Department
for Environment
Food & Rural Affairs

Report on measures for 2016 exceedance of the Target Value for Nickel in Sheffield Urban Area agglomeration zone (UK0007)

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1. Introduction

1.1 Context

Under the EU Directive 2004/107/EC[1], the target value (TV) for nickel (Ni) is an annual mean concentration of 20 nanograms (one billionth of a gram (10^{-9})) per cubic metre (m^{-3}) of ambient air or lower. The Directive requires that Member States shall report on measures in place to address the exceedance of the TV and that all reasonable measures that do not entail disproportionate cost should be taken to ensure this target is not exceeded.

Exceedance of the TV was reported in 2014 in the Sheffield Urban Area and a report on measures was published detailing the exceedance and the measures in place[2].

This document reports the exceedance situation for 2016 reflecting the more recent assessment and updating the 2014 report on measures.

1.2 Status of zone

This is the report on measures required for exceedances of the TV for Ni within the Sheffield Urban Area agglomeration zone identified within the 2016 UK air quality assessment. Exceedances within this zone were identified on the basis of measurement data, with model results on a 1 km x 1 km grid resolution providing supplementary information. Fine scale modelling on a 50 m x 50 m grid resolution located around an identified industrial source provides additional information for this report on measures. This exceedance was reported via e-Reporting dataflow G[3] on attainment and Air Pollution in the UK[4].

Table 1 summarises the spatial extent and associated resident population for the exceedances identified in this zone, as reported via e-Reporting.

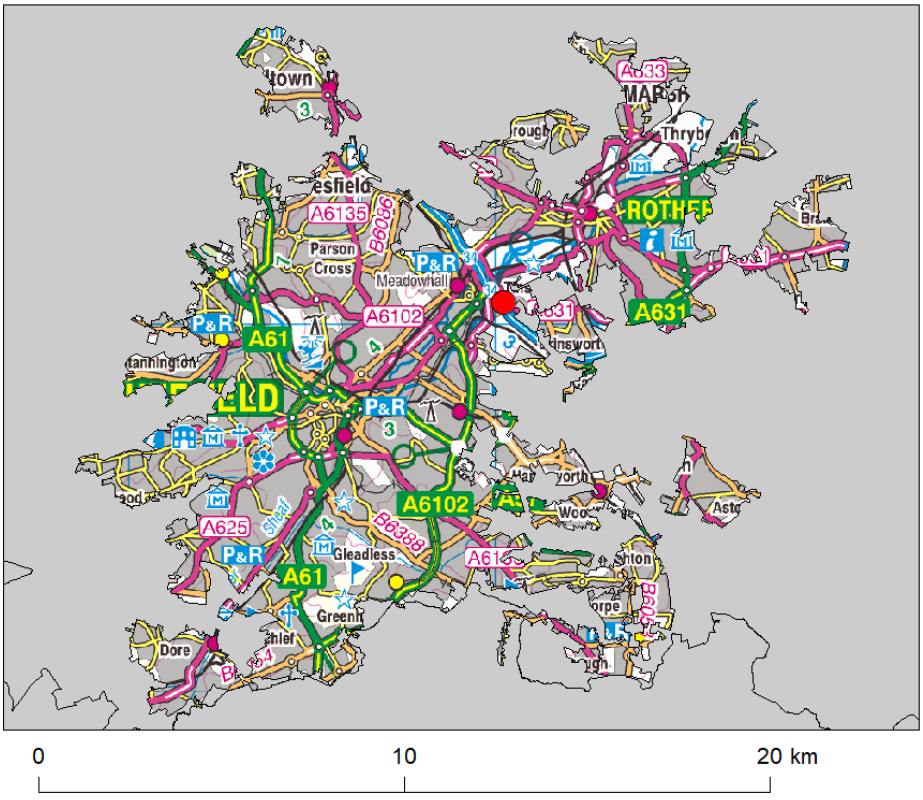
[1] http://eur-lex.europa.eu/LexUriServ/LexUriServ.do?uri=OJ:L:2005:023:0003:0016:EN:PDF
[2] https://uk-air.defra.gov.uk/library/bap-nickel-measures
[3] http://cdr.eionet.europa.eu/gb/eu/aqd
[4] http://uk-air.defra.gov.uk/library/annualreport/index

Table 1. Area exceeding Ni target value in 2016 and associated resident population for exceeding areas within Sheffield Urban Area zone UK0007.

Zone code	Zone Name	Area exceeding TV (km^2)	Population exceeding TV
UK0007	Sheffield Urban Area	None reported	None reported

Figure 1 shows the locations of the exceedances in the context of the zone as a whole.

Figure 1. Location of exceedance of the Ni target value in 2016 in Sheffield Urban Area zone UK0007. Location of the exceeding monitoring station is marked by the red circle. The area of the circle is indicative of the location of the exceedance and does not represent the exceedance area reported.



An initial source apportionment was carried out and this analysis identified one exceedance situation within this zone related to industrial emissions:

- Sheffield [Ni_UK0007_2016_1] related to industrial emissions (measured exceedance at one monitoring station)

This report describes the exceedance situation in the zone. The sections below include a description of the exceedance situation, including maps, information on source apportionment and a list of measures already taken or to be taken. Information on measures is reported within e-Reporting dataflow K.

2 Exceedance situation Sheffield [Ni_UK0007_2016_1] related to industrial emissions

2.1 Description of exceedance

This exceedance situation is located in the valley of the river Don to the North East of Sheffield City Centre in the Sheffield Urban area agglomeration zone. The exceedance was reported on the basis of measurements at the Sheffield Tinsley monitoring station. The exceedance was reported at the location of the measurement station and no population was reported for this exceedance.

Table 2 lists measured annual mean concentrations of Ni from monitoring sites in Sheffield Urban Area agglomeration zone from 2004-2017, and Figure 2 indicates the location of measurement sites. There is one measured exceedance at Sheffield Tinsley (GB0538A) in 2016 for which this report relates. Figure 3 shows the location of the exceedance situation in detail. The concentration of Ni at the other monitoring station within the Sheffield Urban Area agglomeration zone was below the TV in 2016 and no other exceedances have been reported during the 2004-2017 period apart from the measured exceedance reported for 2014.

Figure 3 shows the exceedance situation Ni_UK0007_2016_1 in detail. The figure indicates the location of the measured exceedance. In addition, the figure presents the results of national modelling on a 1 km x 1 km grid resolution that were submitted to the Commission as a supplementary assessment. No modelled exceedance was reported for the Sheffield Urban Area in 2016. Zone boundaries for the 1 km model grid used to assign exceedance situations and associated populations are presented as black hatching. Figure 3 shows the location of several industrial sites located close to Sheffield Tinsley monitoring station.

The measured annual mean concentration of Ni at Sheffield Tinsley (GB0538A) in 2017 was 17 ngm^{-3} (99% data capture). This is below the Ni TV and therefore this exceedance situation does not persist in 2017.

Figure 2: Location of monitoring sites in Sheffield Urban Area.

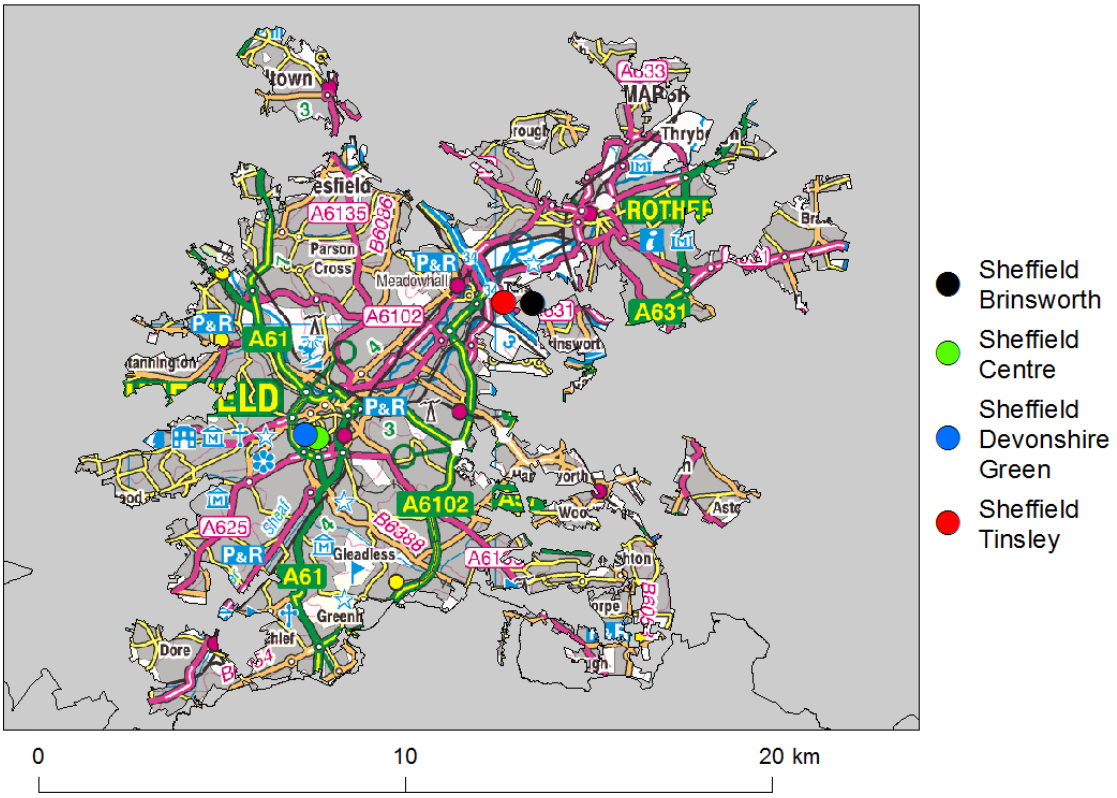
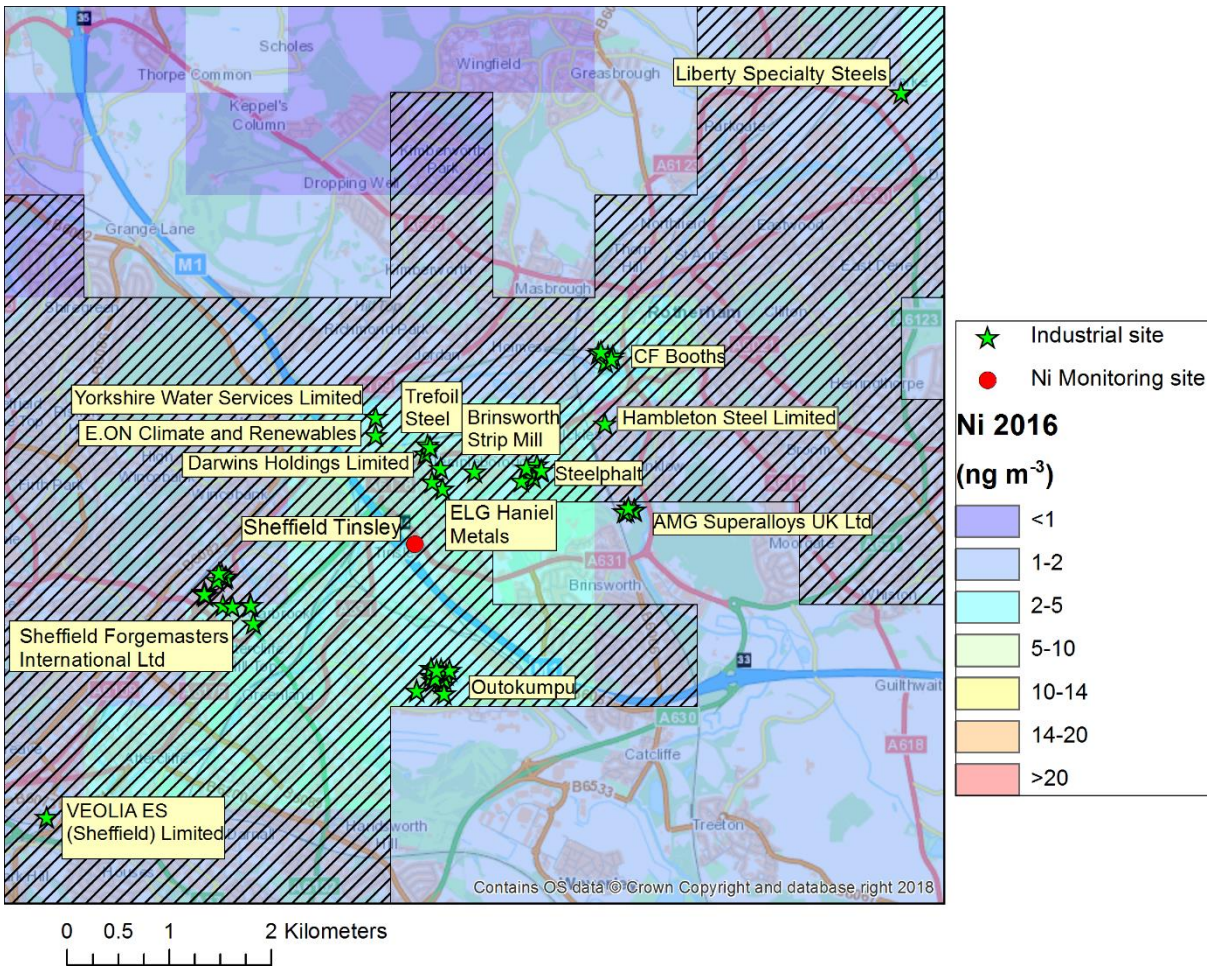


Table 2 Measured annual mean Ni concentrations in Sheffield Urban Area agglomeration zone UK0007 from 2004 to 2017 (ngm^{-3}). (Percentage data capture is shown in brackets).

Station (EoI code)	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015	2016	2017
Sheffield Brinsworth (GB0792A)	20*	14*	12 (98)	11 (100)	12 (94)	9.8 (96)	15 (98)	15 (98)	13 (100)	13 (70)				
Sheffield Centre (GB0615A)					2 (92)	1.7 (98)	2.5 (98)	2.2 (91)	2.6 (88)	3.2 (66)				
Sheffield Devonshire Green (GB1027A)										0.86 (11)	2.6 (99)	1.9 (100)	2.7 (98)	1.7 (100)
Sheffield Tinsley (GB0538A)										14 (81)	21 (96)	18 (94)	24 (89)	17 (99)

* Data capture not available

Figure 3 Exceedance situation Sheffield [Ni_UK0007_2016_1]. The exceeding monitoring station is marked in red. Locations of local industrial sites are also shown. Non-hatched grid squares are assigned to the Yorkshire and Humberside zone UK0034 and do not form part of this exceedance situation. Note that multiple emissions sources are indicated on the map for some industrial sites (Outokumpu, Sheffield Forgemasters International Ltd, AMG Superalloys UK Ltd, E.L.G. Haniel Metals Limited, Harsco Metals Group Limited (Steelphalt), Trefoil Steel Company Limited, and CF Booths Limited).



2.2 Source apportionment

Modelling has been used to determine the annual mean Ni source apportionment for the exceedance situation. National modelling on a 1 km x 1 km grid resolution apportions the Ni concentration to regional and urban background sources. Additional fine scale modelling has also been carried out in support of this Report on Measures to characterise local industrial emissions, this is described in Appendix A1.

Table 3 provides a breakdown of the main emission sources (source apportionment) that have contributed to the grid square in this exceedance. The penultimate column is the total concentration from all emissions sources and is equal to the annual mean Ni concentration measured at the Sheffield Tinsley monitoring site. The total concentrations are presented rounded to integers for consistency with the values reported in the compliance assessment. The values in the other columns have been rounded to two decimal places. The other shaded columns are the subtotals for the regional, urban background and local contributions.

Table 3 identifies that local emissions from industrial sources are the most significant source of Ni. Table 4 gives a more detailed source apportionment for the industry sector based on the fine scale modelling study presented in Appendix A1. This shows local industrial emissions contribute 21.55 ngm^{-3} Ni to the annual mean concentration measured at the Tinsley monitoring site, of which 1.08 ngm^{-3} derives from unidentified local activities. This study also shows that the Outokumpu site is the most significant local industrial emissions source contributing 11.06 ngm^{-3}, as indicated in Table 4, which includes contributions from reported emissions and a contribution attributed within the modelling to diffuse sources on the site.

The source apportionment presented here has been informed by the fine scale modelling carried out in support of this Report on Measures. The contribution from the local industrial sources that were included within the fine scale model were removed from the national model results. Therefore, there are differences between the results of the national model presented in Figure 3 and submitted to the Commission and the background annual mean source apportionment concentrations presented in Table 3.

Table 3. Source apportionment for exceedance situation Ni_UK0007_2016_1. Annual mean Ni concentration (ngm^{-3}).

OS easting (m)	OS Northing (m)	Zone	a) Regional background: Total	Regional background: From within Member State	b) Urban background increment: Total	Urban background increment: Traffic	Urban background increment: Industry including heat and power production	Urban background increment: commercial and residential	Urban background increment: Shipping	Urban background increment: Off road mobile machinery	Urban background increment: Other	c) Local increment: Total	Local increment: Industry including heat and power production	Total for all emissions sources (a+b+c)	Resident population
440500	390500	7	1.00	1.00	1.03	0.03	0.51	0.37	0.00	0.09	0.02	21.55	21.55	24	2422

Table 4. Detailed source apportionment for industrial sources only for exceedance situation Sheffield [Ni_UK0007_2016_1]. Annual mean Ni concentration (ngm^{-3}).

OS easting (m)	OS Northing (m)	Zone	Outokumpu	Scaled contributions from Outokumpu*	Liberty Speciality Steels	AMG Superalloys UK Ltd	Harsco Metals Group Limited, Steelphalt	Other identified industry sources from East**	E.L.G. Haniel Metals Limited	Scaled contributions from North East***	Sheffield Forgemasters International Ltd	Other identified industry sources from West****	Unidentified sources	Local increment: Industry including heat and power production
440500	390500	7	5.82	5.24	0.02	0.03	0.06	0.002	1.47	7.76	0.06	0.01	1.08	21.55

* Contributions from Outokumpu Stainless Ltd (SMACC) attribute to diffuse emissions from roadways and raw material storage areas, scaled to a measurement-model residual (refer to Appendix A1 for details)

** Other industry sources to the East of the Sheffield Tinsley monitoring site identified as contributing <0.01 ngm^{-3} each, including Speciality Steels UK Ltd (Brinsworth Strip Mill) and CF Booths Limited (Clarence Metal Works).

*** Contributions from sources to the North East of the Sheffield Tinsley monitoring site (including E.L.G. Haniel Metals Limited, Darwin Holdings Limited (Fitzwilliam Works), Trefoil Steel Company Limited (Rotherfield Works)) shown as an aggregated total in the source apportionment since the individual contributions are unknown and scaled to a measurement-model residual (refer to Appendix A1 for details)

**** Other industry sources to the West of the Sheffield Tinsley monitoring site identified as contributing <0.01 ngm^{-3} each, including VEOLIA ES (SHEFFIELD) Ltd and E.ON Climate and Renewables UK Biomass Ltd.

2.3 Measures

Improving air quality is a high priority for the Government, including the attainment of EU target values. An exceedance in this zone was reported in 2014 and in 2016, but not in other years since the TV came into force, including 2017. The Government takes any exceedance seriously whilst ensuring that any measures put in place are proportionate to the exceedance. The Government has brought together the regulators and local industrial operators with emissions of Ni to air in pursuit of this aim. Meetings have enabled:

- the Government to communicate to the industrial regulators and operators the extent of the issue and the seriousness with which it is taken;

- the regulators to demonstrate that the operators are applying all cost-effective measures, and in particular are applying best available techniques as required by Council Directive 96/61/EC;

- the operators to cooperate and share best practice in managing their operations; and

- the development of the latest evidence in understanding the predominant sources.

Much of the work in this area has focussed and will continue to focus on the unidentified and scaled source contributions as highlighted in Table 4. Work thus far undertaken has included fine scale modelling (Appendix 1) to model the impact of known emissions to the measurements at Tinsley Monitoring Station and daily and hourly monitoring campaigns at the Tinsley Monitoring station to obtain greater temporal resolution as regards the measurements made at the site (Appendix 2).

Table 5 summarises measures taken or to be taken at local industrial sites identified that may contribute to nickel in ambient air.

Table 5. Table of measures taken or to be taken at local industrial sites.

Measure code	Measure Description	Classification	Implementation dates		Other information		Comment
ELG Haniel Metals Ltd_1	Purchase of shearing machine (@£400K)	Air Quality Planning and Policy Guidance	Start:	Dec 2018	Source affected:	Waste Processing (stainless steel and non-ferrous metals)	The use of the shearing machine will reduce the frequency of oxy-propane cutting, which is carried out in the open. Fugitive emissions (including particulate matter/nickel) will therefore be reduced.
			Expected end:	N/A			
ELG Haniel Metals Ltd_2	Installation of plasma cutting booth with ventilation and filtration system (@11K)	Air Quality Planning and Policy Guidance	Start:	June 2018	Source affected:	Waste Processing (stainless steel and non-ferrous metals)	Previously plasma cutting was carried out in the open. Fugitive emissions containing nickel

			Expected end:	N/A			from this process will now be abated.
ELG Haniel Metals Ltd_3	Monitoring of Densifier Unit by a MCERTS certified monitoring contractor (£2K)	Air Quality Planning and Policy Guidance	Start:	June 2018	Source affected:	Waste Processing (stainless steel and non-ferrous metals)	To determine whether or not the emissions arising from this process contain nickel.
			Expected end:	October 2018			
ELG Haniel Metals Ltd_4	Monitoring of the oxy-propane cutting station (£2K)	Air Quality Planning and Policy Guidance	Start:	June 2018	Source affected:	Waste Processing (stainless steel and non-ferrous metals)	To determine whether or not the emissions arising from this process contain nickel**.**
			Expected end:	October 2018			

Outokumpu SMACC_1	Installation of a new oxy-fuel burner system on the electric arc furnace (£900K)	Air Quality Planning and Policy Guidance	Start:	August 2018	Source affected:	Stainless steel slab, bloom, billet and cast ingot production	Operator to install oxy fuel burners in the EAF to improve the speed and efficiency of melting. The ability to close the slag door will benefit the capture efficiency of the furnace extraction system leading to a reduction in fugitive emissions from the melt shop roof.
			Expected end:	N/A			
Outokumpu SMACC_2	Operator to undertake modelling of the emissions from site to determine whether or not the data collated by Kings College London accounted for all emissions from site or just point sources (£2K)	Air Quality Planning and Policy Guidance	Start:	June 2018	Source affected:	Stainless steel slab, bloom, billet and cast ingot production	Detailed modelling will allow the Operator to focus their efforts on the areas that have the most impact.
			Expected end:	N/A			
Outokumpu SMACC_3	Operator to carry out a dust and PM_{10} monitoring and characterisation assessment for the steel works to	Air Quality Planning and	Start:	April 2018	Source affected:	Stainless steel slab, bloom, billet	Monitoring will determine the concentrations of

	investigate the concentrations of nickel and other materials potentially migrating off site *(Ref Doc. DS/AG/Outokumpu/01*) (£26K)	Policy Guidance				and cast ingot production	nickel and other materials potentially migrating off site
			Expected end:	October 2018			
Outokumpu SMACC_4	Operator to define measurement/monitoring programme for fugitive roof emissions.	Air Quality Planning and Policy Guidance	Start:	May 2018	Source affected:	Stainless steel slab, bloom, billet and cast ingot production	Monitoring will confirm the quantity of fugitive emissions escaping through the melt shop roof
			Expected end:	N/A			
Outokumpu SMACC_5	Operator to carry out measurements as defined in the above monitoring programme for fugitive emissions (10-20K)	Air Quality Planning and Policy Guidance	Start:	October 2018	Source affected:	Stainless steel slab, bloom, billet and cast ingot production	Monitoring will confirm the quantity of fugitive emissions escaping through the melt shop roof

			Expected end	N/A			
Outokumpu SMACC_6	AOD Fume Hood - scheduled maintenance (£120K)	Air Quality Planning and Policy Guidance	Start:	2018	Source affected:	Stainless steel slab, bloom, billet and cast ingot production	AOD Fume Hood Replacement leading to a reduction in fugitive emissions from the melt shop roof - scheduled maintenance
			Expected end:	N/A			
Outokumpu SMACC_7	Refurbishment of main air fan in the Melt Shop - Scheduled Maintenance (£70K)	Air Quality Planning and Policy Guidance	Start: Expected end:	2018 N/A	Source affected:	Stainless steel slab, bloom, billet and cast ingot production	Refurbishment of main air fan to increase efficiency of extraction in the Melt Shop leading to a reduction in fugitive emissions from the melt shop roof
Sheffield Forgemasters International Limited_1	Installation of new Forge Burning extraction (@500K)	Air Quality Planning and Policy Guidance	Start:	August 2018	Source affected:	Steel Processing	Reduction in particulates/nickel emitted to

			Expected end:	N/A			atmosphere is expected.

