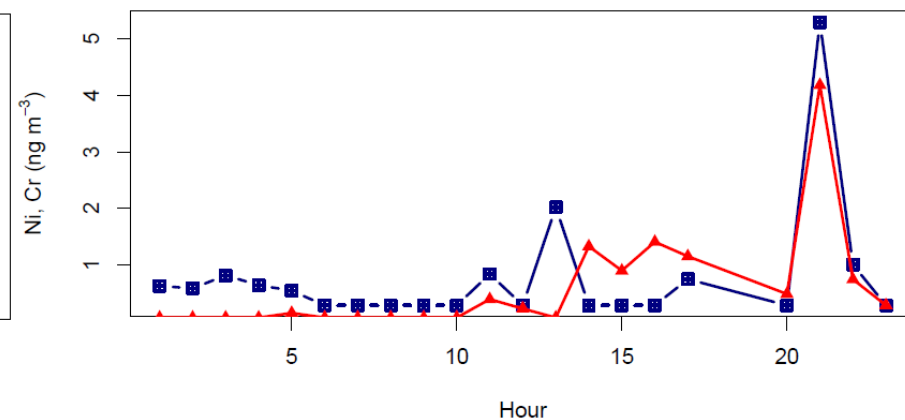


	Melting hours	Non-melting hours	Off
Mean Ni (ng m ⁻³)	75.7	71.6	0.74
Median Ni (ng m ⁻³)	47.9	47.3	0.28
Max Ni (ng m ⁻³)	281.9	176.6	5.3
No. hours	23	9	28
Contribution (%)	72.3	26.8	0.9