2.4 Modelling

Appendix A1 presents fine scale modelling that has identified the emissions sources as potential contributors to the concentrations measured at Sheffield Tinsley monitoring station.

2.5 Monitoring

The Report on Measures for 2014 exceedance of the Target Value for Nickel in Sheffield[5] reported the outputs of a daily heavy metals monitoring campaign at Sheffield Tinsley monitoring station over the period from 25th February 2016 to 9th August 2016. Analysis of measured metal concentrations was undertaken to provide measurement-based evidence to identify emissions sources contributing to Nickel concentrations measured in the Tinsley area. This study identified contributions to the measured concentration from sources to the South and sources to North East. The source to the South was consistent with emissions from the Outokumpu site, but the sources to the North East were not identified. The study identified that monitoring to a higher time resolution might provide further insight into dominant sources.

During 2017 King's College London were commissioned to undertake a ten-week high time resolution (hourly) measurement campaign. This campaign took place January and March 2017 with the aim of providing further evidence to identify sources of Ni measured at the Tinsley AURN site. This work identified two sources of Nickel: one related to point source emissions which was characterised by molybdenum and manganese and one fugitive source type, characterised by chromium and calcium, likely to be associated with material handling or transport.

Wind speed and direction measurements were used to quantify where these source types were emitted from. There were three broad source directions –East, West and South. The source from the South, which contributed 47% to the Nickel concentrations measured during the study, was associated with emissions from the Outokumpu facility. This contribution was associated mainly with point source type emissions of Nickel, with a smaller contribution from fugitive source type emissions.

[5] Report on measures for 2014 exceedance of the Target Value for Nickel in Sheffield Urban Area agglomeration zone (UK0007), https://uk-air.defra.gov.uk/assets/documents/reports/bap-nickel-measures/ni_sheffield_UK0007_reportonmeasures_2014.pdf

The source to the East contributed 40% to the measured Nickel concentrations and was related mainly to industrial sources to the North East. The source from the West represented emissions from over half of the industries in Sheffield, which lie in that direction and was dominated by the point source type emissions. The sources to the West provided the smallest contribution to measured Ni concentrations.

The widespread nature of point source emissions across industries in Sheffield makes this challenging to tackle. However, the high time resolution measurements help to focus resources and identify specific emissions from industrial sources.

3. Industrial Sources of Nickel

3.1 Environment Agency Regulated Plant Part A

Further information about operating processes at individual regulated plant can be found in Appendix A1 and A2. From the industrial sites identified to date, Outokumpu has been identified as making the most significant contribution from regulated industry to the levels of Ni measured at Tinsley monitoring site. Outokumpu is regulated by the Environment Agency and is declared as using BAT. Ongoing further analysis of emissions samples from the area is being undertaken, in conjunction with Outokumpu to assist in identification of other potential sources of fugitive emissions that are currently unidentified. Actions to tackle Nickel emissions from Outokumpu are presented in Table 5.

3.2 Local Authority Regulated Plant Part B

Further information about operating processes at individual sites can be found in Appendix A1 and A2. The Local Authority has advised that these are all operating within the terms and conditions of their permits.

3.3 Unregulated plant – Local Authority

Sheffield City Council has provided information that none of the other industrial sites identified as potential contributors to Ni emissions in the region fall within the scope of the regulations and as such there are no relevant measures to put forward.

A1. Local scale modelling of the industrial point sources

This annex summarises supplementary modelling work carried out to investigate the sources of the measured exceedance of the 4th Daughter Directive (Directive 2004/107/EC, DD4) annual mean target value (TV) for nickel (Ni) of 20 ng m^{-3} at the Sheffield Tinsley monitoring station for the year 2016. Under DD4 Member States are required to identify zones and agglomerations where exceedances of the TV occur. Exceedance of the TV triggers a requirement within the Directive to prepare a report on measures. Source identification is not a formal requirement for this report on measures but is clearly a prerequisite for demonstrating that all measures not entailing disproportionate costs have been taken, and modelling can be useful to evaluate source contributions.

The following sources of information were used to compile a list of the potential sources of Ni relevant to this exceedance:

- a review of the results from high time resolution monitoring campaigns at the Sheffield Tinsley monitoring station
- sources present in the National Atmospheric Emissions Inventory (NAEI) and Pollution Climate Mapping (PCM) national modelling
- sources identified by the Environment Agency (EA), Sheffield City Council (SCC) and Rotherham Metropolitan Borough Council (RMBC).

The data provided are described in the next section.

This annex also describes the modelling approach and model results, including concentration maps, comparison of the model output with observations, modelled source apportionment and compliance situation as modelled. It concludes with recommendations for further work to build on the output of this modelling study to further improve understanding of the Sheffield Ni TV exceedance reported in 2016.

A1.1. Ni emissions data and data from related studies

A1.1.1. Review of NPL reports

Information from National Physical Laboratory (NPL) monitoring at Sheffield Tinsley considered in this study derives from the presentation to the Nickel in Air Review

Meeting, Environment Agency, Rotherham, 24th January 2018[6]. Further information also considered derives from the NPL draft 2016 report for the metals network[7].

Key information from our review of the NPL reports:

- Exceedance of Ni TV at Sheffield Tinsley for 2016 (24 ng m^{-3}), prior exceedances in Sheffield during 2004 (at Brinsworth) and 2014 (Tinsley) and an upward trend in concentrations over the last 10 years.
- Re-location of site from Brinsworth to Tinsley in order to better fit 4th Daughter Directive micro-siting requirements. The Brinsworth monitoring site was too close to building façade. Tinsley is an existing established AURN site (opened 1990), meets DD4 siting requirements, and is located close to significant point sources and sensitive receptors.
- 25th February – 10th August 2016, and 18th January – 5th April 2017 daily sampling at Tinsley (normal sampling frequency is weekly) – illustrates high short-term peaks not evident in weekly sampling – short-term peaks can contribute significantly to annual mean and indicative sources contributing (e.g. weekday/weekend behaviour, relationship with meteorology/pollution roses, correlations with other metals).
- Analysis from the 2016 daily monitoring shows:
    - Weekday concentrations were elevated compared to the weekends and the largest contributions were from the South and North East.
    - Some residual elevated concentrations on the weekends along similar directions, which could be indicative of fugitive/diffuse emissions from similar sources.
    - Correlations between Ni, and Cr, Mn, Fe, Cu: Cr and Mn mainly from the South, other metals also sources to N/NE/E.
- NPL draft 2016 report for metals network identifies Outokumpu Stainless Ltd, Sheffield, as the dominant local industrial source (located to South of Tinsley).

A1.1.2. Review of KCL reports

Kings College London (KCL) undertook a 10-week high time resolution (hourly) measurement campaign (19th January – 26th March 2017) to identify the sources of Ni measured at the Sheffield Tinsley AURN site[8]. Information from this campaign and source apportionment study has been derived from the final report of that study[9],

[6] "Measured Concentrations of Nickel in Sheffield", S. Goddard, NPL. Presentation to the Nickel in Air Review Meeting, Environment Agency, Rotherham, 24th January 2018.
[7] "Annual Report for 2016 on the UK Heavy Metals Monitoring Network", NPL, draft report received 06/03/2018
[8] https://uk-air.defra.gov.uk/networks/site-info?uka_id=UKA00181
[9] "Source Apportionment of Nickel Sources at Sheffield Tinsley"; David C Green, Anna Font, Max Priestman & Anja H Tremper, Environmental Research Group, King's College London; November 2017.

and the presentation on that study delivered to the January 2018 Nickel in Air Review Meeting[10].

Key information from our review of the KCL reports:

- A range of chemical components of particulate matter (PM) were measured, in addition to meteorology using the KCL Mobile Atmospheric Research Platform (MARPL), complementing measurements at the AURN site.
- Analysis of the 19th January – 26th March 2017 campaign results shows:
    - Representativity – Ni and Cr concentration measurements from the campaign were confirmed to be representative of the long-term time series; the frequency of wind speeds and directions at the Tinsley site during the 2017 campaign were confirmed to be representative of those observed at Sheffield Airport during 2016. It is noted that conclusions on the representativity of the observations during the study is limited by a lack of knowledge of behaviour of the emission sources.
    - Identifying the locations and descriptions of local industrial sources – distances and bearings to Ni sources along with the process descriptions were used to inform the Positive Matrix Factorisation (PMF) and K-means cluster analysis used to isolate likely dominant sources.
    - Time variation – the overall Ni time series (also the time series for other metals) is characterised by short term peak concentrations, and diurnal variation shows a morning peak driven by reduced dispersion and increased emissions at this time of day. By day of the week, concentrations were highest on weekdays and low on weekends, this is attributed to reduced industrial activity. Concentrations of other pollutants (NO_2, Black Carbon, particle number) in contrast are characteristic of traffic sources i.e. morning and afternoon peaks driven by rush hours, weekday concentrations elevated over weekends driven by reduced weekend road traffic.
    - Bivariate polar plots (BPPs) and conditional probability function (CPF) BPPs – these highlight sources contributing at the highest concentration levels (concentrations greater than the 95th percentile) are to the South (particularly) and North East, while sources contributing at lower concentration levels (concentrations greater than the 25th and 50th percentile) are present to the South, West and North East. The results are comparable to the results from the period of daily sampling by NPL (25th February – 10th August 2016) however the KCL CPF BPP results provide further information by distinguishing those directions and wind speeds relevant to different concentration levels.

[10] "Quantification of Nickel Sources at Sheffield Tinsley", D.C. Green, A. Font, A.H. Tremper, M. Priestman, KCL. Presentation to the Nickel in Air Review Meeting, Environment Agency, Rotherham, 24th January 2018.

- PMF source apportionment – two predominant, chemically and physically distinct Ni source types were identified in the 13 and 14 factor PMF solutions. One of these is rich in Mo (Ni/Mo), contributing 73% or 72% of the Ni to the selected PMF solutions respectively, and the other is rich in Cr (Ni/Cr), contributing 22% of the Ni to both selected PMF solutions. The PMF solutions had 5-6% of the Ni concentration unexplained and not assigned to specific sources. Examining time variation and BPPs for these two sources:
    - Ni/Mo source type – largest contributions from South and North East, concentrations highest weekdays, in morning with temperature inversions, attributed to a local buoyant source, and conversely also at higher wind speeds attributed to either more distant sources or atmospheric mixing increasing ground level concentrations from nearby sources. The likely dominant industrial sites highlighted based on directional analysis were Darwin Holdings and/or Trefoil Steel to the North (10°), and Outokumpu to the South. Other less significant sources to the East were highlighted as contributing to the mean.
    - Ni/Cr source type – largest contributions from South, and some to the North, no diurnal variation hence behaviour independent of industrial activity. Again, likely sources highlighted were Darwin Holdings and/or Trefoil Steel to the North (10°), and Outokumpu to the South. Wind speed was found to be highly influential with the strength of the source to the South increasing with wind speed, indicative of wind driven resuspension (e.g. stockpiles, vehicle movement, material handling). The source type also contains Ca indicative of the process (Ca used to purify alloys as sinter and is retained in slag after processing). Again, other less significant sources to the East were highlighted as contributing to the mean.
- K-means cluster analysis of CPF BPPs – a 3 cluster solution was derived for the 75th percentile CPF BPP of the Ni/Mo and Ni/Cr, 13 and 14 factor PMF solutions. This separates contributions into three broad source directions – South (S to SSE), East (NNW to SSE), West (S to NNW).
    - South – this was identified as the dominant source direction contributing 46.9% to the Ni concentrations measured (31.4% Ni/Mo and 15.5% Ni/Cr) and “confidently” attributed to the Outokumpu site (in this direction and accepted to be the largest emitter of Ni in the area).
    - East – identified as contributing 39.6% to the Ni concentrations measured (34.6% Ni/Mo and 5% Ni/Cr) and attributed to Darwin Holdings and/or Trefoil Steel (two facilities to the east, closely aligned with the peak concentrations identifiable in the BPPs).

- West – identified as contributing the smallest contribution (13.6%) to the Ni concentrations measured (10.7% Ni/Mo and 2.9% Ni/Cr) and attributed to emissions from over half of the Ni emitting industries in Sheffield, which lie in that direction.

A1.1.3. Review of sources present in the NAEI and national modelling, data on local industry from regulators, and data from the 2014 study

In addition to the information on likely significant sources derived from the review of the recent NPL and KCL studies (sections A1.1.1 and A1.1.2), a variety of data sources have been reviewed and combined for the current study for 2016. These include:

- The NAEI, which provides Ni emission estimates and plant data for industrial sites (e.g. operator names, site names, location information), and is a key source of data for the Pollution Climate Mapping model (PCM) which is applied in the UK national air quality compliance assessment.
- The PCM modelling for Ni concentrations, which incorporates contributions from area sources, point sources (stack releases plus fugitive emission estimates) and non-inventory contributions like resuspension (regional PM dust contributions from soil re-suspension, local PM dusts from vehicle re-suspension) and long-range transport of primary particulate matter.
- Data on local industry from regulators.
- The previous local study of point source contributions to Ni in Sheffield during 2014 (see Brookes (2016)[11]; Defra et al., (2016)[12]).

Further information on how data from these sources was handled and incorporated into the current study is given in the following sections.

A1.1.3.1. Review of sources present in the NAEI and national modelling

The PCM modelling of Ni concentrations for 2016 serves as the background for this local study. Due to reporting timescales, the 2016 PCM compliance assessment modelling took NAEI 2015 emission estimates with projections to 2016 as input. For this study GIS analysis was used to identify “local” Ni point sources within the NAEI 2015 and 2016 that are within 15 kilometres of either the Sheffield Tinsley or Sheffield Devonshire Green monitoring stations. The contribution from local point

[11] Brookes, D. and R. Rose (2016). Local study of point source contributions to Nickel in Sheffield, 2014, Ricardo Energy & Environment.

[12] Department for the Environment Food and Rural Affairs (Defra), Welsh Government (WG), Ricardo Energy & Environment (2016), 2014 Reports on Measures, Zonal report for the Sheffield Urban Area (UK0007), "Report on measures for 2014 exceedance of the Target Value for Nickel in Sheffield Urban Area agglomeration zone (UK0007)", https://uk-air.defra.gov.uk/library/bap-nickel-measures-2014.

sources of Ni based on the NAEI 2015 were subtracted from the national modelling in order to avoid double counting of these contributions.

Local point sources of Ni based on the NAEI 2016 were reviewed in terms of if there was further local data from either EA and local authority data (see Section A1.1.3.2) or the 2014 study[11] (see Section A1.1.3.3) to avoid duplication. If there was no further local data to allow detailed treatment, the contribution from these sources were modelled at 1 km x 1 km spatial resolution using the PCM modelling approach including NAEI 2016 emissions and local meteorology and added to the background Ni concentrations for 2016 from the national modelling (see Section A1.2).

A1.1.3.2. Review of EA and local authority data

In response to the 2016 Ni TV exceedance and informed by the NPL and KCL local monitoring campaigns, the Environment Agency (EA) coordinated a project with Sheffield City Council (SCC) and Rotherham Metropolitan Borough Council (RMBC) during 2018 to identify and inspect Ni sources in the Sheffield Road area of Tinsley/Templeborough, as well as the Outokumpu Stainless Limited (SMACC) site. Information from the project report[13], reports on industrial sites inspected and the presentation the EA delivered to the January 2018 Nickel in Air Review Meeting[14] were reviewed for this study and combined with the information on sources present in the NAEI and national modelling (see Section A1.1.3.1), and the sources treated in the 2014 study (see Section A1.1.3.3). The sites identified in the EA/SCC/RMBC 2018 project report are reproduced here in Table A1.1.

[13] "Report on measures for 2016 exceedance of the Target Value for Nickel in Sheffield Urban Area Agglomeration Zone (UK0007)", Environment Agency, report received 26/07/2018

[14] "Outokumpu Stainless Ltd -SMACC", Environment Agency. Presentation to the Nickel in Air Review Meeting, Environment Agency, Rotherham, 24th January 2018.

Table A1.1 – Sites identified in the EA/SCC/RMBC 2018 project

Operator	Regulator
E.ON Climate and Renewable UK Biomass Limited, Blackburn Meadows, Alsing Road, Sheffield, S9 1HF	Environment Agency
E.L.G. Haniel Metals Limited, Sheffield Road, Tinsley, Sheffield, S9 1RT	Environment Agency
Yorkshire Water Services Limited, Blackburn Meadows STW, Alsing Road, Tinsley, Sheffield. S9 1HF	Environment Agency
Outokumpu Stainless Ltd (SMACC), Europa Link, Sheffield, S9 1TZ	Environment Agency
Harsco Metals Group Limited, Steelphalt, Sheffield Road, The Ickles, Rotherham, S60 1DR	Environment Agency
AMG Aluminum Ltd & AMG Superalloys Ltd, Fullerton Road, Rotherham, South Yorkshire, S60 1DL	Environment Agency / Rotherham MBC
Speciality Steels UK Ltd, Sheffield Road, Rotherham, S60 1BN	Environment Agency
Darwins Holdings Limited, Fitzwilliam Works, Sheffield Road, Tinsley, S9 1RL (notification of closure August 2018)	Sheffield City Council
Trefoil Steel Company Limited, Rotherfield Works, Dead Man's Hole Lane, Tinsley, S9 1QQ	Sheffield City Council
CF Booths Limited, Armer St, Rotherham S60 1AF	Rotherham MBC
Hambleton Steel Limited, Rotherham S60 1DJ*	Rotherham MBC

*Note: No information was available on Hambleton Steel Limited

A1.1.3.3. Review of the 2014 study and compilation of sources considered in the 2016 study

The previous local study of point source contributions to Ni in Sheffield during 2014 (Brookes (2016)[11], Defra (2016)[12]) provides a basis for the modelling approach for 2016. The information gathered for the 2014 modelling on emissions, processes and release parameters has been combined with the emission data from the NAEI 2016, EA and local authority data to compile the input for the 2016 modelling.

For a small number of industrial sources or potential releases, 2016 Ni emissions data were indicated as being low and unspecified; these sites have been mapped but not modelled (see Table A1.2 and Figure A1.1). Those sites that have been modelled at higher resolution in the current study are listed in Table A1.3 and mapped in Figure A1.1. Table A1.3 includes descriptions of whether emissions were treated as line (e.g. along a roof vent), point (e.g. from a chimney stack) or volume releases (e.g. diffuse emissions from a storage area or building). The bearings from the Sheffield Tinsley monitoring station to each release point have been calculated and used to relate each source to the three broad source directions identified in the K-means cluster analysis of CPF BPPs in the KCL study (Green et al., 2017)[9]. Temporal emission profiles have been applied where information was available on

operating hours from the EA 2018 site reports. A categorisation for modelling (a)-(c) has also been made to indicate the level of confidence in the emissions data, where:

a) Indicates reported emissions and release parameters
b) Indicates derived emissions and/or release parameters based on the EA 2018 site reports
c) Indicates scaled contributions from uncertain local point/fugitive/diffuse sources with release parameters based on the 2018 EA site reports

Table A1.2 – Identified Ni emitters or emission points that were not modelled due to low emissions rates or lack of information

Operator	Address	Postcode	Process Type	Emission point description	Data provider
E.L.G. Haniel Metals Limited	Sheffield Road, Tinsley, Sheffield	S9 1RT	Started Operating in 2012 - Shredding of Metal	Densifier Outfeed building – 2018 EA site report provides results of short-term monitoring (June 2018) which indicate minimal if any fugitive emissions for this emission point.	EA
Yorkshire Water Services Limited	Blackburn Meadows STW, Alsing Road, Tinsley, Sheffield.	S9 1HF	Prior to October 2013: Incineration of non-hazardous waste. Since March 2016: sewage sludge is anaerobically digested in a bio-energy digestion plant (BED).	Prior to October 2013 a sewage sludge incinerator operated. A composting facility was then used to process sewage sludge from 2014 to early 2016 and could have contributed diffuse Ni emissions during this period. The 2018 EA site report indicates that Ni emissions from the BED operating since March 2016 are negligible.	EA
Harsco Metals Group Limited, Steelphalt	Sheffield Road, The Ickles, Rotherham	S60 1DR	EA regulated – Crushing and screening of metallurgical slag from steel works. RMBC regulated – Road stone coating activity - asphalt plant which involved the use of bitumen mixed together with varying proportions of aggregate, filler and fibre pellets to produce asphalt.	Roadstone coating plant - stack A1. 2018 EA site report indicates Ni emissions are not quantified, abatement is in place for PM emissions for which there is continuous monitoring, this shows PM emissions are significantly below the emission limit.	EA
				Storage of limestone product. EA site report provides no information on Ni emissions.	
				Open roadways. Emissions from roadways are continuously abated which indicates Ni would be minimal compared to open storage areas.	
Hambleton Steel Limited	Hambleton Steels, Fullerton Road, Ickles, Rotherham	S60 1DJ	RMBC regulated – No data.	No data.	EA

Table A1.3– Identified Ni emission points included in the modelling study. Emission rates are not specified for category c sources.

Operator	Site Name	Stack Name/Description	Stack Location (description)	Ni emissions, kg, 2016	Release type	Bearing to Sheffield Tinsley (°)	Temporal profile?	Categorisation for modelling (description) and KCL cluster assignment	Data provider
Outokumpu	Stainless Melting and Continuous Casting	A1	Melt Shop Bag Filter	519.00	Line	173	No	**a** (Emissions split between releases derived from 2014 releases in combination with NAEI 2016 emission total and information on 2017 emissions from the EA.), **KCL South cluster**	EA/NAEI
		A2	DC Arc Furnace	50.91	Point	173	No		
		A3	Grinder Bag Filter	2.16	Point	169	No		
		A4	Grinder Bag Filter	2.38	Point	168	No		
		A5	Grinder Bag Filter	2.16	Point	166	No		
		A6	Radial Saw Bag Filter	0.00	Point	168	No		
		A13	Cast Product cut-off Bag Filter	24.55	Point	169	No		
		A14	Grinder Bag Filter	1.24	Point	164	No		
		A15	Melting Shop Scanvenging Filter (West)	33.55	Point	179	No		

		A16	Melting Shop Scanvenging Filter (East)	38.64	Point	179	No		
		A17	EAF Dust Storage Silo Filter	0.00	Point	172	No		
		N/A	West vent melt shop roof	72.83	Line	178	No		
		N/A	East vent melt shop roof	141.59	Line	173	No		
		N/A	Roadways - Traffic		Volume	171	No	**c** (Modelled contribution scaled after unit emissions applied distributed over the volume of each source derived from the mapped surface area and estimated height.), **KCL South cluster**	EA
		N/A	Raw materials storage area - storage of waste dust		Volume	170	No		EA
Sheffield Forgemasters International Ltd	Sheffield Forgemasters Brightside	A1	Melting Shop, Bag Filter Plant Roof Vents	2.01	Line	244	No	**a** (Emissions split between releases derived from 2014 releases in combination with NAEI 2016 emission total.), **KCL West cluster**	EA/NAEI
		A2	Snow Grinder and Melt Shop Flame Cutting Facility	1.34	Point	251	No		

		A3	Forge Ingot Burning, Bag Filter and Plant Stack	2.71	Point	260	No		
		A4	Gas Fired Boiler Plant Stack	1.20E-04	Point	250	No		
		A5	Gas Fired Boiler Plant Stack	1.20E-04	Point	252	No		
		A6	Gas Fired Boiler Plant Stack	1.20E-04	Point	250	No		
		A7	Gas Fired Boiler Plant Stack	1.20E-04	Point	250	No		
		A8	Forge Heating Furnace No.1 Stack	2.39E-04	Point	260	No		
		A9	Forge Heating Furnace No.7 Stack	1.80E-03	Point	261	No		
		A11	Heavy Forge Roof Vents (exhausts from forge furnaces2, 14, 17, 28, selas furnace	4.19E-03	Line	261	No		

			and heat treatment furnaces NTP1 to 16, 18 and 20a/b)						
		A13	Foundry Shot Blast Stack	0.55	Point	257	No		
		A15	Foundry Burning Booth Stack	10.00	Point	257	No		
		A20	Foundry Heat Treatment Furnace Stacks	3.59E-04	Point	256	No		
		A21	Foundry Heat Treatment Furnace Stacks	5.99E-04	Point	256	No		
		A22	Foundry Heat Treatment Furnace Stacks	3.59E-04	Point	257	No		
		A28 (251-255)	Melting Shop Low Casting Bay Roof Vents (Furnaces 251-255)	5.15	Line	250	No		
		A31	Forge Heating	8.38E-04	Point	262	No		

			Furnace No.3 stack						
Liberty Speciality Steels	Aldwarke Lane	-	-	112.49	Point	47	No	**a** (Modelling parameters from PCM and NAEI 2016 emissions.), **KCL East cluster**	PCM/NAEI
VEOLIA ES (SHEFFIELD) LIMITED	Sheffield Energy Recovery Facility	Release Point A1	Main Stack	5.00	Point	233	No	**a** (modelling parameters from 2014 study and NAEI 2016 emissions), **KCL West cluster**	EA/NAEI
E.ON Climate and Renewables UK Biomass Ltd	Blackburn Meadows Renewable Energy Plant	Release Point A1	Main Stack	5.00	Point	341	No	**a** (Modelling parameters from 2014 study and NAEI 2016 emissions.), **KCL West cluster**	EA/NAEI
AMG Superalloys UK Ltd	Fullerton Road	A1	Arc Furnace	2.12	Point	81	No	**a** (Emissions split between releases derived from 2014 releases in combination with NAEI 2016 emission total, locations based on EA 2018 site report in combination with aerial imagery.), **KCL East cluster**	EA/NAEI
		A2	Arc Furnace	9.20	Point	81	No		
		Mix filter 65	Mix filter 65	0.11	Point	81	No		
		Pangborne Shotblast	Pangborne Shotblast	0.13	Point	81	No		
		Arc Furnace Shop Roof Vent	Arc Furnace Shop Roof Vent	6.49	Line	80	No	**b** (Release parameters derived from EA 2018 site	EA

								report, height based on EA LIDAR derived building heights, emissions estimated based on EA 2018 site report.), **KCL East cluster**	
E.L.G. Haniel Metals Limited	Sheffield Road, Tinsley, Sheffield	Oxy-propane Cutting Area	Oxy-propane Cutting Area		Point	27	Yes	**c** (Modelled contribution scaled after emissions and release parameters estimated from 2018 short term monitoring of fugitive emissions.), **KCL East cluster**	EA
		Plasma Cutting Area	Plasma Cutting Area	63.26	Point	16	Yes	**b** (Release parameters and emissions derived from EA 2018 site report.), **KCL East cluster**	EA
Harsco Metals Group Limited, Steelphalt	Sheffield Road, The Ickles, Rotherham	Open stockpile storage of slag	Storage of slag prior to crushing (South of crushing plant)	3.27	Volume	61	No	**b** (Emissions derived from EA 2018 site report applied distributed over the volume of each source derived from the mapped surface area and estimated	EA
		Open storage of crushed/screened slag	Storage of slag prior to coating	3.27	Volume	57	No		EA

			(North of coating plant)					height.), **KCL East cluster**	
		Open storage of crushed/screened slag	Storage of slag prior to coating (South West of coating plant)	3.27	Volume	59	No		EA
		Enclosed crushing plant	Crushing plant	1.31	Volume	60	No		EA
Speciality Steels UK Ltd, Brinsworth Strip Mill	Sheffield Road, Rotherham	A1	Hot Mill Reheat Furnace	0.33	Point	40	Yes	**a** (Modelling parameters from 2014 study and 2016 emissions for A1 stack from EA 2018 site report. A potential fugitive release from the F1 hot mill roof is noted but not treated, because the 2018 site report indicates these emissions are suppressed by BAT process.), **KCL East cluster**	EA
Darwins Holdings Limited, Fitzwilliam Works	Sheffield Road, Tinsley	Roof vents, roller shutter doors etc.	Roof vents, roller shutter doors etc.		Volume	8	Yes	**c** (All processes vent internally into the foundry. Modelled contribution scaled after unit emissions	EA

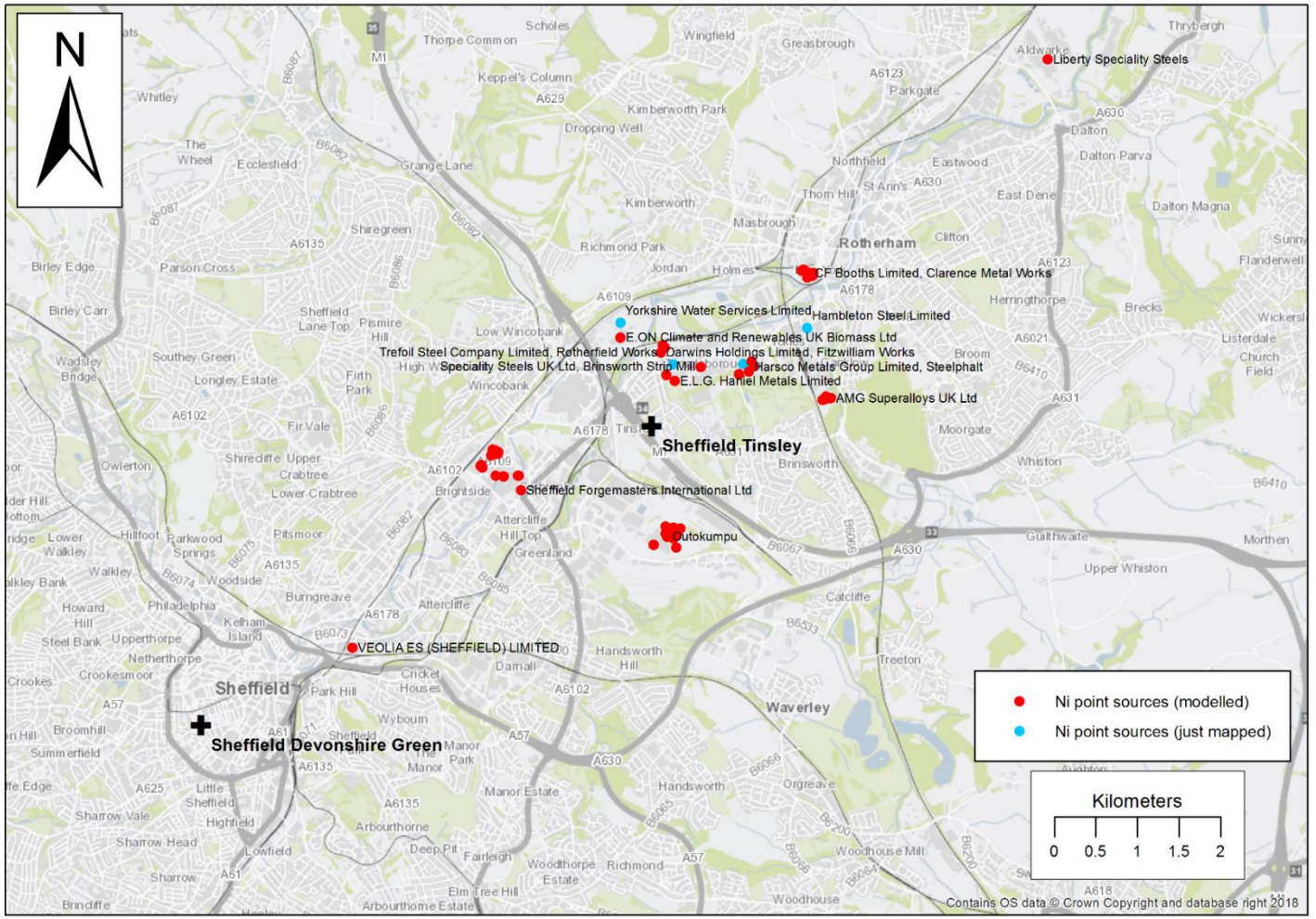
								applied distributed over the volume of the building derived from the mapped surface area and height based on EA LIDAR derived building heights.), **KCL East cluster**	
Trefoil Steel Company Limited, Rotherfield Works	Dead Man's Hole Lane, Tinsley	Melting shop roof vents (release melting, tapping and finishing emissions which vent internally)	Melting shop roof vents		Line	8	Yes	**c** (Modelled contribution scaled after unit emissions applied distributed over the length of roof derived from aerial imagery and at height derived from EA LIDAR derived building heights and Google Earth. Temperature of release assumed near ambient, flow estimated based on reported flows for other EAF roof vents), **KCL East cluster**	EA
		Arc air cutting cartridge filter grille	Arc air cutting cartridge filter grille		Point	9	Yes	**c** (Modelled contribution scaled after estimated emissions applied	EA

								with release parameters based on EA 2018 site report. Temperature of release assumed near ambient, position of release from aerial imagery, height of release from Google Earth.), **KCL East cluster**	
		DCE shotblasting cartridge filter	DCE shotblasting cartridge filter		Point	9	Yes	**c** (Modelled contribution scaled after estimated emissions applied with release parameters based on EA 2018 site report. Temperature of release assumed near ambient, position of release from aerial imagery, height of release from Google Earth.), **KCL East cluster**	EA
CF Booths Limited, Clarence Metal Works	Armer St, Rotherham	Decontamination units: Addax 1 (rotary gas/oil fired dryers which de-grease by volatilisation)	Addax 1	0.34	Point	46	Yes	**b** (Release parameters derived from EA 2018 site report in combination with stack monitoring reports from the	EA

		Decontamination units: Addax 2 (rotary gas/oil fired dryers which de-grease by volatilisation)	Addax 2	0.14	Point	46	Yes	2014 study. Emissions derived from stack monitoring reports from the 2014 study.), **KCL East cluster**	
		Decontamination units: C4 (gas oil fired box type batch furnaces, 1000kg capacity)	C4	0.08	Point	46	Yes		
		Furnaces: F3 (gas oil heated crucible furnace <=5 t capacity)	F3	0.10	Point	47	Yes		
		Furnaces: combine F1, F2, F4, F8 (electric induction furnaces), with F5 and F6 (oxy-oil fired rotary furnaces <5 t capacity)	F1, F2, F4, F8, F5 and F6	0.06	Point	47	Yes		
		Furnaces: F9 and F10 (electric induction furnaces <5 t capacity)	F9 and F10	0.08	Point	44	Yes		
		Combined fugitive nickel emissions for the Addax facilities and furnaces	Addax facilities and furnaces	0.09	Volume	46	No	**b** (Volume of the source derived from the mapped surface area and height based on EA LIDAR	EA

								derived building heights. Emissions derived from EA 2018 site report.), **KCL East cluster**	
		Combined diffuse nickel emissions for Raw Materials Storage Area, road transport/Fork lift trucks/diesel cranes and mobile plant	Raw Materials Storage Area, road transport/Fork lift trucks/diesel cranes and mobile plant	0.11	Volume	44	No	**b** (Volume of the source derived from the mapped surface area and height based on Google Earth. Emissions derived from EA 2018 site report.), **KCL East cluster**	EA

Figure A1.1 – Map of local industrial sources of Ni including modelled sources and sources that were not modelled (just mapped). The locations of the Sheffield Tinsley and Sheffield Devonshire Green monitoring stations are also marked.



A1.2. Modelling approach

ADMS v5.2.1 was used for the current modelling study. Detailed source characteristics for the release points summarised in Table A1.3 were derived from data received from the EA, the PCM and the previous 2014 modelling study as discussed in Section A1.1.3.3.

Model input datasets including terrain and meteorology are briefly described below. Table A1.4 summarises generic modelling parameters applied for each model run.

Table A1.4 – Generic modelling parameters

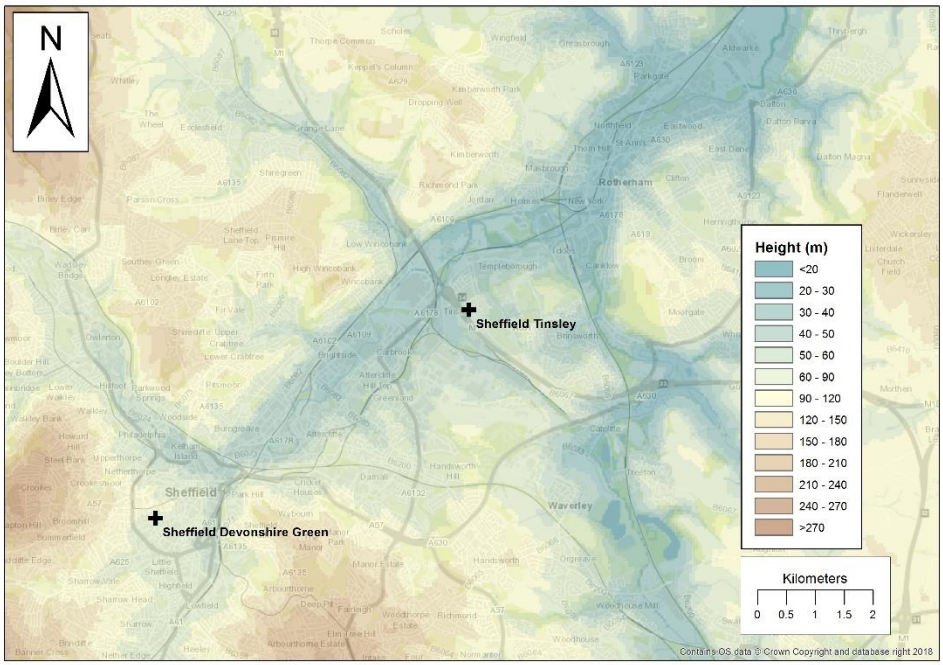
Variable	Parameters
Complex terrain	Y
Terrain grid resolution setting	64x64
Surface roughness at dispersion site	1.0 m[15]
Minimum Monin-Obukhov Length (LMO) at dispersion site	30 m[16]
Surface roughness at met site	0.3 m[17]
Minimum Monin-Obukhov Length (LMO) at met site	20 m[18]
Model output grid resolution	50 m

A1.2.1. Terrain

To treat the effects of terrain on dispersion detailed local terrain data based on OS Terrain 50 was incorporated (see Figure A1.2).

[15] ADMS recommended value for cities, woodlands
[16] ADMS recommended value for cities and large towns
[17] ADMS recommended value for airports
[18] ADMS recommended value for airports

Figure A1.2 - Detailed local terrain based on OS Terrain 50



A1.2.2. Meteorology

An analysis of available meteorological data in the vicinity of Sheffield (not detailed here) was undertaken using the open source R package openair[19]. Data from Sheffield Doncaster Airport and RAF Waddington were evaluated for comparability. Meteorological data for Sheffield Doncaster Airport were used primarily (as the nearest airport meteorological station) and a gap filling procedure based upon the US EPA protocol[20] was followed to compensate for missing data within the Sheffield Doncaster Airport dataset. The protocol was as follows: 1 hour gaps were filled based upon the previous hour, gaps up to 3 hours were filled by interpolation, and larger gaps (>3 hours) were filled with measurements from RAF Waddington.

A1.2.3. Combining model data

As noted in Section A1.1.3, local Ni sources from the NAEI 2016 for which there was no further local data were updated with emissions from the NAEI 2016 and modelled at 1 km x 1 km resolution. The contribution of local sources categorised as (a) and (b) in Table A1.3 were modelled in detail with output on a 50 m x 50 m resolution grid.

The contribution of local sources categorised as (c) in Table A1.3 have also been output on a 50 m x 50 m resolution grid. However, since the emissions rates are unknown, these sources were

[19] https://github.com/davidcarslaw/openair

[20] EPA-454/R-99-005, Meteorological Monitoring Guidance for Regulatory Modeling Applications, 2000, https://www3.epa.gov/scram001/guidance/met/mmgrma.pdf

initially modelled with unit emission rates. The contributions from these sources were then scaled in order to provide source apportionment for the annual concentration measured at Sheffield Tinsley.

The scaling factors applied to these sources were derived by:

1. Multiplying the annual mean measured Ni concentration for 2016 at the Sheffield Tinsley monitoring station (i.e. 23.6 ng m^{-3}) by the percentages allocated to the source direction clusters in the KCL study (Green et al., 2017)[9], in order to derive contributions concentrations from each cluster (11.1 ng m^{-3} for South, 9.3 ng m^{-3} for East and 3.2 ng m^{-3} for West). No scaling has been applied to contributions from the West.
2. Allocating the local sources within this study to the clusters.
3. Scaling the contributions for category (c) sources in the South and East clusters to match the residual between the measured proportion allocated to the clusters and the summed contributions of category (a) and (b) sources in the clusters. No scaling has been applied to contributions from the West.

In the KCL study[9] the South cluster contribution is attributed to Outokumpu Stainless Ltd (SMACC), hence the modelled South cluster contribution in this study has been derived by subtracting the modelled contributions from Outokumpu category (a) components from the measured proportion (0.469 x $[Ni]_{measured,\ 2016}$ = 11.1 ng m^{-3}) to determine a residual. The modelled diffuse contributions from roadways and the raw material storage area (category (c) contributions) have then been scaled to match this residual. Attributing a proportion of the contribution from Outokumpu to the as yet unquantified diffuse sources is consistent with the KCL study, which noted wind driven resuspension as a factor driving elevated concentrations at the Sheffield Tinsley monitoring station.

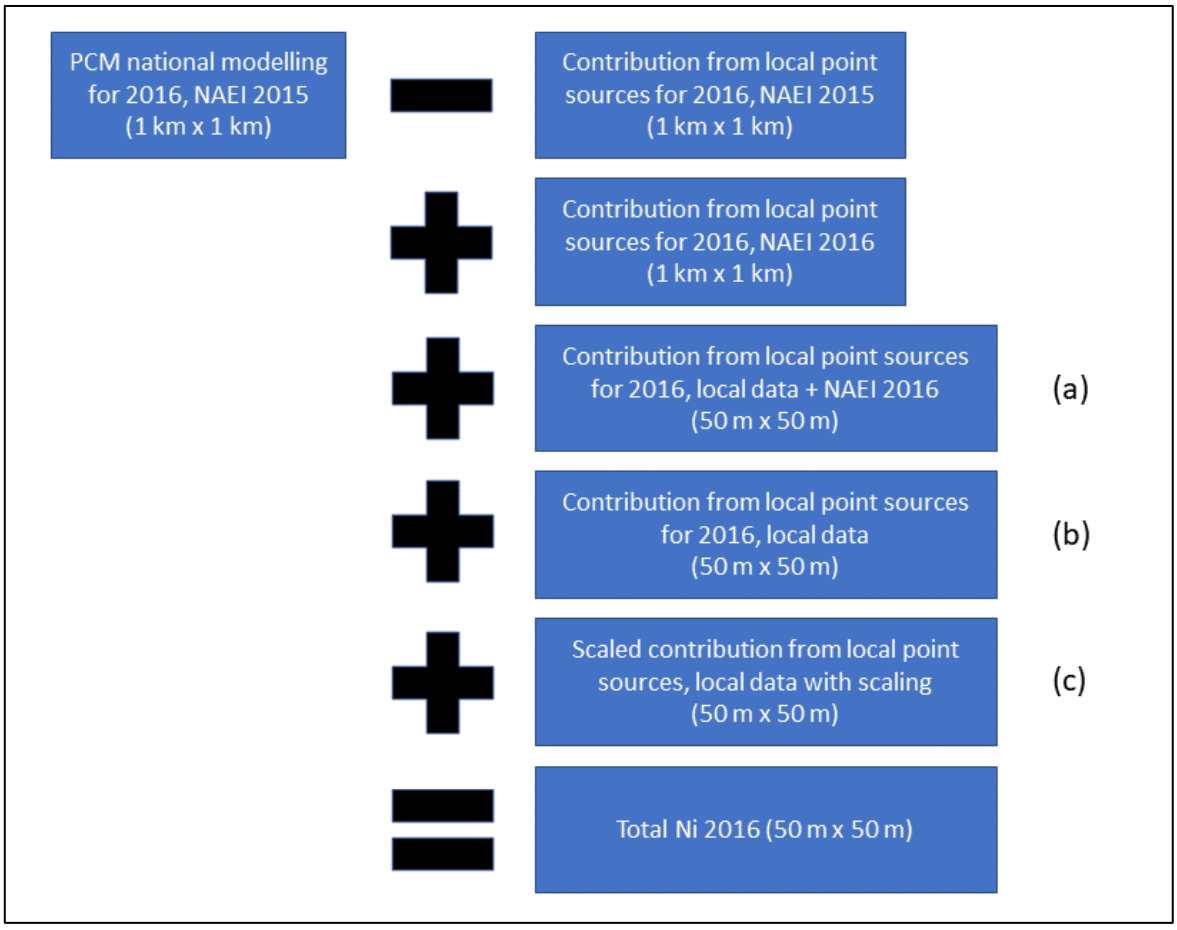
The KCL study attributes the East cluster contributions to Darwin Holdings and/or Trefoil Steel along with other sources to the East contributing to the mean. The EA/SCC/RMBC 2018 project[13] further identified E.L.G. Haniel Metals Ltd as a Ni source in close proximity and in a similar direction from the Sheffield Tinsley monitoring station (see bearings in Table A1.3). In this study the modelled East cluster contribution has therefore been derived by subtracting the modelled contributions from category (a) and (b) sources from the measured proportion (0.396 x $[Ni]_{measured,\ 2016}$ = 9.3 ng m^{-3}) to determine a residual. Since the three unknown contributions within the East cluster are not uniquely identified, and in the absence of other information, the modelled contributions from category (c) sources are combined and a single constant scaling factor has been applied to make the summed contributions match this residual.

The KCL study attributes the remainder of the concentration observed at the Sheffield Tinsley monitoring station to the West cluster contributions, corresponding to emissions from over half of the Ni emitting industries in Sheffield. In this study, the modelled West contribution has been derived from those local sources within this cluster without scaling, and the remaining background contributions from other sources from the PCM national modelling have been added to this and the South and East contributions to make the total modelled Ni concentration for 2016. No attempt

has been made to assign the small residual within the West cluster that is not accounted for by the modelled components.

Figure A1.3 shows how different modelled contributions have been combined. It must be noted that the source apportionment derived in this study depends on the representativeness of the KCL study for the year 2016. Within the results (Section A1.3) the combined output is referred to as Ni 2016c.

Figure A1.3 – Schematic of process to combine modelled contributions



A1.3. Model results

The results from the modelling study are presented in terms of concentration maps including a review of compliance impacts within the study domain (Section A1.3.1), and source apportionment in comparison to observations (Section A1.3.2).