A. working hours



B. non-working hours

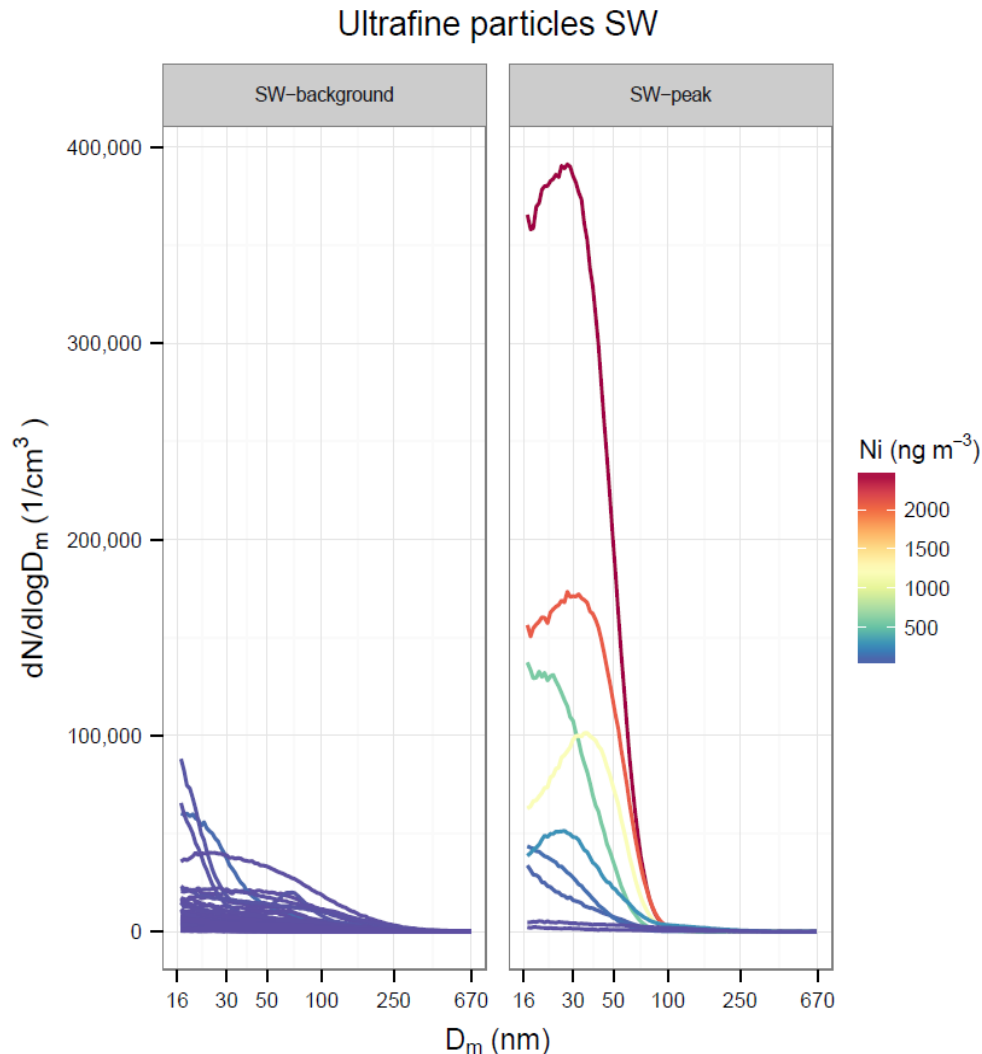


Results - Transient plumes from the SW

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)

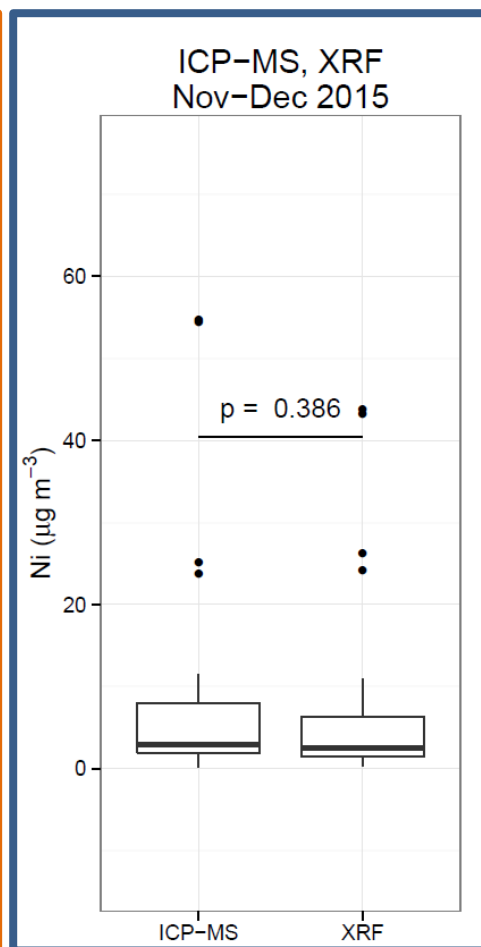
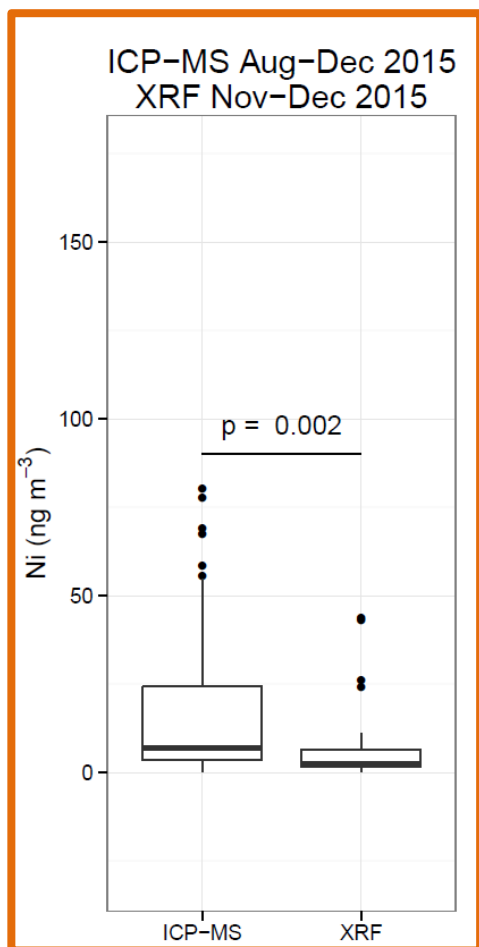
Thank you for listening