A1.3.1. Concentration maps and compliance impact

Figure A1.4 presents a subset of the 2016 annual mean Ni concentration map for the Sheffield area from this study that excludes the contributions from the scaled sources. It is notable that even

excluding the scaled contributions, exceedances of the Ni TV (20 ng mg^{-3}) are modelled in the vicinity of the Outokumpu site to the South of the Sheffield Tinsley monitoring station and in the vicinity of sources to the North and North East. The footprint of the modelled exceedance in this case does not extend to the location of the Sheffield Tinsley monitoring station.

Figure A1.5 presents the modelled total 2016 annual mean Ni concentration map for the Sheffield area from this study including the contributions from the scaled sources. The contribution of scaled sources in the East cluster to the mapped total concentration is based on the use of a single constant scaling factor as noted in Section A1.2.3. Including the scaled contributions (noting this adds point, fugitive and diffuse contributions to the local sources identified in the KCL study (Green et al., 2017)[9] and the EA/SCC/RMBC 2018 project[13]) the area of exceedance of the Ni TV (20 ng mg^{-3}) extends from the sources to the North of the Sheffield Tinsley monitoring station down to the Outokumpu site to the South, with the footprint of the modelled exceedance including the location of the Sheffield Tinsley monitoring station. An inspection of the area of modelled exceedance compared to 1 km gridded population (2011 census) indicates population exposure from the area surrounding Outokumpu in the South to the Meadow Bank Road in the North. The model results also suggest the area of exceedance extends across the zone boundary to the South of Outokumpu into the neighbouring Yorkshire and Humberside non-agglomeration zone (UK0034). Further work will keep this exceedance situation under review, including the possibility of the exceedance extending into the Yorkshire and Humberside non-agglomeration zone (UK0034).

A1.3.2. Source apportionment

Figure A1.6 shows the modelled Ni contribution from different sources at Sheffield monitoring site locations based upon the combined modelling output for 2016 (Ni 2016c). Measured concentrations at the sites are also presented, giving an indication of the level of agreement between modelled and measured concentrations. As noted in Section A1.2.3 the contribution of local sources categorised as (c) in Table A1.3 are uncertain and have been scaled such that the total modelled from the South and East clusters in this study match the percentages apportioned to these clusters in the KCL study[9]. This approach attributes the main industrial sources of Ni at the Sheffield Tinsley monitoring station to the South cluster (Outokumpu) and the East cluster (E.L.G. Haniel Metals, Darwin Holdings, Trefoil Steel). Since the unknown contributions in the East cluster are not separable and have been scaled using a single factor, their contribution is shown as an aggregated total in the source apportionment (labelled “Scaled contributions from North East (c)”). It is notable that excluding the scaled components, the Outokumpu site remains the main industrial source of Ni at both the Sheffield Tinsley and Sheffield Devonshire Green monitoring stations.

With no scaling applied to sources in the West cluster or the other background contributions from the national modelling, a small under prediction remains. The combined modelling output represents 95% of the observed concentration at Sheffield Tinsley, and 70% of the observed concentration at Sheffield Devonshire Green.

Figure A1.4 - Map of annual mean Ni concentrations for 2016 from local fine-scale modelling of industrial sources based on reported (a) or derived (b) emissions added to the background Ni concentrations from the national model. The locations of modelled industrial sources and additional industrial sources not modelled (just mapped) are also shown.

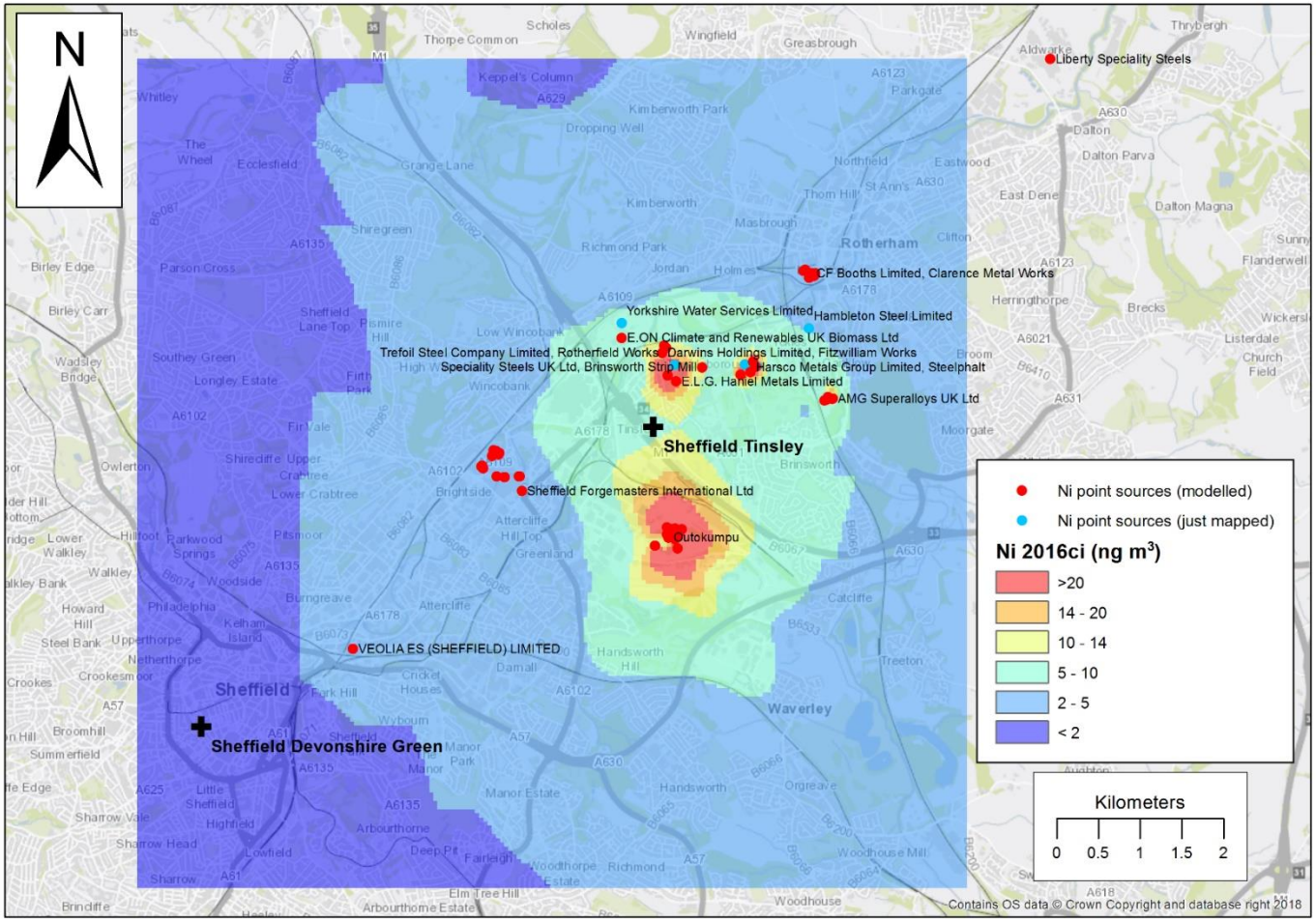


Figure A1.5 – Map of total annual mean Ni concentrations for 2016 from local fine-scale modelling of industrial sources based on reported (a) or derived (b) emissions, plus scaled contributions from uncertain local point/fugitive/diffuse sources (c) added to the background Ni concentrations from the national model. The locations of modelled industrial sources and additional industrial sources not modelled (just mapped) are also shown.

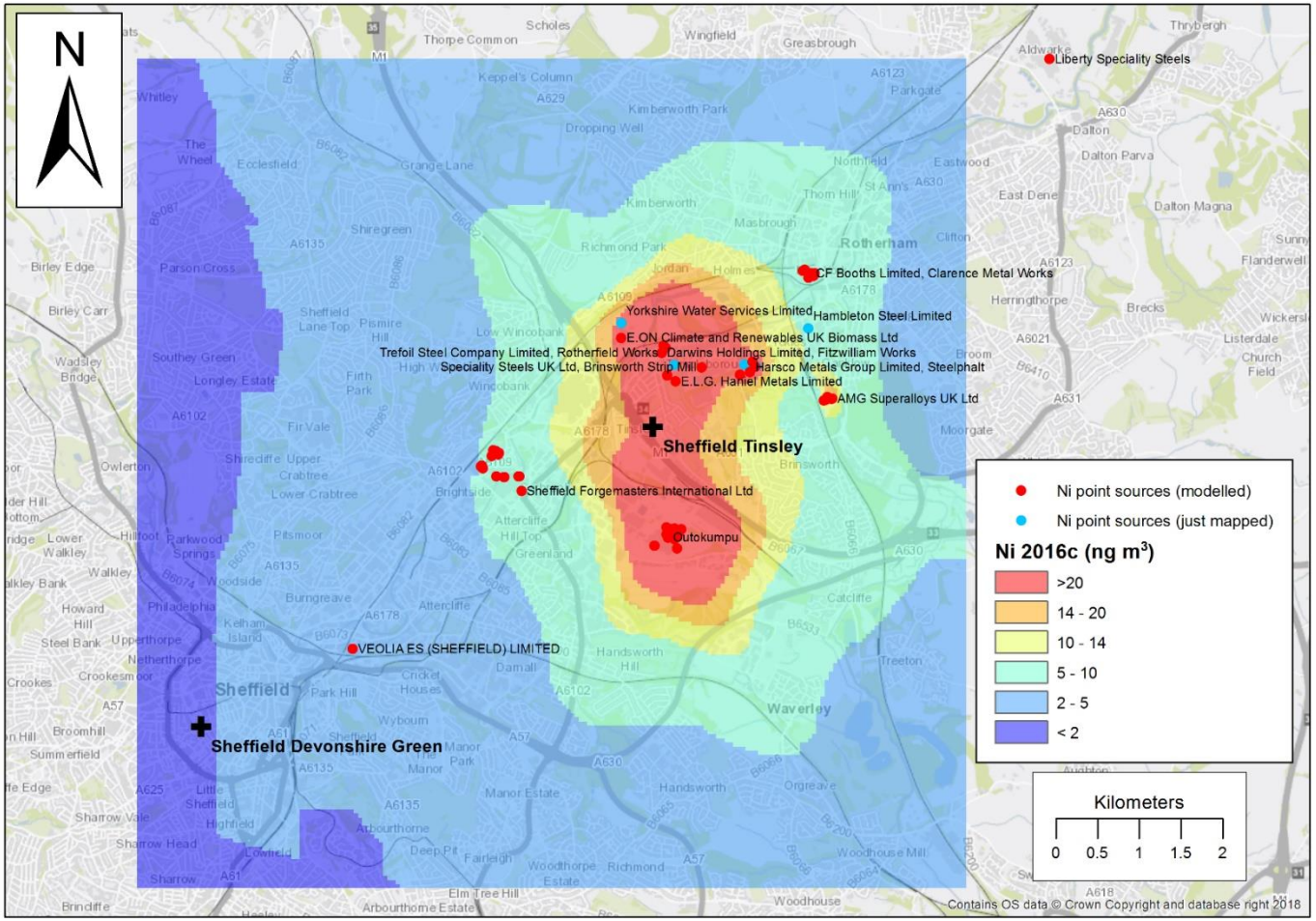
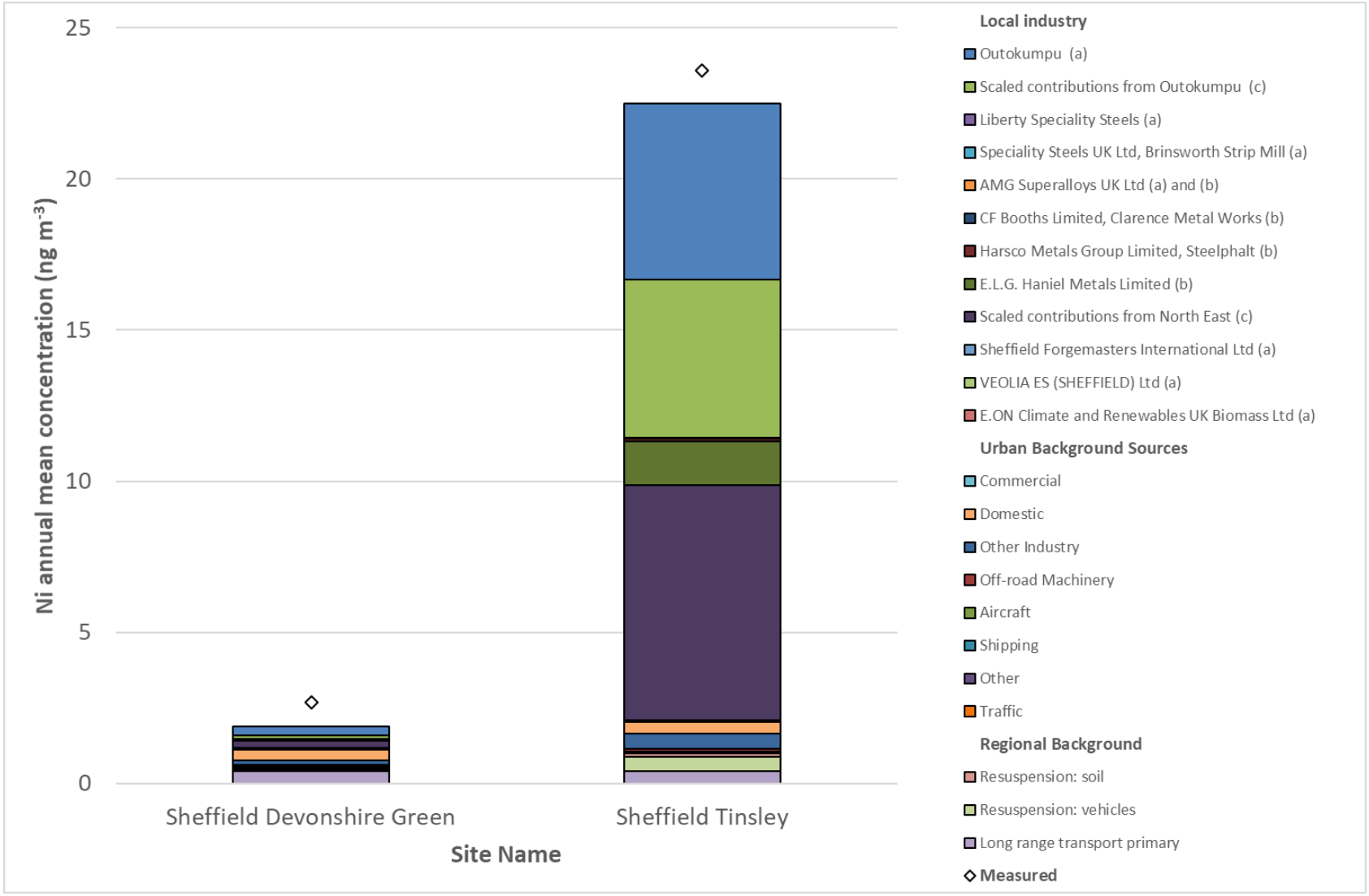


Figure A1.6 - Annual mean Ni source apportionment at Sheffield monitoring sites in 2016 (combined detailed and national modelling output)



A1.4. Conclusions

Based upon the results of the detailed modelling study present here:

- The detailed modelling indicates exceedances of the Ni TV (20 ng mg^{-3}) associated with the Outokumpu site and sites to the North of Sheffield Tinsley (including E.L.G. Haniel Metals, Darwin Holdings, and Trefoil Steel) although the individual contributions of the sources to the North East are not represented, and the magnitude of contributions and spatial extent of exceedances depends on the representativeness of the analysis in the KCL study (Green et al., 2017)[9] for the 2016 annual mean.
- The footprint of the modelled exceedance includes the Sheffield Tinsley monitoring station and inspection of the area of modelled exceedance compared to 1 km gridded population (2011 census) indicates population exposure from the area surrounding Outokumpu in the South to the Meadow Bank Road in the North. The model results also suggest the area of exceedance extends across the zone boundary to the South of Outokumpu into the neighbouring Yorkshire and Humberside non-agglomeration zone (UK0034). Further work will keep this exceedance situation under review, including the possibility of the exceedance extending into the Yorkshire and Humberside non-agglomeration zone (UK0034).
- The source apportionment analysis suggests that the main industrial source of Ni at both the Sheffield Tinsley and Sheffield Devonshire Green monitoring stations is Outokumpu, with sites to the North of Sheffield Tinsley (including E.L.G. Haniel Metals, Darwin Holdings, and Trefoil Steel) contributing to the measured exceedance there.
- The combined modelling output represents 95% of the observed concentration at Sheffield Tinsley, and 70% of the observed concentration at Sheffield Devonshire Green.

Recommendations:

- A significant proportion of the total Ni concentration modelled in this study has been derived by scaling contributions from uncertain point, fugitive and diffuse emissions from the industrial sites noted above. There is scope for further improving understanding of the emissions, activity levels and timing of operations identified in KCL study[9] and the EA/SCC/RMBC 2018 project[13], which would focus attention on the main Ni emitters and provide information for modelling studies.
- The high temporal resolution monitoring conducted by NPL and KCL has been valuable in that it enables directional analysis and informs source apportionment. Should work be needed to interpret future exceedances or to analyse the impact of measures such monitoring campaigns would be recommended.

- The national modelling for compliance assessment does not capture the observed exceedance because not all of the sources identified in this study are fully captured by the NAEI. Data gathered in this study and resulting from measures to quantify and reduce emissions from industry in Sheffield, could be used to inform future modelling and compliance assessments.

A2. Monitoring studies

Source Apportionment of Nickel Sources at Sheffield Tinsley

KING'S College LONDON

November2017

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Environmental Research Group, King's College London

Title	Source Apportionment of Nickel Sources at Sheffield Tinsley

Customer	Department for Environment, Food & Rural Affairs

Customer Ref	

File Reference	ERG\ AIRQUALI\Defra\Sheffield\SheffieldNickelReport_Final.docx

Report Number	-

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Executive Summary

Concentrations of Nickel in PM_{10} measured at the Sheffield Tinsley monitoring stations have exceeded the EU Target Value in 2004, 2014 and 2016. The nearby Outokumpu steel manufacturing plant, producing steel strip and coil products, was highlighted as the potential source of the elevated Ni concentrations at these sites due to its locality as well as it being the largest nickel emissions source in the UK but there are many other sources of Ni in the Sheffield area. The aim of this study was to identify the sources of Nickel in PM_{10} measured at this location and data was collected during a 10 week measurement campaign using the latest high time resolution measurement techniques.

This work identified two sources of Nickel: one related to point source emissions which was characterised by molybdenum and manganese and one fugitive source type, characterised by chromium and calcium, likely to be associated with material handling or transport.

Wind speed and direction measurements were used to quantify where these source types were emitted from. There were 3 source directions – East, West and South. The source was from the south, which contributed 47% to the Nickel concentrations measured during this study, can confidently be associated with the Outokumpu facility. This contribution can be viewed as 31% from the point source type and 16% from the fugitive source type.

The source from the West made the smallest contribution (14%) and represented the emissions from over half of the industries in Sheffield, which lie in that direction and was dominated by the point source type.

The source to the East contributed 40%. Of this, 35% was related to the point source type most likely and 5% from the fugitive source type.

The widespread nature of the point related source type across industries in Sheffield makes this challenging to tackle. However, focusing resources to identify specific processes from the identified industrial sources would be a useful initial step towards reducing Nickel emissions. The fugitive source type was clearly most influenced by the local Outokumpu plant and further work to identify the processes and / or activities which are leading to these emissions may be the most cost-effective way of ensuring that the measurements at the Sheffield Tinsley site remain below the annual mean EU Target Value for nickel.

Introduction

Nickel (Ni) concentrations in the UK are regulated under the 4th Daughter Directive (Directive 2004/107/EC, DD4); this stipulates a Lower Assessment Threshold (LAT), an Upper Assessment Threshold (UAT) and Target Value (TV) (see Table 1). Exceedances of the UAT and LAT must be determined based on concentrations during the previous five years. An assessment threshold will be deemed if it has been exceeded during at least three years out of the previous five. The assessment threshold determines subsequent assessment measures. Member States are required to identify zones and agglomerations where exceedances of the TV occur. Exceedance of the TV triggers a requirement within the Directive to prepare a report on measures. In the case of industrial emissions, measures not entailing disproportionate costs, i.e., Best Available Technology (BAT), must be applied to attain the TV. Source identification is not a formal requirement but is clearly a prerequisite for demonstrating that all measures not entailing disproportionate costs have been taken.

Table 1: Target Value, upper and lower assessment thresholds for Ni (Directive 2004/107/EC)

	Nickel
Target Value	20 ng m^{-3}
Upper assessment threshold in percent of the target value	70% (14 ng m^{-3})
Lower assessment threshold in percent of the target value	50% (10 ng m^{-3})

The UK Heavy Metals network measures the Ni concentrations on filters sampled over a 2-week period. Annual mean Ni concentrations measured in Sheffield city centre (Centre and Devonshire Green monitoring stations) have remained consistently below the LAT since monitoring began in 2004. However, annual mean Ni concentrations at the Brinsworth and Tinsley monitoring stations have ranged from 10 to 21 ng m^{-3} during this time indicating a localised enhancement of Ni.

A scoping assessment and supplementary modelling work (Brookes and Rose 2016) were carried out to investigate the source of the measured exceedance of the TV for Ni during 2014. These studies identified that the annual mean Ni concentrations at these stations were typically greater than the LAT of 10 ng m^{-3} across all years (2004-14). Further, the annual mean Ni concentrations were between the TV and UAT in 2005, 2010, 2011 and 2013. Exceedances of the TV were only measured in 2004 and 2014 but has since exceeded again in 2016. The nearby Outokumpu steel manufacturing plant, producing steel strip and coil products, was highlighted as the potential source of the elevated Ni concentrations at these sites due to its locality as well as it being the largest nickel emissions source in the UK.

An enhanced daily measurement study undertaken in 2016 (Butterfield and Goddard 2016) also identified the Outokumpu facility as the most likely source but accepted that hourly time resolution measurements of Ni combined with local meteorological measurements would be required to provide further insight.

The aim of this study was to identify the sources of Ni with size < 10 µm (PM_{10}) measured at the Tinsley Defra measurement station. For that, data was collected during a 10 week measurement campaign using the latest high time resolution measurement techniques. The location of the Tinsley measurement station and also the main industrial sources of Ni are shown in Figure 1.

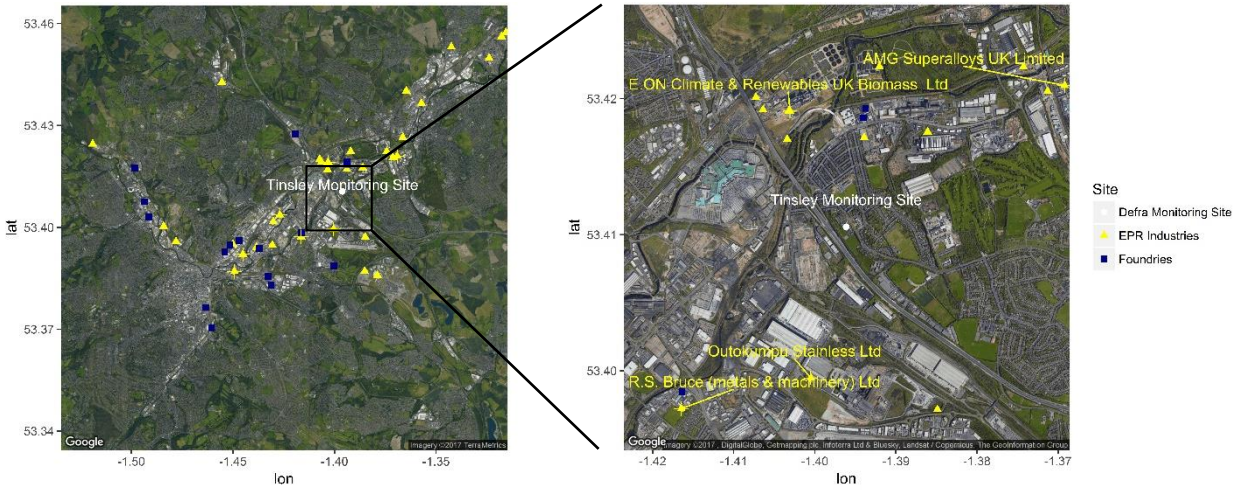


Figure 1: Map of showing the Sheffield Tinsley measurement station location and surrounding industrial sources

Methods

Measurement Campaign

Between the 19th January and the 26th March 2017, a range of chemical components of Particulate Matter (PM) were measured at the Tinsley measurement station using the King's Mobile Atmospheric Research Platform (MARPL) (Figure 2). The Tinsley measurement station (53° 24' 38'' N; 1° 23' 46 ''W) is an affiliated site on the DEFRA Automatic Urban and Rural Network (AURN) and is also a Heavy Metals Network site. The equipment is held within the grounds of the Tinsley Community Centre approximately 200 metres east of the M1 motorway. The surrounding area is generally open, with residential areas to the east of the M1 and light industrial premises to the west of the M1.