david.c.green@kcl.ac.uk
anna.font_font@kcl.ac.uk

SUPPLEMENTARY SLIDES

Relationship between XRF and ICPMS

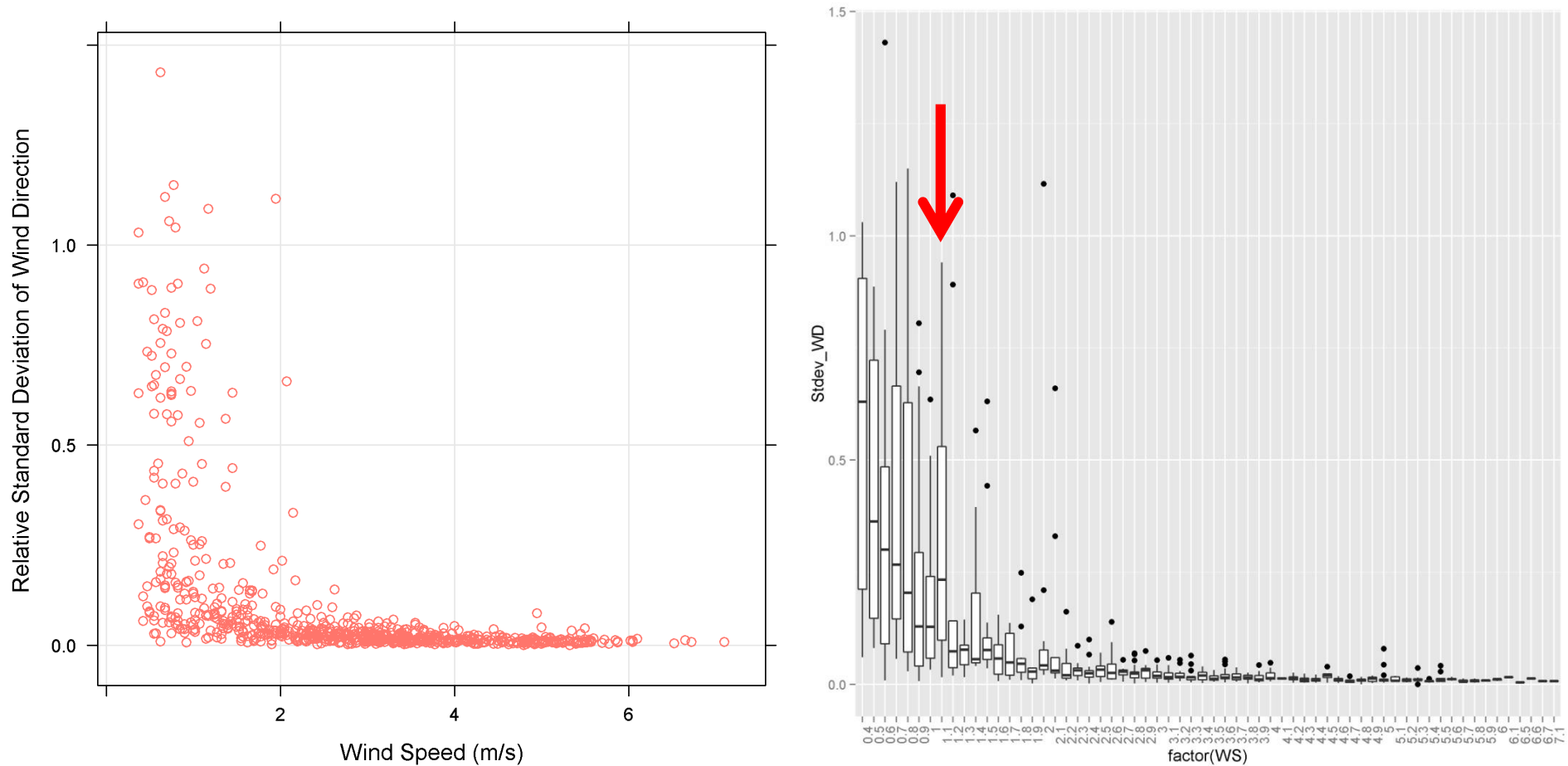
Daily measurements by ICP-MS between Aug-Dec and daily measurements by XRF between Nov – Dec' 15 were *statically different*



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

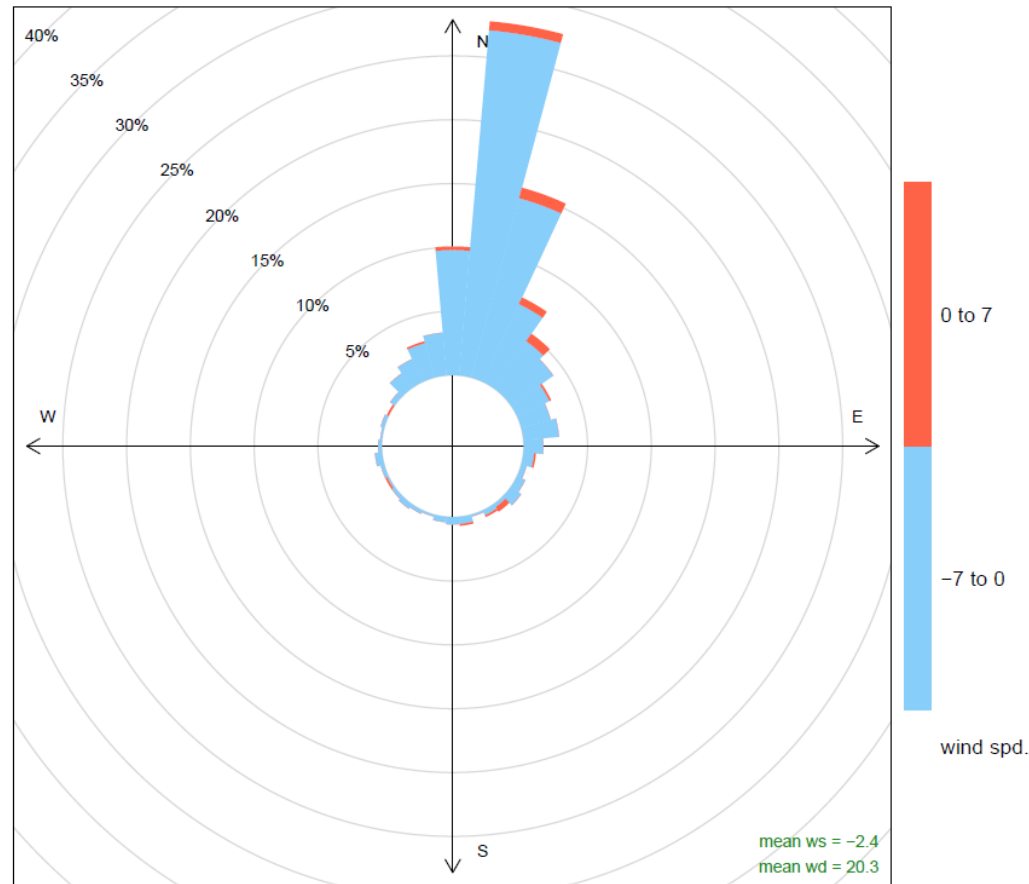
Ni (ng m^{-3})	Min	1 st Q	Median	Mean	3 rd Q	Max
ICP-MS (1 st Aug – 23 rd Dec)	0.19	3.39	6.82	20.92	24.26	420.60
XRF (28 th Nov – 23 rd Dec)	0.28	1.50	2.49	20.44	6.36	319.20