Concentrations of nitrogen oxides (NO_X = NO + NO_2) were available for the duration of the campaign at hourly basis for this location from the AURN (https://uk-air.defra.gov.uk/data/). During the campaign, the National Physical Laboratory (NPL) increased the time resolution of the filter measurement from bi-weekly to daily at the Tinsley site. Also, the measurement of regulatory metals was complemented with a small suite of additional metals. This was done to ensure that the XRF technique was comparable to the longer term measurements using ICP-MS because a short number of weekly samples would not have produced the number and the diversity in concentrations to establish a robust correlation between measurement techniques.

Figure 2: MARPL at Tinsley monitoring station (left) and inside MARPL (right)

Instrumentation

The instrumentation deployed in MARPL is listed below.

Meteorological Measurements

Wind speed, wind direction and temperature were measured at a height of 10 m using a Met One AIO2 weather sensor at 15-minute-mean time resolution.

Aethalometer AE21

The Magee-32 aethalometer measured Black Carbon (BC) in PM with diameter <2.5 µm ($PM_{2.5}$) at a 15 minute resolution. The measurement technique is based on the transmission of light at 880 nm through a sample collected onto a quartz tape. The instrument calculates the absorption coefficient of the sample by measuring the attenuation of the light passing through the sample relative to a clean piece of filter. The change in the attenuation is converted to BC concentration using a mass extinction coefficient of 16.6 $m^2\ g^{-1}$ chosen by the manufacturer to give a good match to Elemental Carbon. In practice this mass extinction coefficient varies with factors such as particle size, sample composition and quantity of material already on the filter. The effect of this nonlinearity due to filter loading was corrected using the model developed by Virkkula et al (2007).

X-ray fluorescence (XRF)

The Cooper Environmental Services Xact™ 625 automated multi-metals monitor is based on reel-to-reel filter tape sampling followed by non-destructive X-ray fluorescence (XRF) analysis of metals. In this study it was used for continuous measurements of twenty $PM_{2.5}$ elemental components: Arsenic (As), Barium (Ba), Calcium(Ca), Cerium (Ce), Chromium (Cr), Cooper (Cu), Iron (Fe), Potassium (K), Manganese (Mn), Nickel (Ni), Lead (Pb), Sulphur (S), Antimony (Sb), Selenium (Se), Silicon (Si), Strontium (Sr), Titanium (Ti), Vanadium (V) and Zinc (Zn). Sampling and analysis was performed continuously and simultaneously, except for the time required to advance the tape (~20 s). Concentrations for the 20 elements were reported at hourly basis. Daily automated quality assurance checks were performed every night at midnight with this hour missing for ambient measurements. Quality assurance and quality control (QAQC) including internal (palladium) and external standards checks (for all analysed metals); field and instrument blanks (Teflon tape); energy calibration; metals upscales (for Cd, Cr, and Pb) for baseline; and flow calibration was performed to ensure the sensitivity, precision and accuracy of the measurements.

Particle Size Distribution

Particle size distribution was measured using a Scanning Mobility Particle Sizer (SMPS – TSI model 3080) for particles with diameters 14 – 673 nm; and using an Aerodynamic Particle Sizer (APS – TSI model 3321) for particles between 370 nm and 20 µm. The SMPS consisted of an electrostatic classifier and a Condensation Particle Counter (CPC - TSI model 3775). The electrostatic classifier contained a source of Kr-85 charge and a Differential Mobility Analyser (DMA – TSI model 3081). The former brings the particles in the sample to a known steady state charge distribution; and the latter allows particles of a single electrical mobility (a quantity related to particle diameter) to pass to the CPC to be counted. By varying the operating voltage of the DMA the size of particles sent to the CPC can be varied and a size distribution obtained. The APS measured the aerodynamic size of a particle by its rate of acceleration, with larger particles accelerating more slowly due to increased inertia using two partially overlapping laser beams.

Emissions from local industrial processes

Understanding the location of the local industrial sources is vital when allocating source contributions using highly time resolved ambient and meteorological measurements. Both the Environment Agency (who regulate Part A1 processes) and Sheffield City Council (who regulate Part A2 and B processes) provided detailed source information and this is shown in Figure 1; the descriptions are reproduced from (Butterfield and Goddard 2016). Routine monitoring, where carried out, is based on the measurement of total suspended particles.

Part A1 processes regulated by the Environment Agency

Sheffield Forgemasters **International Limited**: Steel scrap, other raw materials and alloys are melted in a 100 tonne charge weight Electric Arc Furnace. The molten steel is tapped from the furnace into a pre-heated ladle which is then transferred into one of the secondary steelmaking units; a Vacuum Arc Degassing unit, a Vacuum Oxygen Decarburising unit and depending on the process route being used, a Ladle Furnace. The function of the secondary steelmaking units is to refine the metallurgical properties of the steel. The molten steel is then cast into ingots, some of which are unprocessed and sold direct to customers whilst others undergo further processing including surface treatment, heat treatment, ingot burning, forging and finishing. Molten steel is also transported in the ladles to the Foundry operations for casting.

Outokumpu (SMACC): The main purpose of the installation is the manufacture of stainless steel from high quality ferrous scrap metal. In full production, a maximum of 600,000 tonnes per annum of steel can be produced, which has a high chromium content (average 18.5%). Steel scrap and other raw materials are melted in an electric arc furnace, which has a nominal capacity of 130 tonnes. The melt is tapped into a ladle for transfer to the secondary steel making unit; all steel is transferred to an argon-oxygen decarburisation vessel for reducing the carbon content of the liquid steel and, depending on the process route being used, to a ladle arc furnace or to an argon rinse station. Lime is added to produce a lime-based slag which extracts, by chemical reactions, unwanted impurities from the molten steel. The function of the secondary steel making units is to improve the metallurgical properties of the steel by refining. Metal

alloying additions are made to achieve the correct steel analysis to meet specifications. The specific sources on the local Outokumpu site are shown in Figure 3.

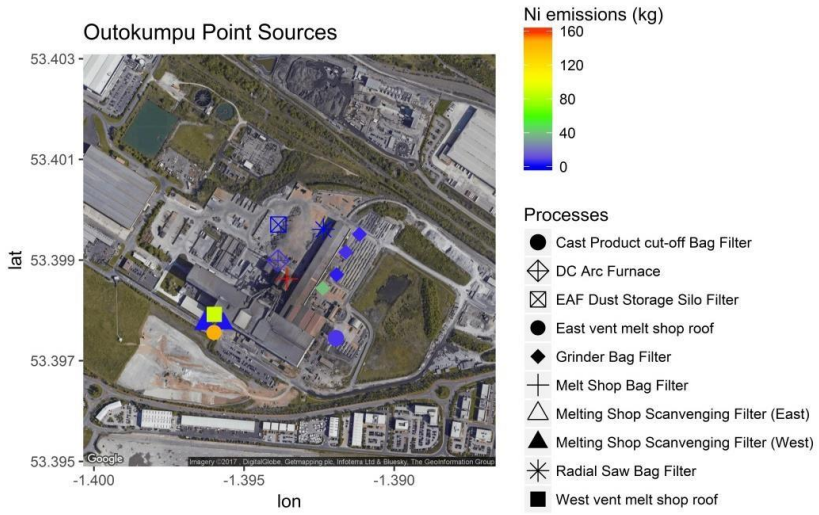


Figure 3: Sources on Outokumpu site

TATA Steel – Brinsworth Strip Mill: The Brinsworth Strip Mill, part of the TATA Special Steels business, operates a hot mill producing narrow strip. The business also undertakes acid pickling of rolled strip to achieve the desired surface cleanliness. The hot mill produces hot rolled strip (up to 515 mm wide) in carbon and alloy steels including certain non-ferrous materials. It produces approximately 160,000 tonnes of hot coiled strip per annum. The Strip Pickling Plant operates in conjunction with the Hot Mill to remove mill scale and clean the surface of the strip using dilute hydrochloric acid prior to sale or subsequent cold rolling and/or heat treatment.

AMG Superalloys: The installation covers the production of nickel, cobalt and copper shot using an electric arc furnace; and the production of ferro boron, chrome boron and nickel boron in three smaller electric arc furnaces.

Part B and A2 processes regulated by Sheffield City Council

Darwin Holdings: The melting of steel scrap, ferro alloys and pre-melt ingots in four high frequency electric induction Inductotherm furnaces two of which have 2 tonne capacity, one with a 1 tonne capacity and one with 0.5 tonne nominal capacity. All furnaces vent internally so emissions are fugitive. All their fettling/shot blasting activities vent internally to the foundry.

Trefoil Steel: The production of stainless steel, carbon steel and low alloy steel melting clean pig iron and steel scrap with the addition of ferro manganese, ferrochromium, ferro molybdenum, ferro silicon and calcium silicomanganese as alloying elements, using two high frequency electric induction Inductotherm furnaces. The furnace capacities are 600 kg and 920 kg. The furnaces vent internally to the foundry so emissions are fugitive. They have shot blasting and welding benches that vent internally but one arc air unit vents externally.

Norton Cast Products: The production of carbon steel, low alloy steel, stainless steel and nickel alloys in six furnaces. This foundry has no stacks to atmosphere from the melting furnaces, the fumes are fugitive within the foundry and then released via roof holes/cracks or roller shutter doors if these are open. They have recently installed a 5 tonne furnace and this also vents internally. They have arc air, fettling and welding benches which are extracted to filters which emit to atmosphere.

Atomising Systems: The process operates two main production atomisers. Atomisation is a process used to produce powders of metal alloys to very high tolerance levels with respect to shape, size and consistency. The metal powders are used in many industries and many applications ranging from solder and brazing pastes to catalytic converters and nanotechnology. The main alloys produced on site are copper alloys. Other alloys include ferrous, nickel and precious metal alloys. The production capacity is 2000 – 5000 tonnes of powder per annum.

Thessco Limited: Silver and base metals are melted in either electric or gas-fired furnaces of various sizes ranging from 0.035 to 1.5 tonne capacity. Molten metal alloys from the melting furnaces are then cast, using continuous casting units or hand casting, into iron moulds.

Source identification

In order to identify the source contributing to the highest concentration of Ni, the bearings from the Tinsley monitoring station to each registered process were calculated and are shown in

Table 2; information on the process was not always available and is therefore not included in section 0 above. The nickel and chromium feedstock used by the industries near Tinsley as in March 2016 are summarized in Table 3.

Table 2: Mean distance and range of bearings to each Ni emitting process in the Sheffield area

Company	Distance (m)	Bearing
Darwins Holding Ltd	903	9
Trefoil Steel Company Ltd	983	9
AMG Superalloys UK Limited	2130	57
Outokumpu - Grinder Bag Filter	1327	168
Outokumpu - Cast Product cut-off Bag Filter	1488	169
Outokumpu - Melt Shop Bag Filter	1341	173
Outokumpu - DC Arc Furnace	1299	173
Outokumpu - Melting Shop Scanvenging Filter (West)	1429	180
Outokumpu - Melting Shop Scanvenging Filter (East)	1429	180
Outokumpu - West vent melt shop roof	1429	180
Outokumpu - East vent melt shop roof	1429	180
Sheffield Forgemasters International Ltd	2180	249
Atomising Systems Ltd	2448	186
Outokumpu Stainless Ltd	1270	193
Orchid Orthopedic Solutions Sheffield Ltd	3855	217
William Cook Integrity Ltd	3693	221
R.S. Bruce (metals & machinery) Ltd	2008	222
Castings Technology International	6182	224
Norton Cast Products Ltd	1903	225
The Alloy Steel Melting Company Ltd	5868	230
Veolia ES Sheffield Limited	4391	233
F E Mottram Ltd	3298	236
Thessco Ltd	3849	238
Brass Founders Sheffield	4321	243
Durham Foundry (Sheffield) Ltd	4067	245
ATI Allvac Ltd	3736	245
Transition International Ltd	6377	262

Symmetry Medical Sheffield Ltd	6478	267
ELG Carrs stainless steels	6816	277
Tata Steel UK Ltd	15204	302
Tivac Alloys Ltd	2430	321
E.ON Climate & Renewables UK Biomass Ltd	1052	334

Table 3: Nickel and Chromium feedstock used by surrounding industries in March 2016

Company	Direction from monitoring site to emission source	Emissions Regulation Part	Ni (tonnes)	Cr (tonnes)
Outokumpu	160-220˚	Part A	1636.66	3479.75
Brinsworth Strip Mill	30-60 ˚	Part A	204.69	
Sheffield Forgemasters	230-260 ˚	Part A	23.33	
Atomiser Systems Ltd	200-220 ˚	Part B	5.46	17.43
Norton Cast Products	210- 230 ˚	Part B	1.69	0.83

Results

The following sections describe the measurements made using the different techniques during the campaign.

Temporal representativity

A key question when examining measurements from a relatively short sampling campaign is how representative of the long term measurement they are. This question can be addressed by comparing the meteorological and ambient measurement between the campaign and those measured over the long term. However, conclusions should be drawn with some caution as, although the seasonal and meteorological variability can be somewhat characterised, little is known about any changes in the emission patterns.

The long term weekly concentration of Ni is plotted in Figure 4 alongside the high time resolution measurements averaged to a weekly mean. The long term means are stable except for a period between March and June 2016 where Ni concentrations attained values > 100 ng/ m^{-3}. Measurements for the period when the high-time resolve measurements were undertaken (January – March 2017; shaded red rectangle) lie within the range of routinely measured concentrations. The mean Ni concentration measured by routine filters was 19 ng m^{-3} (excluding those measurements marked <LOD; Limit of Detection) while the mean concentration as measured by the XACT was 23.8 ng m^{-3} (shown in Table 4).

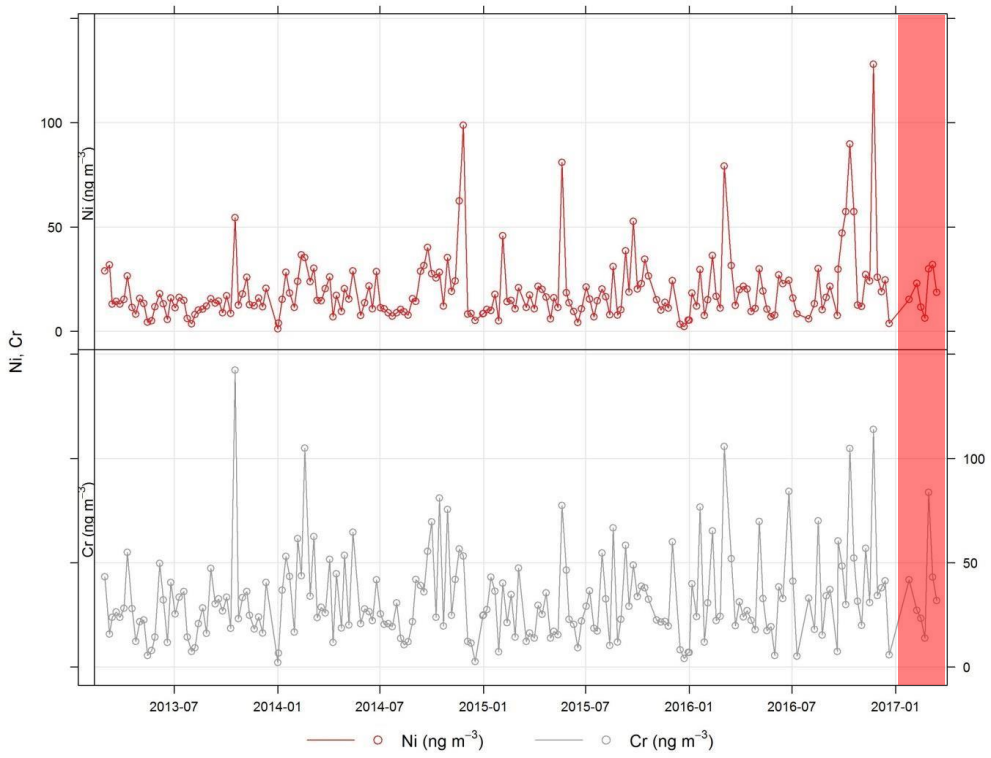


Figure 4: Long term weekly measurements of Ni and Cr alongside measurements from the campaign (shaded red)

To assess whether the meteorological conditions experienced during this campaign were unusual, the wind speed and wind direction measured during the campaign by the met mast at MARPL were compared to those measured at Sheffield Airport for the whole of 2016; this comparison is shown in Figure 5. Generally, the two frequency plots are in agreement, however there are large discrepancies in winds from 330˚, 360˚ and 150˚. Fortunately, none of these wind directions align with any of the significant industrial sources and the campaign can be regarded as representative of the typical wind speed and directions and therefore of industrial point sources. The broader seasonal variability, especially drier summer conditions which may result in stronger fugitive sources, will not be reflected by this winter campaign.

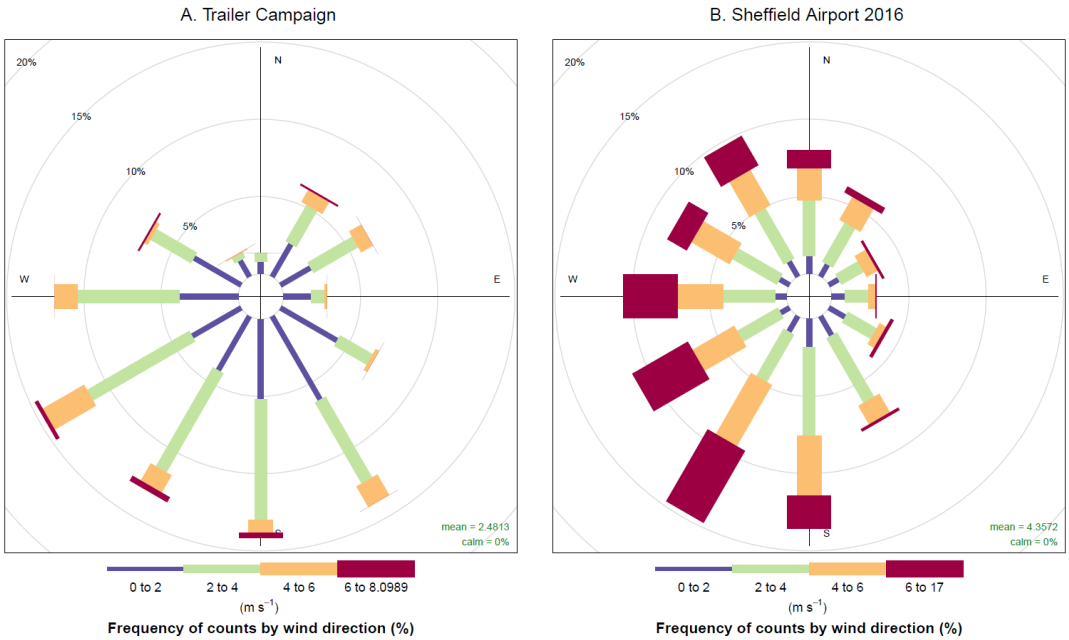


Figure 5: Frequency plots of wind speed and direction as measured during the campaign (Jan-Mar 2017) (A) and Sheffield Airport for 2016 (B)

PM mass concentrations and chemical composition

Campaign overview

The statistics for the hourly and daily mean concentrations for the metals measured by the XACT instrument are summarized in Table 4. The mean Ni concentration was 23.8 ng m^{-3} (calculated from hourly means); this was above the annual mean TV (20 ng m^{-3}).

Table 4: PM chemical speciation data summary

Element	Mean (ng m^{-3})	Median (ng m^{-3})	Min (ng m^{-3})	Max (ng m^{-3})
As	2.9	0.4	0.0	670.8
Ba	2.7	1.1	1.1	160.1
Ca	402.0	248.5	1.7	4307.8
Cd	4.2	4.1	4.1	72.4
Ce	0.8	0.4	0.4	27.0
Cl	1364.5	761.2	4.8	9949.7
Cr	52.1	8.5	0.0	1520.0
Cu	18.0	11.4	0.3	203.1
Fe	685.7	453.5	10.9	15503.6
K	141.5	108.1	3.7	1020.0
Mn	47.2	14.6	0.2	1202.0
Mo	14.7	0.9	0.9	1794.6
Ni	23.8	3.1	0.3	1333.6
Pb	22.2	8.2	0.3	1310.4
Pt	0.2	0.2	0.2	1.8
S	782.2	492.0	24.9	4850.8
Sb	0.2	0.0	0.0	142.1
Se	0.9	0.2	0.1	34.8
Si	216.5	85.7	85.7	3545.2
Sr	1.2	0.5	0.5	9.3
Ti	27.4	11.3	0.4	2036.7
V	1.3	0.2	0.2	123.2
Zn	100.7	25.5	0.2	4873.8

The hourly time series, diurnal and weekly variations alongside a bivariate polar plot for Ni are shown in Figure 6. This demonstrates the transient nature of the impact of the Ni emission at the Tinsley location; emissions combine with meteorological factors to create a time series characterised by short term peak concentrations. This is in marked contrast to the typical traffic signature exhibited by the NO_2, Black Carbon (BC) and particle number (PCNT) measurements shown in Figure 7, Figure 8 and Figure 9, respectively. All of these showed a bi-peak diurnal variation consistent with the morning and afternoon rush hour peaks; and showed lower concentrations during the weekend consistent with both reduced traffic and reduced industrial activity. The early morning peak was common to all pollutants shown here and was the result of reduced dispersion and increased emissions at this time of day.

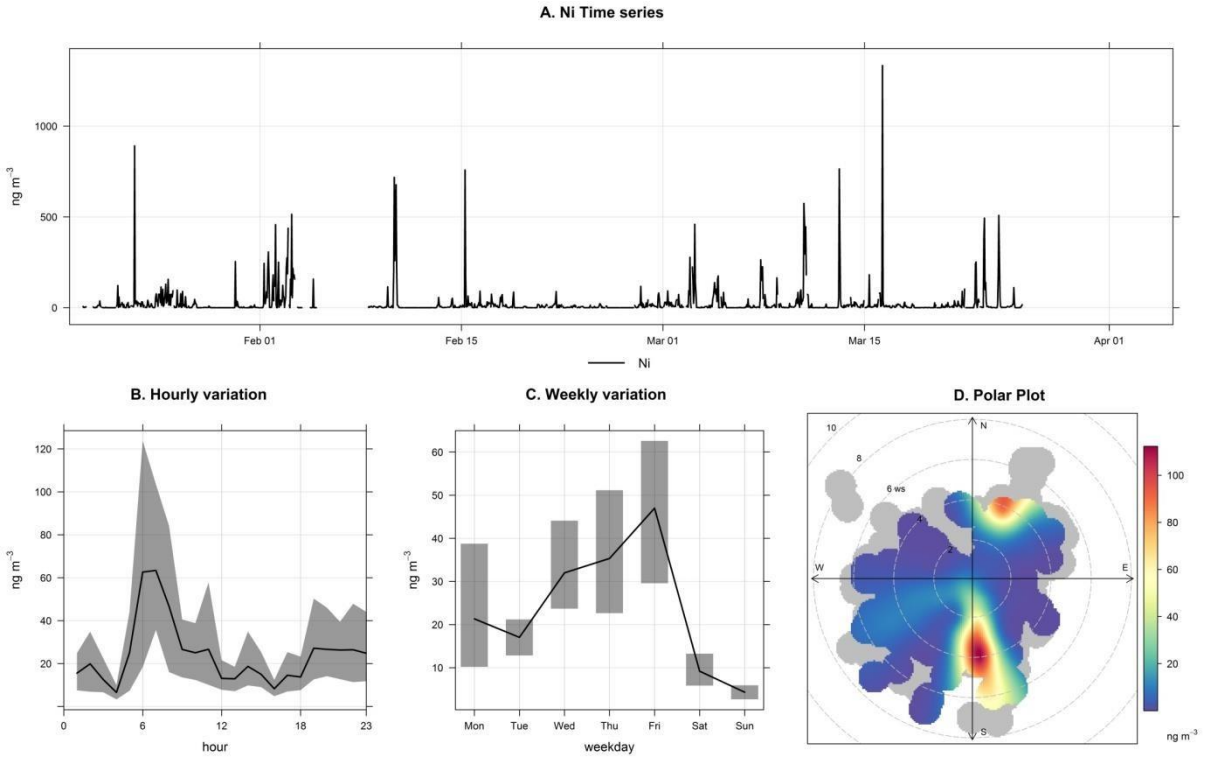


Figure 6: Hourly time series, diurnal variation, weekly variations and bivariate polar plot for Ni

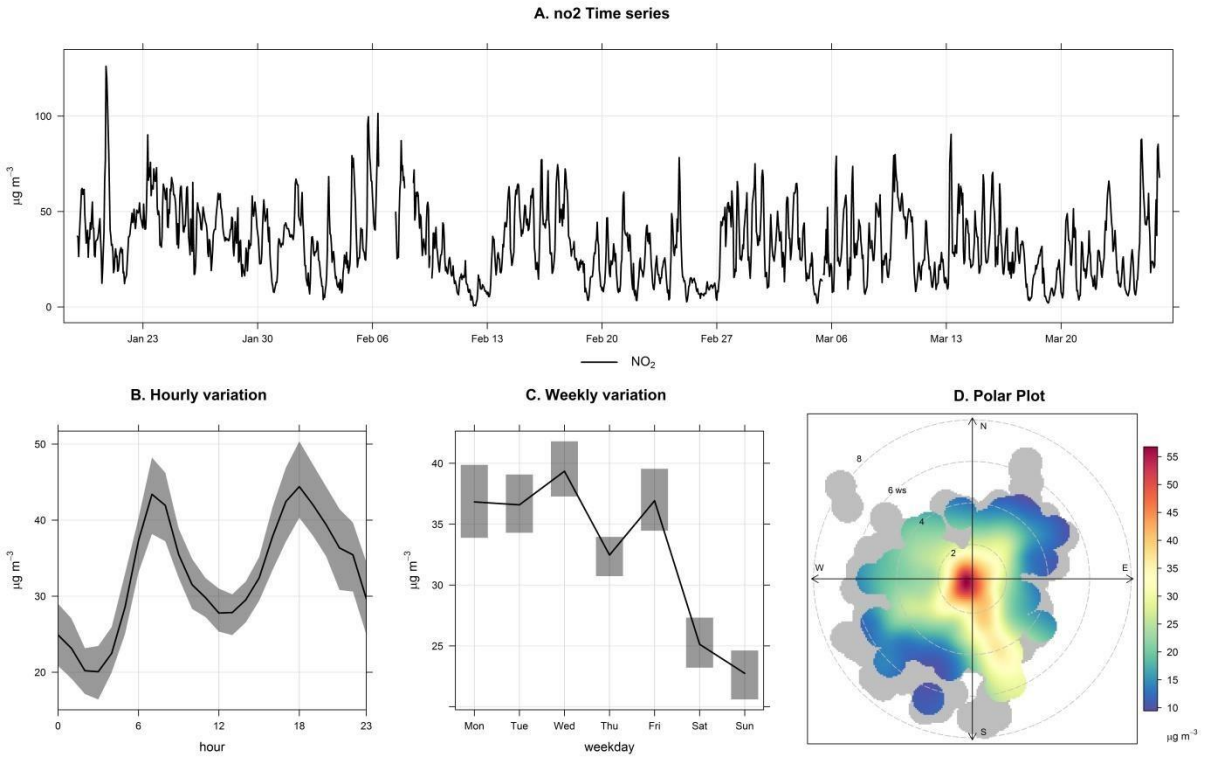


Figure 7: Hourly time series, diurnal variation, weekly variations and bivariate polar plot for NO_2

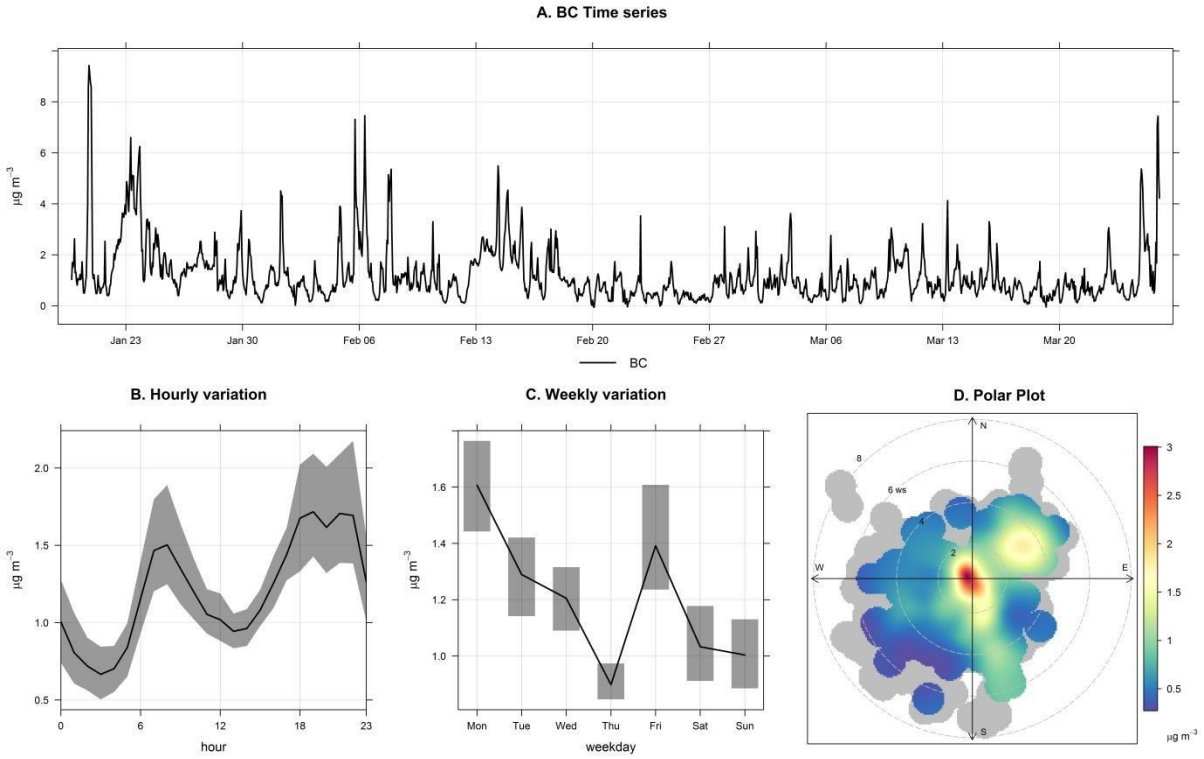


Figure 8: Hourly time series, diurnal variation, weekly variations and bivariate polar plot for Black Carbon

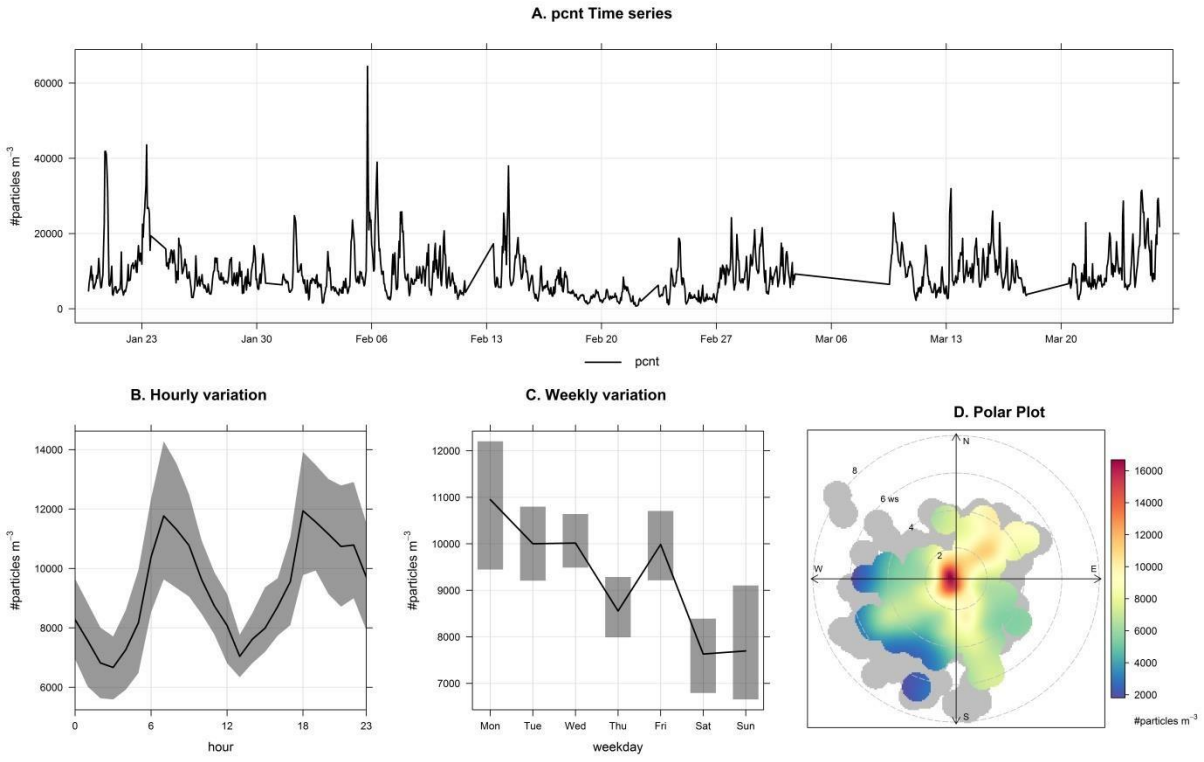


Figure 9: Hourly time series, diurnal variation, weekly variations and bivariate polar plot for Particle Number

Comparison with daily measurements

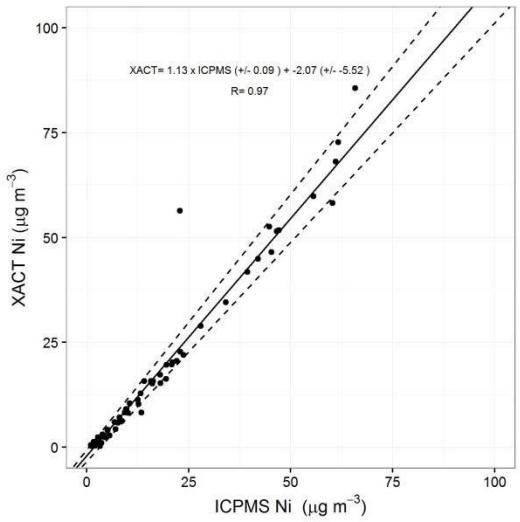
The comparison of daily mean, median, minimum and maximum metal concentrations as measured by the ICP-MS and the XRF techniques is shown in Table 5. The overall means and peak concentrations were indeed comparable. Notably,

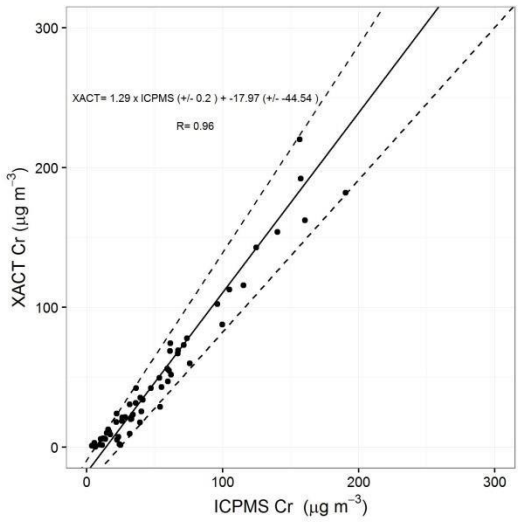
the Ni mean reported using the XRF technique (24.6 ng m^{-3}) compared extremely well to that reported using ICP-MS (24.3 ng m^{-3}); as did the maximum concentration (113.5 and 113.2 ng m^{-3}, respectively).

Table 5: Daily mean elemental measurements

Element	XRF Daily (ng m_{-3})				ICP-MS Daily (ng m_{-3})			
	Mean	Median	Min	Max	Mean	Median	Min	Max
As	2.8	1.3	0.0	33.3	1.5	0.9	-0.2	26.2
Ba	2.7	1.8	1.1	28.4	0.8	0.3	0.0	11.7
Ca	396.6	368.1	37.2	1104.1	1.9	0.6	0.1	65.8
Cd	4.2	4.1	4.1	7.3	-	-	-	-
Ce	0.8	0.7	0.4	1.6	-	-	-	-
Cl	1370.8	1142.0	35.8	5129.1	-	-	-	-
Cr	52.8	29.7	0.4	345.8	54.7	37.9	2.7	251.6
Cu	17.5	14.6	2.3	46.8	19.8	16.5	3.0	56.0
Fe	672.8	572.3	82.1	1952.7	706.7	584.4	91.8	1759.5
K	138.5	107.6	16.8	416.6	-	-	-	-
Mn	47.4	32.4	1.6	286.9	40.8	29.4	1.8	241.2
Mo	15.1	7.1	0.9	129.8	-	-	-	-
Ni	24.6	14.0	0.3	113.5	24.3	13.4	1.0	113.2
Pb	22.0	13.1	1.3	124.6	23.2	14.5	1.2	111.3
Pt	0.2	0.2	0.2	0.3	-	-	-	-
S	777.8	548.6	126.0	3436.2	-	-	-	-
Sb	0.2	0.0	0.0	6.2	-	-	-	-
Se	0.9	0.3	0.1	5.5	1.9	1.2	0.3	6.2
Si	211.7	167.8	85.7	770.6	-	-	-	-
Sr	1.2	1.1	0.5	3.6	-	-	-	-
Ti	22.8	14.3	1.4	223.5	-	-	-	-
V	1.2	0.6	0.2	12.9	1.5	1.1	0.2	9.6
Zn	99.9	58.2	4.5	624.8	102.1	56.5	3.8	605.4

Figure 10 shows the Reduced Major Axis (RMA) regression analysis comparing key metallic elements using XRF and ICP-MS. All showed excellent agreement correlation coefficients (R) between 0.95 and 0.99. Slopes were generally greater than 1 and varied between 1.06 and 1.29; this is consistent with previous comparisons (Furger, Minguillón et al. 2017) and work undertaken in the UK (Font, Priestman et al. 2016). These inconstancies are likely due to differences in sampling and calibration but are within expected between method variability. The consistency demonstrated by the high correlation coefficients indicates that all sources were equally well captured by the different techniques and therefore the hourly measurements undertaken by the XRF technique would accurately capture these sources in source apportionment analysis.





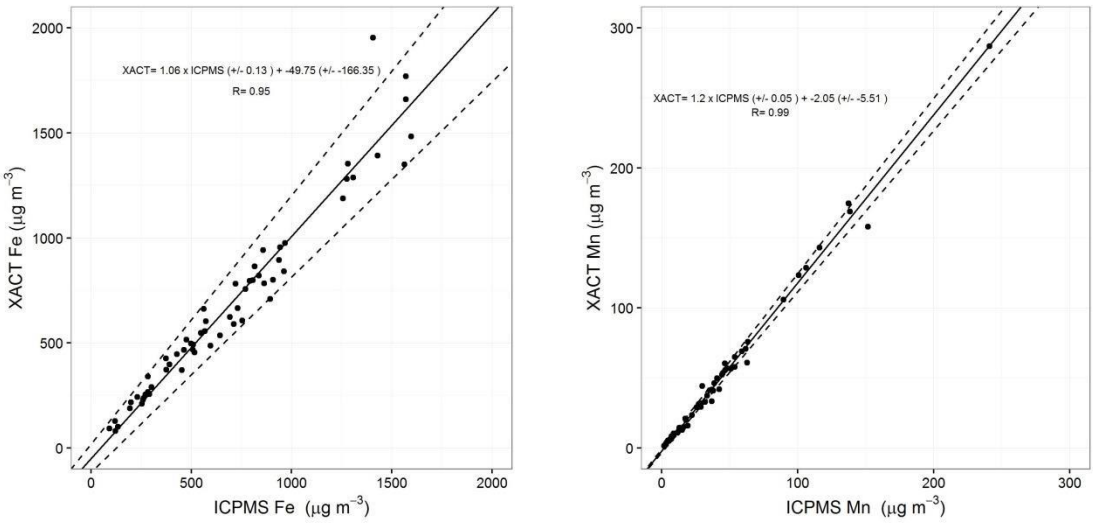


Figure 10: RMA regression analysis comparing XRF and ICPMS measurements key metallic elements (clockwise from top left) Ni, Cr, Mn and Fe

Highly Time Resolved Ni Measurements

Measuring the chemical composition of airborne particulate matter (PM) can provide valuable information on the concentration of regulated toxic metals and their sources and assist in the identification and validation of abatement techniques. Undertaking these at a high time resolution (1 hour or less) enables receptor modelling techniques to be more robustly linked to emission processes. Some indication of the primary Ni sources can be gained from a more detailed analysis of the highly time resolved Ni concentrations in association with meteorological measurements. Figure 11 show a bivariate polar plot of the mean Ni concentrations superimposed on a map indicating the various sources described for the Outokumpu site. It is clear that the dominant source lay in the direction of the Outokumpu site south of Tinsley site although there was clearly an additional source to the north-east.

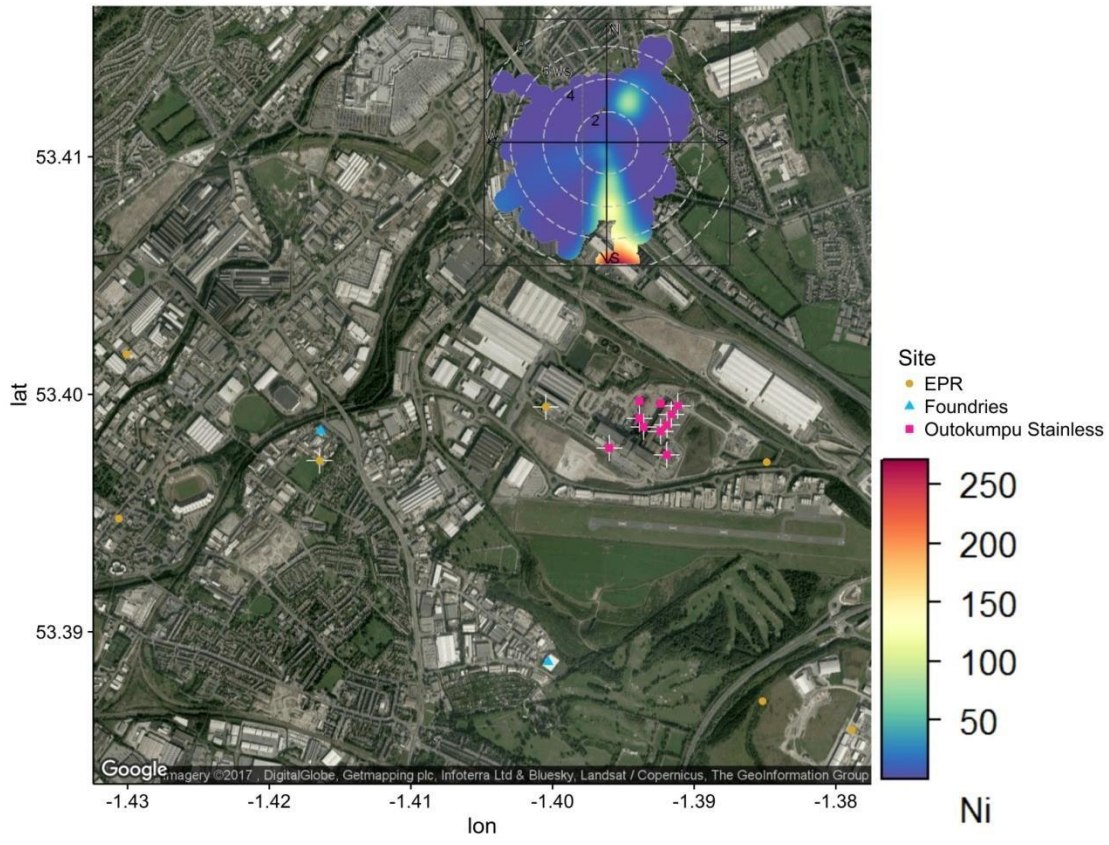


Figure 11: Bivariate polar plot of Ni concentrations superimposed on map showing Outokumpu emission sources

This type of bivariate polar plot accentuates the influence of peak concentrations on the mean. Further insight into the potential wide range of sources in the area can be gained by examining the same data as a conditional probability function bivariate polar plot. The Conditional Probability Function (CPF) BPP shows the probability (0-1) of any specific point on the polar plot of exceeding a set percentile. The more likely that that point exceeds the percentile the greater the intensity. This method appears to be very useful to identify sources of pollutants in complex areas where multiple sources are located as those tend to occupy concentration intervals at given wind direction and conditions (Uria-Tellaetxe and Carslaw 2014). CPF BPPs of Ni at the 25th, 50th, 75th and 95th percentiles are shown in Figure 12; the high colour intensity to the south and north-east was consistent with the mean polar plot in Figure 11, Figure 6. However, at lower concentrations, the influence of other sources became clear. At the lowest concentrations, below 0.3 ng m^{-3}, three directional sources were apparent but as concentrations increased through the 50th percentile (3.2 ng m^{-3}) and 75th percentile (14 ng m^{-3}) the influence of this westerly source decreased leaving only the sources to the south and north-east. It is interesting to note that the source to the north-east was only prevalent at higher wind speeds – this may be consistent with a fugitive ground level source which was only detectable under strong winds.