Sensitivity test wind data



Wind direction significant whenever wind speeds $> 1\text{m/s}$

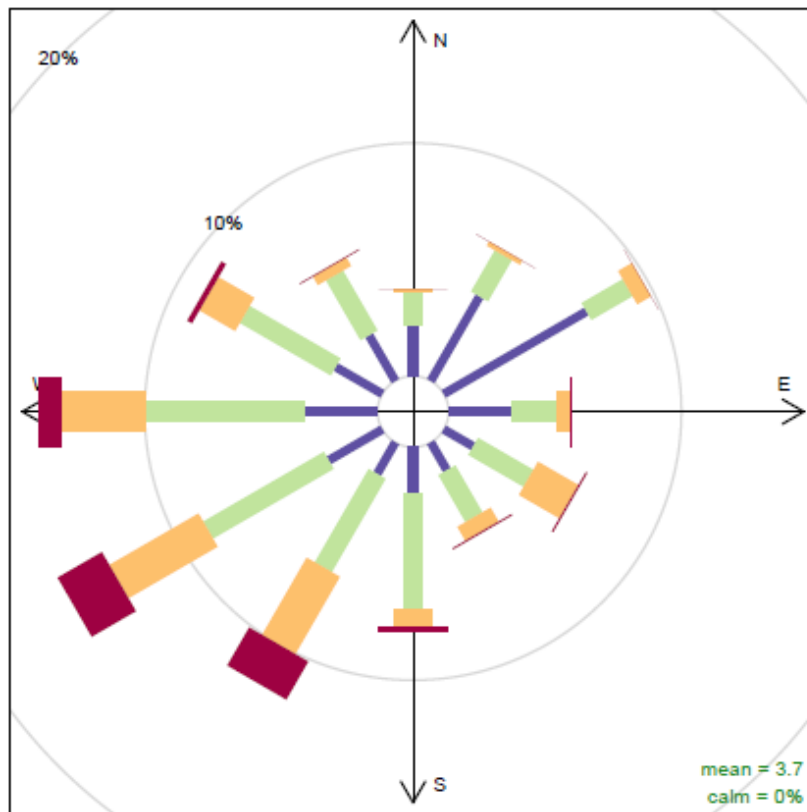
Meteorological Measurements



Frequency of counts by wind direction (%)

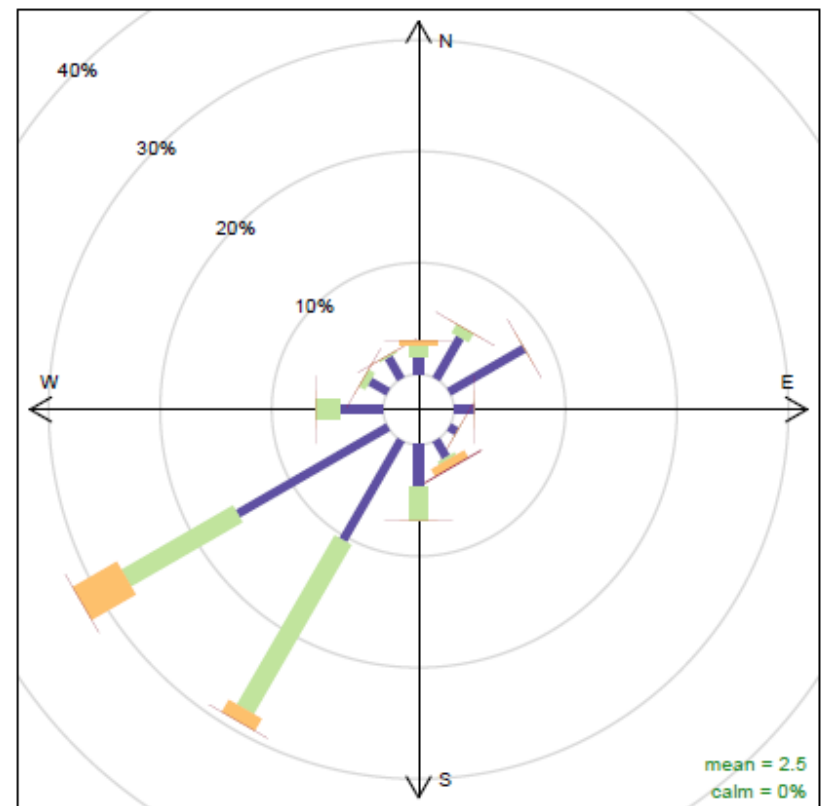
Meteorological Measurements

Swansea



Frequency of counts by wind direction (%)

Pontardawe



Frequency of counts by wind direction (%)