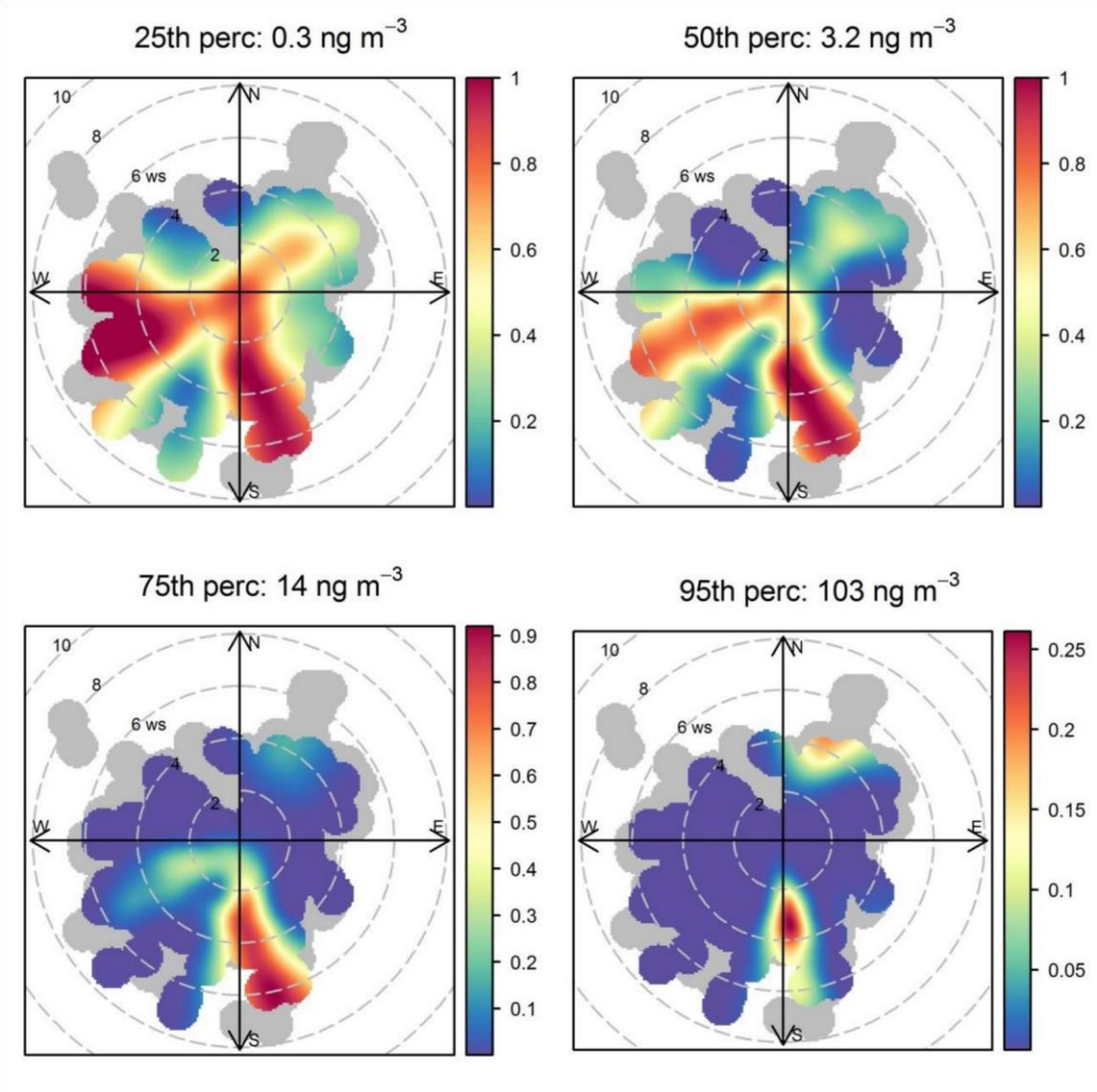


Figure 12: Conditional probability function bivariate polar plots showing Ni concentrations at the 25th, 50th, 75th and 95th percentiles

Positive Matrix Factorisation (PMF) Source Apportionment

Source apportionment techniques have been widely used to quantitatively determine PM sources. The main source apportionment models include chemical mass balance (CMB) and positive matrix factorization (PMF). CMB uses *a priori* knowledge of source profiles and assumes that the composition of all sources is well defined and known (Henry, Lewis et al. 1984). This technique is ideal when changes between the source and the receptor are minimal, although this rarely happens in real atmospheric conditions and the constraints may add a high level of uncertainty. PMF is a least-squares approach based on a receptor-only multivariate factor analytic model (Paatero and Tapper 1994). The main difference between PMF and CMB is that the first does not require any prior information about the sources as input to the model and the profiles and contributions are uniquely modelled by the solver (Paatero, Hopke et al. 2002).

In this instance, we are not seeking to quantify the contribution of the different sources to total PM_{10} mass concentrations; instead we are attempting to understand the contribution of each source to the Ni concentration. This therefore requires a slightly modified approach and many sources, identified by the PMF algorithm, may contribute significantly to the mass of PM_{10} (e.g. marine aerosol) but contain no Ni and therefore can be ignored. The important aspect of the PMF solver in this study remains in those source outputs that contributed to Ni concentration.

PMF source apportionment was undertaken on the combined data set of XACT data; the chemical components included were Ba, Ca, Ce, Cl, Cr, Cu, Fe, K, Mn, Mo, Ni, Pb, Pt, S, Se, Si, Sr, Ti, V. PMF runs were configured to yield between 1 and 15 sources. The resulting sources produce both an 'explained variation' and 'percentage contribution' for the overall factors to the measured concentration of PM_{10} (shown in Figure 13). The "explained variation" provides information about which factors were more important in describing either the mass or the factor while the relative contribution quantifies which factor or element dominated the measured mass.

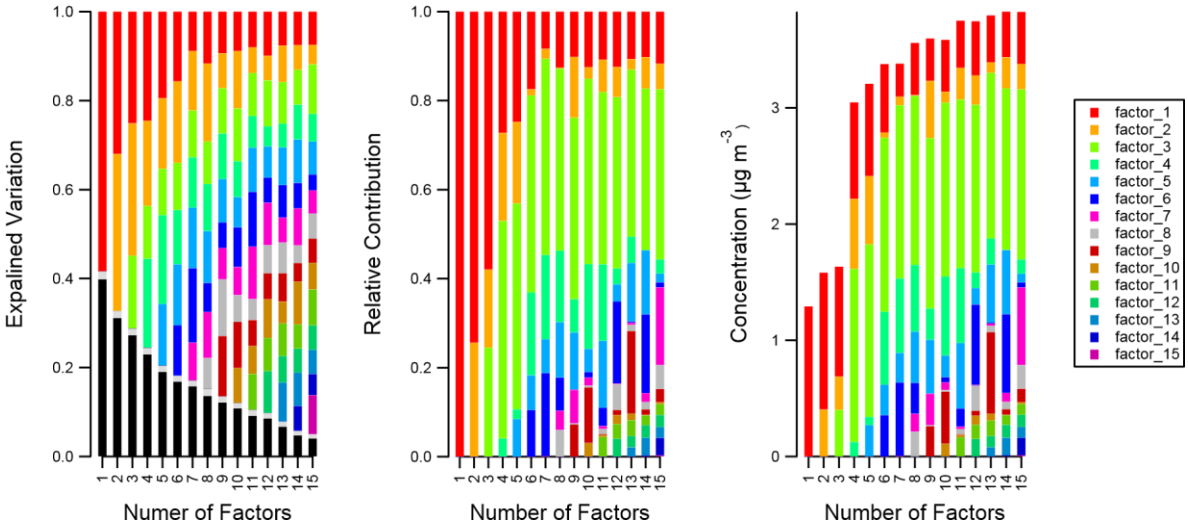


Figure 13: Explained variation, relative contribution and mass contribution of the different factor solutions (black is unexplained)

The optimum number of sources was chosen based on a number of model diagnostic outputs and attributes of idealised expected solutions:

1. Q/Qexp is a measure of the model residuals and reduces as the model explains more of the variability in the input measured data.
2. The maximum correlation between factor time series (TS_R^2) measures whether two of the factors are temporally correlated, identifying therefore factors that potentially describe the same source.
3. The maximum percentage Ni contribution. A solution which reflects the geographical distribution of Ni sources as identified in the Bivariate Polar Plots (three as observed in Figure 11, Figure 12) was therefore sought.

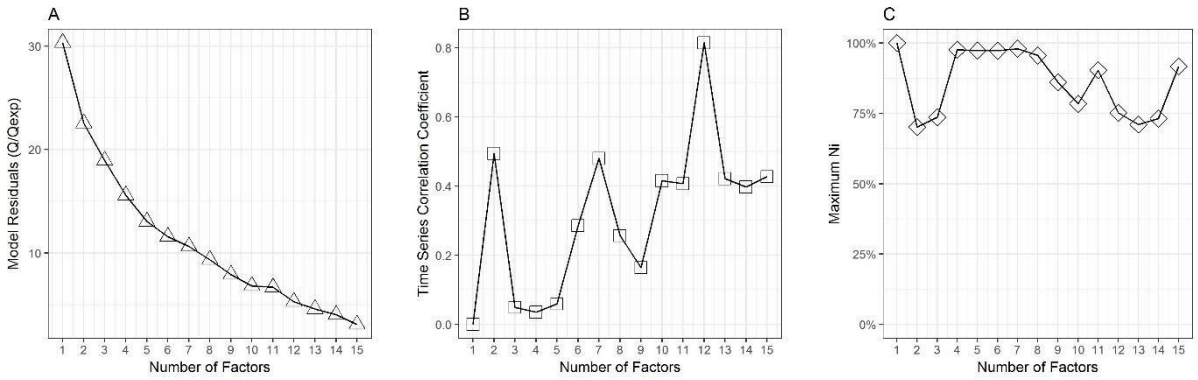


Figure 14: PMF diagnostic outputs – Q/Q_{exp} (A), factor times series correlation coefficient (B) and the maximum percentage Ni contribution (C)

The results of these diagnostics are shown in Figure 14. Q/Q_{exp} reduces as more factors are defined and the model explains more of the measurements. Ideally a solution with the lowest Q/Q_{exp} is chosen however the solutions need to be physically meaningful so it is not just a matter of choosing the solution with the largest number of factors.

The maximum correlation between factor time series (TS_R^2) increased beyond 9 factors and then stabilised (with the exception of the 11 factor solution). Although there was some correlation between factors, there were not two factors describing a single emission.

The maximum percentage Ni contribution from a single source decreased after 8 factors, indicating that as more factors were introduced the Ni was apportioned to more than one single factor. Looking in detail at the solutions with more than 9 factors, two distinct sources of nickel were common across the solutions (except for the 11 factor solution; Table 6). There was one factor rich in Cr and Mn and also, to a lesser extent, in Cu. It accounted for 25-30% of Ni. The other was rich in Mo and to a lesser extent in Fe and accounted for 70-80% of the Ni. At 13 and 14 factors the maximum contribution of Ni stabilised at approximately 70% before rising at 15 factors. The 15 factor solution allocated most of the Ni to the Cr factor and distributed the remainder across several different factors. At a higher number of factors the PMF algorithm did not distribute the Ni into additional sources. A stability in the factor solutions was therefore achieved at 13 and 14 factors accompanied by a low Q/Q_{exp}. These solutions are examined in more detail below.

Table 6: Relative contributions to the different elements from solution with more than 9 factors

Element	Ni, Mn and Cr rich factors							Ni and Mo rich factors						
	Number of Factors							Number of Factors						
	9	10	11	12	13	14	15	9	10	11	12	13	14	15
Ba	22%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	1%
Ca	0%	23%	9%	9%	17%	15%	21%	0%	0%	0%	0%	0%	0%	0%
Ce	0%	0%	0%	0%	0%	0%	0%	0%	0%	1%	0%	0%	0%	0%
Cl	84%	0%	0%	0%	0%	0%	0%	0%	0%	3%	0%	0%	0%	0%
Cr	20%	95%	98%	95%	99%	99%	74%	16%	5%	0%	5%	1%	1%	0%
Cu	3%	17%	14%	8%	21%	15%	27%	11%	9%	20%	4%	7%	7%	0%
Fe	3%	3%	14%	0%	2%	5%	2%	27%	26%	0%	26%	18%	16%	6%
K	77%	0%	0%	0%	0%	1%	0%	1%	0%	58%	0%	0%	0%	1%
Mn	0%	78%	68%	77%	76%	72%	51%	8%	6%	6%	5%	0%	0%	33%
Mo	13%	0%	16%	0%	0%	0%	0%	80%	83%	54%	77%	75%	82%	96%
Ni	53%	22%	90%	25%	29%	27%	0%	86%	78%	7%	75%	71%	73%	2%
Pb	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
Pt	0%	0%	0%	1%	1%	1%	0%	0%	0%	3%	0%	0%	0%	1%

S	0%	2%	2%	5%	0%	2%	0%	4%	2%	0%	2%	4%	2%	9%
Se	2%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%	0%
Si	0%	1%	1%	0%	0%	0%	1%	1%	1%	20%	1%	2%	1%	0%
Sr	0%	0%	0%	0%	0%	0%	0%	0%	1%	0%	1%	0%	0%	0%
Ti	0%	0%	0%	0%	0%	0%	0%	1%	1%	52%	0%	0%	1%	2%
V	70%	0%	0%	0%	0%	0%	0%	0%	0%	99%	0%	0%	0%	0%
Zn	0%	23%	12%	23%	0%	0%	41%	0%	0%	0%	0%	0%	0%	0%

Nickel Sources in the 13 and 14 Factor Solutions

The two Ni sources types were identified in both the 13 and 14 factor solutions. One was rich in Mo (Ni/Mo) and the other in Cr (Ni/Cr). The Ni/Mo source type was the largest of the two sources contributing 73% and 72% of the assigned Ni in factor 13 and 14, respectively. The Ni/Cr source type contributed 22% to both factor 13 and 14 (Figure 15). A 5-6% of the Ni measured remained unexplained by the PMF algorithm and cannot be assigned to a specific source.

The different chemical composition; and the relative elemental contributions (i.e. how much of the total measured concentration does the factor explain) can help to identify the different source types. However, much more information relating to the scrap steel melted and composition of the alloys produced would be needed to categorically assign these factors to specific industrial processes.

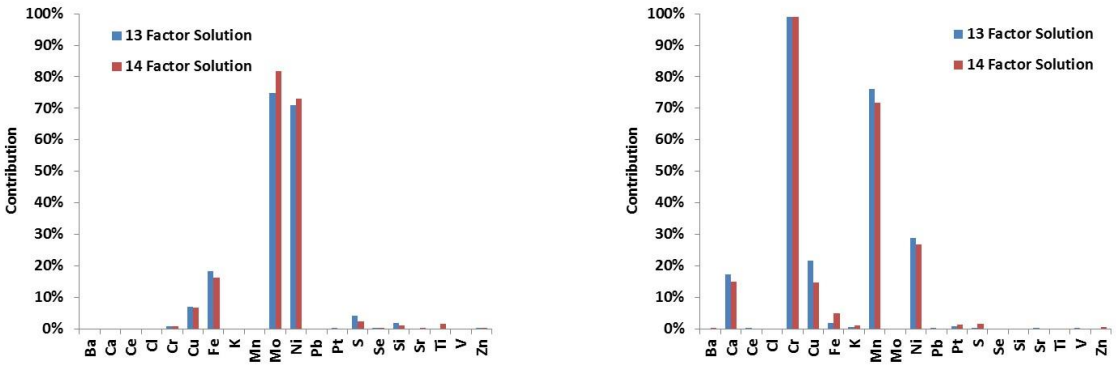


Figure 15: Relative elemental source contributions of Ni/Mo source type (left) and Ni/Cr source type (right)

Nickel / Molybdenum (Ni/Mo) source type

Figure 16 and Figure 17 show the hourly time series, diurnal variation, weekly variations and bivariate polar plot for 13 and 14 factor Ni/Mo source respectively. The solutions are very similar, having an R^2 of 0.99. The hourly time series demonstrates the typical episodic response expected from a nearby industrial source. The diurnal variation shows that the concentrations were elevated on the early morning suggesting that at least some of the peak concentrations occurred during still stable conditions; this was confirmed by the bivariate polar plot, with a colour intensity in the centre – typical of elevated concentrations due lack of dispersion. However, there were also stronger influences at higher wind speeds from both the south at approx. 180˚ and at approx. 10˚. This indicates two separate sources emitting PM_{10} of a similar chemical composition. This was not unexpected as there are many similar industrial processes in the Sheffield area. Concentrations were much lower on weekend days; this indicates that emissions were related to human and industrial activity cycles.

Examining the description of the local industrial activity in section 0 and the bearing of these processes from the Tinsley measurement station in section 2.4, it is clear that the source from approximately 10˚ was associated with Darwin Holdings and / or Trefoil Steel. Their processes are consistent with a release of Fe, Mo and Ni. Outokumpu is the

dominant emitter to the south so was expected to be the source in this direction. Other sources to the east also contributed towards the mean concentration.

To investigate the behaviour of this source type with wind speed and direction the Ni/Mo source strength in µg m^{-3} was analysed as a pollution rose disaggregated into days of the week and are shown in Figure 18. In general, the Ni/Mo source type was more prevalent on weekdays than on Sundays. However the frequency of winds from the south was low (<5%) on Sundays, Mondays, Tuesdays and Thursdays but only Mondays and Sundays showed a contribution less than 1 µg m^{-3} to the Ni/Mo source type. It is clear from the polar plot and the Thursday pollution rose that concentration were elevated even at low wind speeds; this indicates a local source whose concentration increased during periods of reduced dispersion. Conversely, elevated concentrations of this source type were predominantly seen during high wind speeds from the south and north-east. This indicates that wind speed was also be important in the transport of the source from more distant locations or the atmospheric mixing of the source in the atmosphere to increase ground level concentrations from more nearby sources.

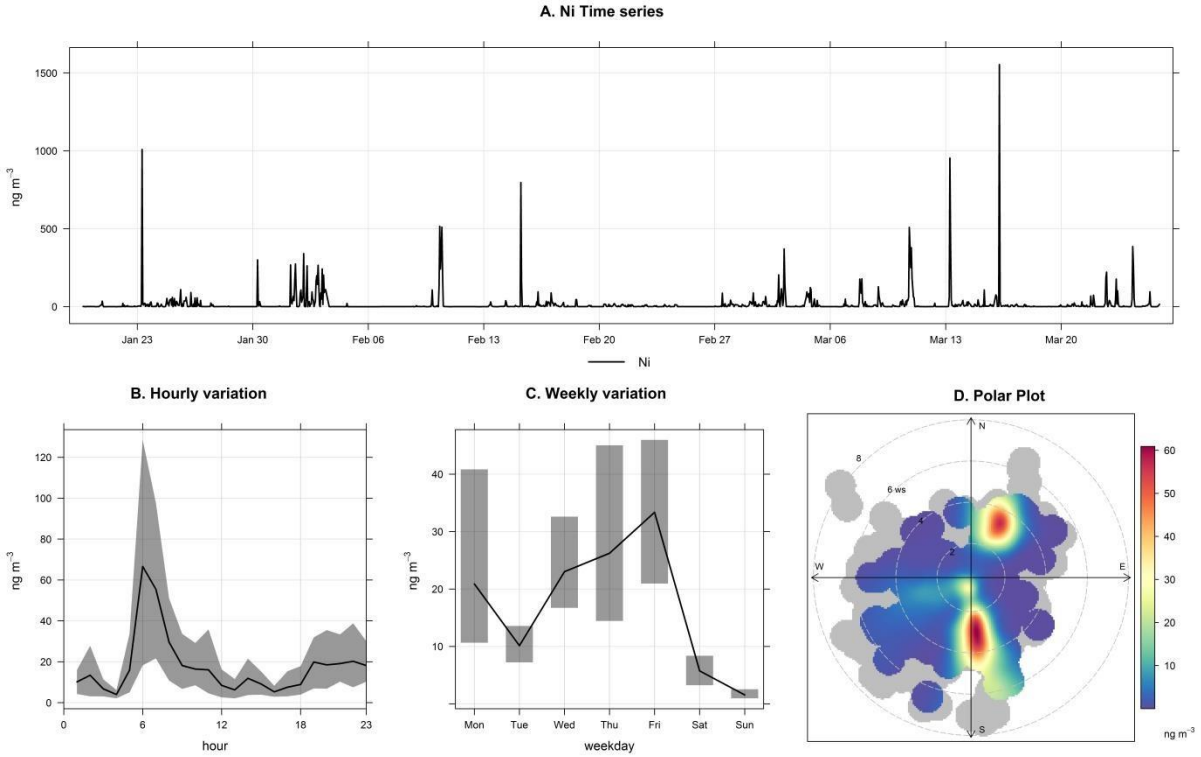


Figure 16: Hourly time series, diurnal variation, weekly variations and bivariate polar plot for the 13 factor Ni/Mo source

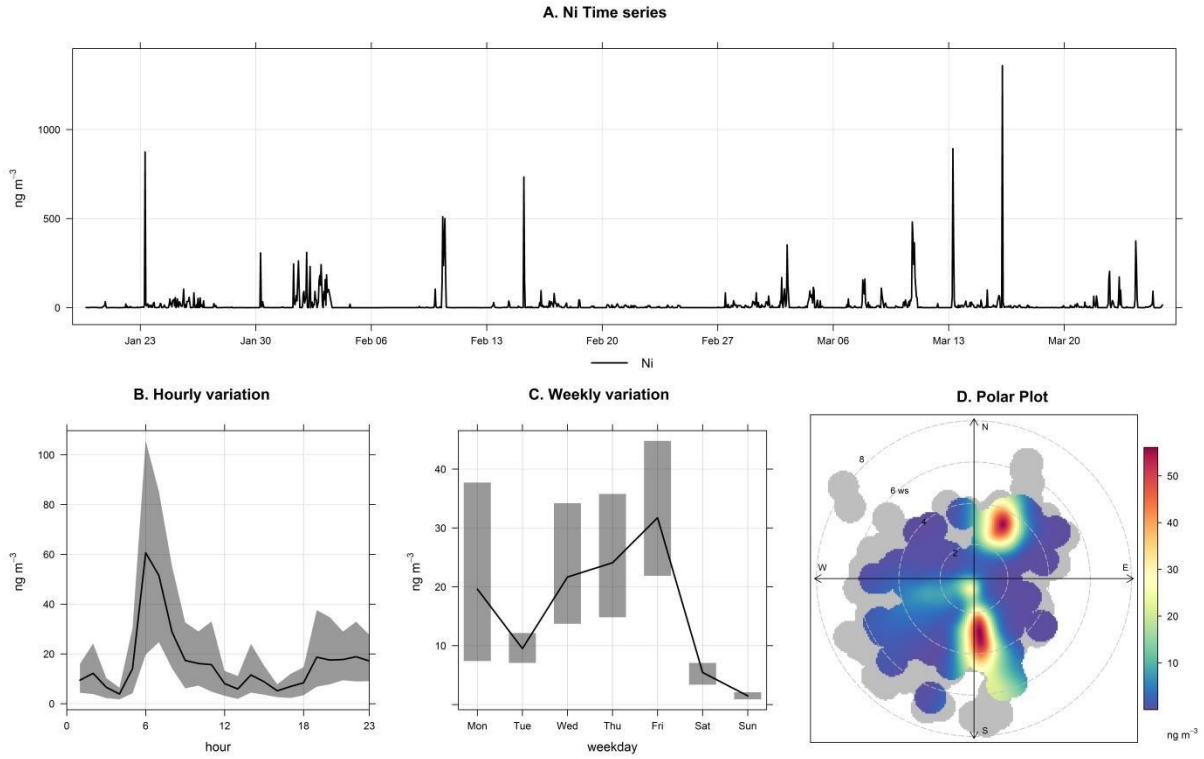


Figure 17: Hourly time series, diurnal variation, weekly variations and bivariate polar plot for the 14 factor Ni/Mo source

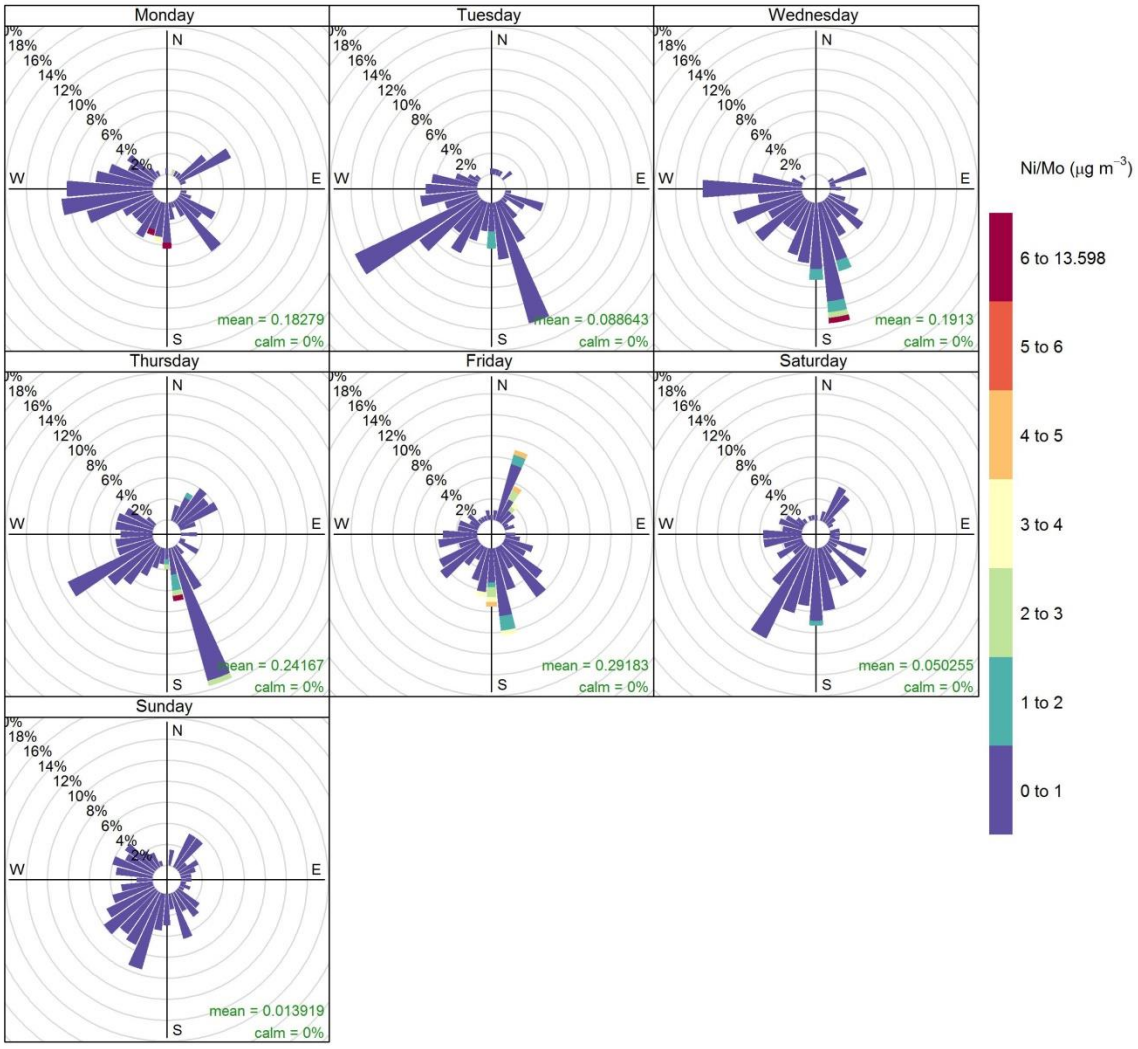


Figure 18: Ni/Mo source strength pollution rose disaggregated by day of week

Nickel / Chromium (Ni/Cr) source type

Figure 19 and Figure 20 show the hourly time series, diurnal variation, weekly variations and bivariate polar plot for 13 and 14 factor Ni/Cr source respectively. The solutions were very similar, having an R^2 of 0.99. The hourly time series demonstrates the typical episodic response expected from a nearby industrial source in a similar way to the Ni/Mo source. However, the diurnal profile was somewhat different, with no morning and evening elevations which are associated with reduced dispersion from local sources. Instead mean concentrations remained uniform throughout the day suggesting that emissions from this source were independent of typical daily urban activity cycles. The strongest source was clearly from the south although there were also signs of a source at approximately 10˚. Again, this indicates two separate sources emitting PM_{10} of a similar chemical composition: Darwin Holdings and / or Trefoil Steel to the north; and Outokumpu to the south; although in this case the source to the south was stronger than for the Ni/Mo source. Again, other sources to the east also contributed towards the mean concentration.

To investigate the behaviour of this source type with wind speed and direction the Ni/Cr source strength in µg m^{-3} was analysed as a pollution rose disaggregated into days of the week and are shown in Figure 21. In general, the Ni/Cr source type was more prevalent on weekdays than on Sundays, however the frequency of winds from the south was low (<5%) on Sundays, Mondays, Tuesdays and Thursdays but only Tuesdays and Thursdays showed a contribution greater than

1 µg m^{-3} to the Ni/Cr source type. This source type therefore appeared to be more strongly related to wind speed than the Ni/Mo source type.

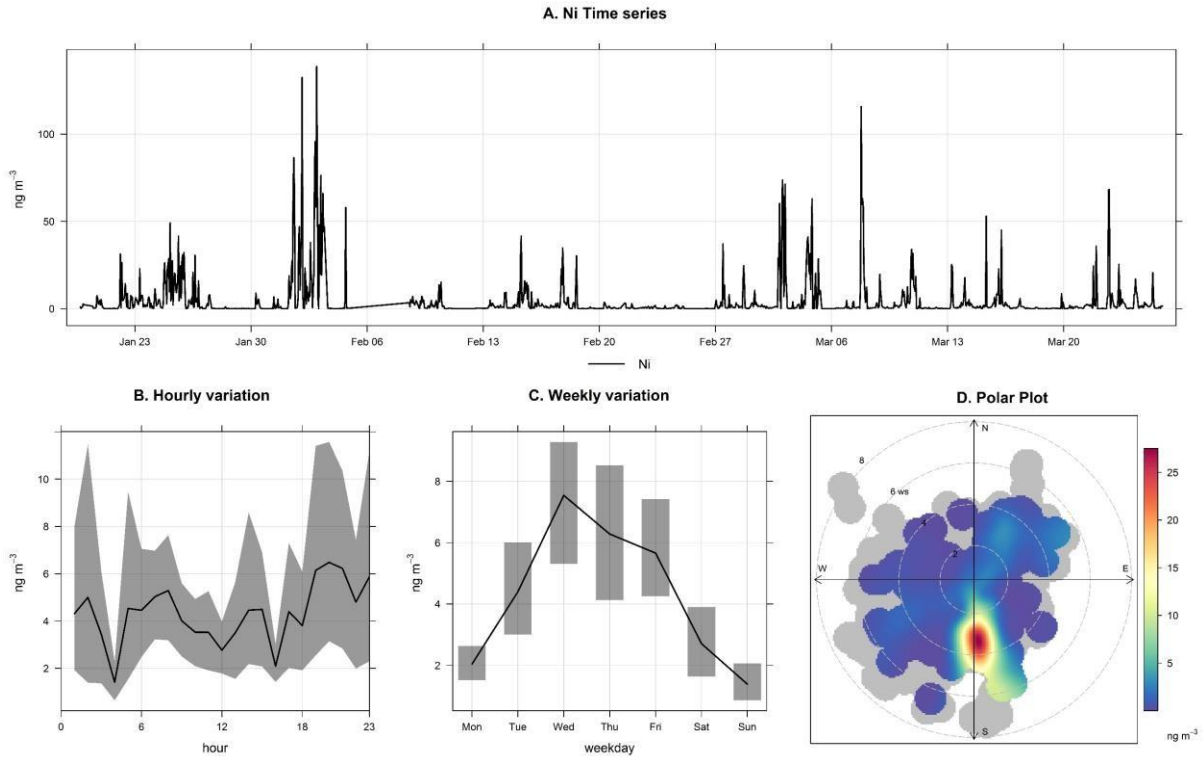


Figure 19: Hourly time series, diurnal variation, weekly variations and bivariate polar plot for the 13 factor Ni/Cr source

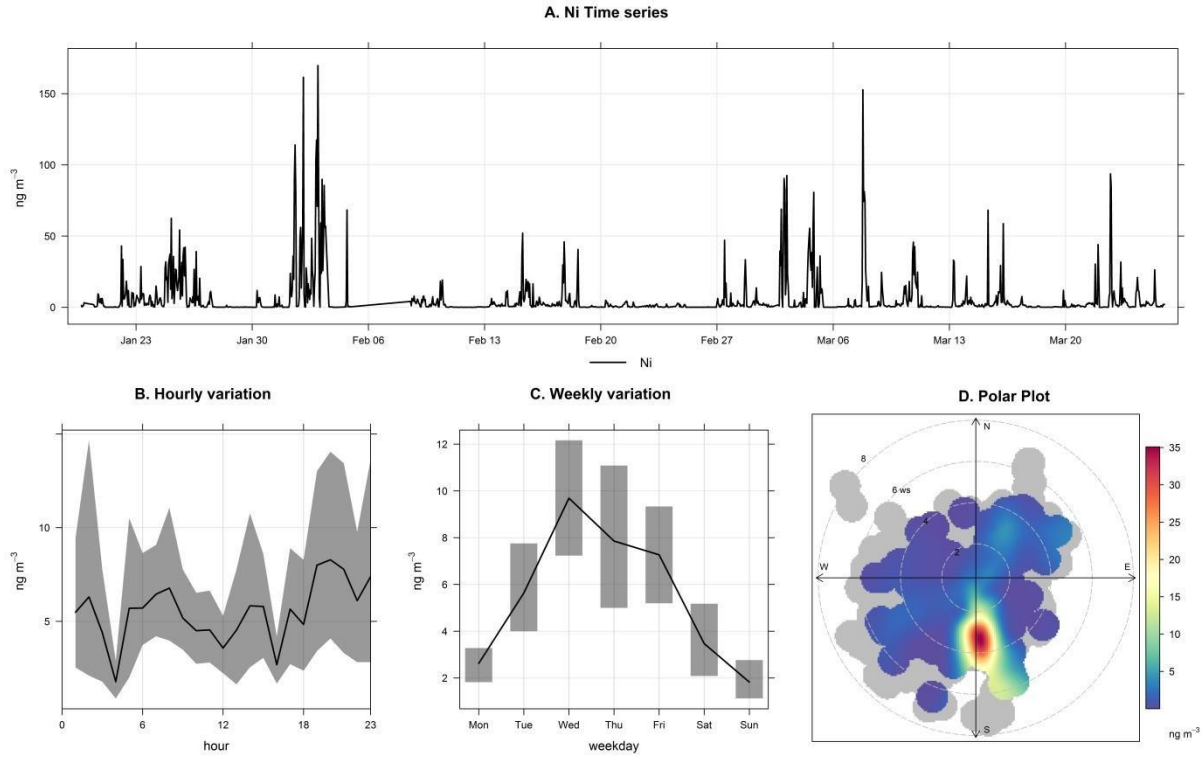


Figure 20: Hourly time series, diurnal variation, weekly variations and bivariate polar plot for the 14 factor Ni/Cr source

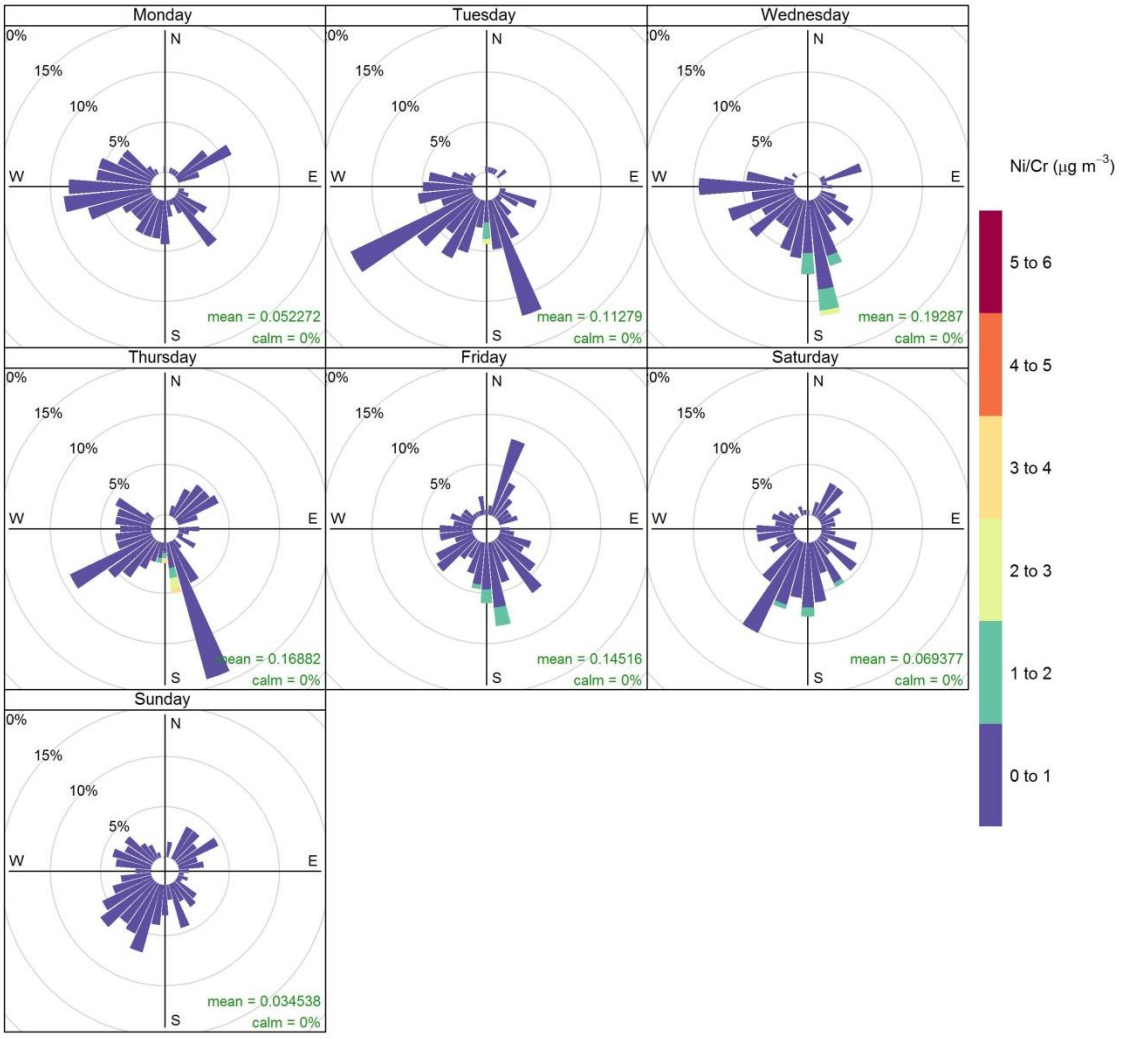


Figure 21: Ni/Cr source strength pollution rose disaggregated by day of week

To assess whether wind speed influenced the strength of this source, the winds from the south (from 170 to 190 degrees) were taken and binned by wind direction. The resulting plot is shown in Figure 22 and demonstrates that the strength of the source from the south increased with wind speed. Although elevated wind speeds enhance the mixing and dispersion from the source points to the measurement location, the lack of elevated concentrations at low wind speeds (as was the case for the Ni/Mo source) indicates that wind resuspension clearly played a role. The industrial activity / process which may be leading to these emissions was therefore likely to be related to fugitive emissions from stockpiles, vehicle movements or material handling. The presence of Ca in the elemental signature for this source type may help to identify the activity / process as it is used in the steel making and is a component of the slag produced as a by-product.

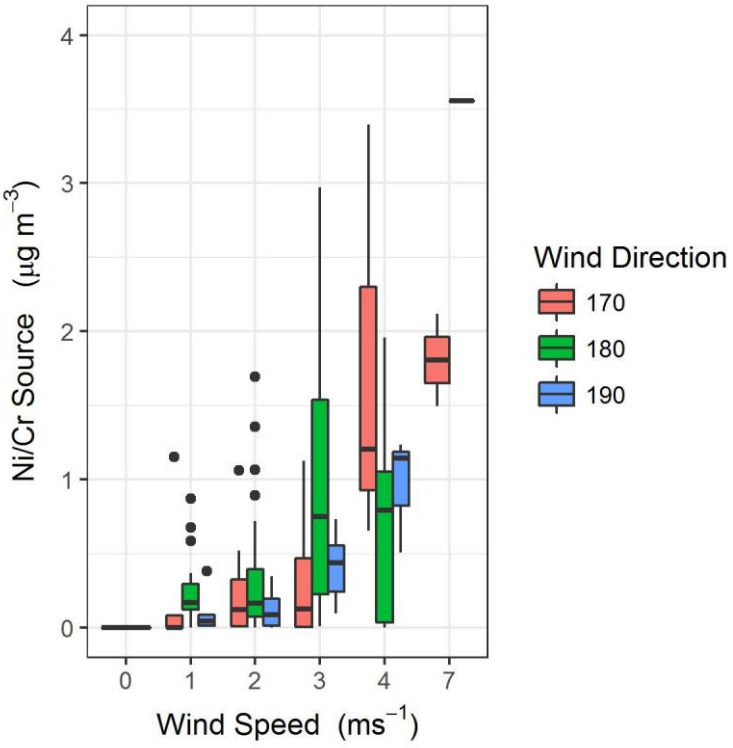


Figure 22: Ni/Cr source strength vs wind speed coloured by wind direction (170-190 only)

Apportionment of Ni measurements using k-means cluster analysis of bivariate polar plots

K-means cluster analysis of condition probability function (CPF) bivariate polar plots (BPPs) was successfully applied to source apportion Ni concentrations at Pontardawe in the Swansea Valley, where they routinely exceed the EU Target Value (Font, Priestman et al. 2016). This approach relies upon the combination of high time resolution measurements and meteorological measurement combined into bivariate polar plots; from where they can be grouped into clusters based on the influencing meteorological variables (Carslaw and Beevers 2013). Using a CPF BPP better represents the influence of different sources at low concentrations as BPPs using the mean are skewed by a small number of high concentrations and tends to accentuate the influence of sources which contribute to the peak concentrations; this is shown in Figure 12. A modified approach was used here using the results of the PMF model rather than the unprocessed Ni data and allows the PMF solutions with multiple sources to be quantified by source direction.

The process of clustering data proceeds as follows. First, *k* points are randomly chosen from the data space which represents the initial group centroids. Each data point is therefore assigned to the group based on the closest centroid point. When all objects have been assigned, the position of *k* centroids is recalculated. The two steps are repeated until the centroids no longer move.

One of the disadvantages of the method is the subjective choice of the number of *k* clusters. While many methods exist to determine the optimum number of clusters applied to time series datasets, these methods do not work effectively when applied to bivariate polar plots. The choice of the number of appropriate clusters is therefore heuristic and is best determined by post-processing. The number of clusters might be chosen based on a priori knowledge of the area of study (e.g. different known sources); or by repeating the *k*-means clustering with different numbers of groups (Carslaw and Beevers, 2013).

Here the CPF percentile and the number of clusters was varied to achieve the optimum cluster solution. This was tested using the Ni/Mo source from Factor 13; *k*-means clustering between 2 and 10 clusters was undertaken on CPF BPPs at percentile values at 5% intervals between 50th and 75th percentiles; these results are included in the appendix. The optimum cluster solution was chosen based on source relevance – the clusters needed to clearly distinguish between the three source directions while still being physically meaningful. At low percentile values the southerly and easterly sources were not adequately distinguished below 6 clusters, by which point the number of clusters exceeded the meaningful sources. Only at the 75th percentile did the southerly, easterly and westerly sources resolve at low number of clusters - here, 3 clusters were adequate to distinguish between the different source directions and provide three broad source directions: South, East and West. *K*-means clustering was repeated on the remaining factor solutions at the 75th percentile to ensure that this was an optimum solution; these are also included in the Appendix. The 75th percentile CPF BPP and the resulting 3 source solution for the Ni/Mo and Ni/Cr sources for both the 13 and 14 factor solutions are shown in Figure 23.

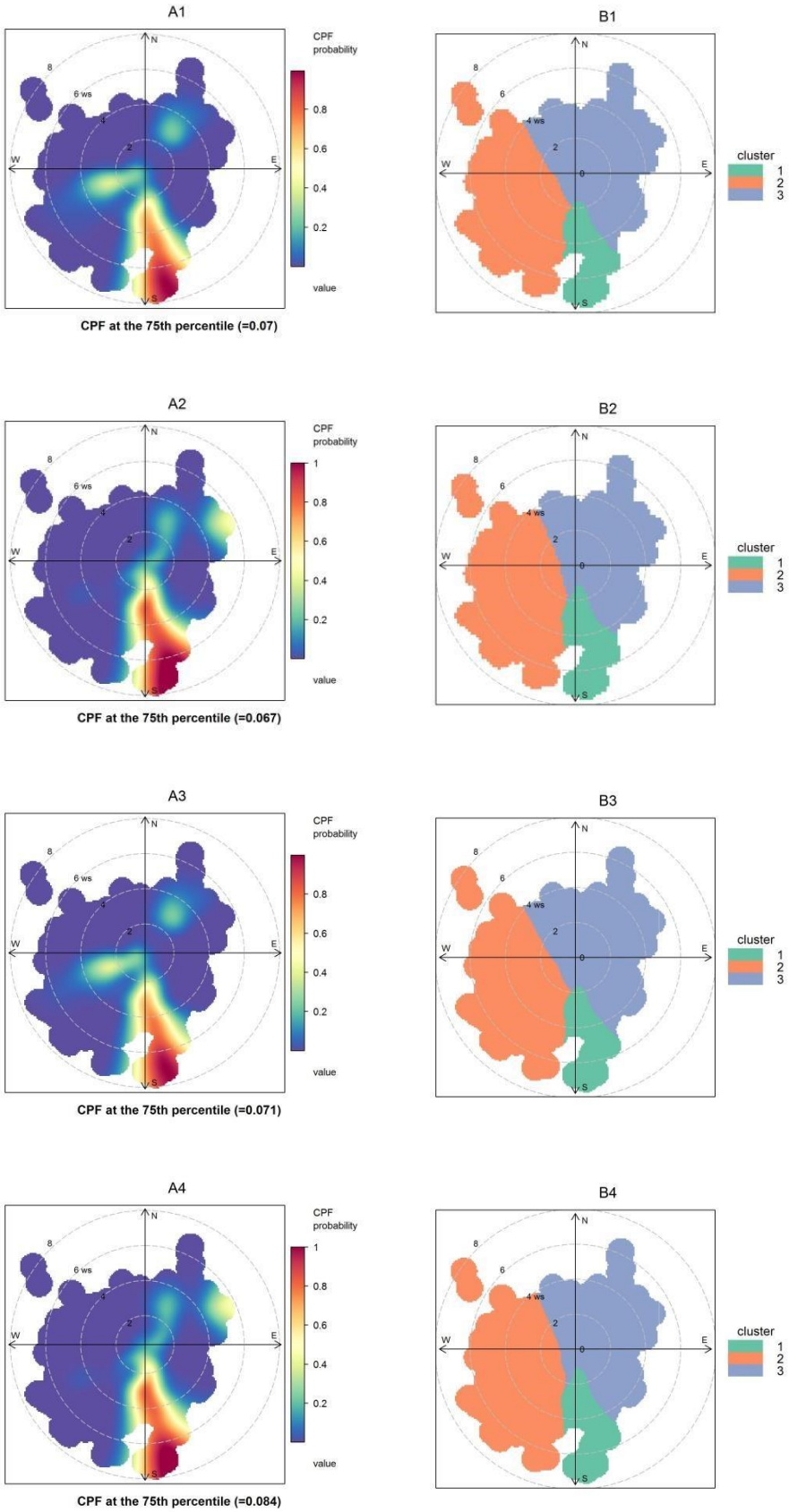


Figure 23: CPF BPP for 75th percentile (A) and the resulting 3 source solution (B) for the 13 factor Ni/Mo solution (1), 14 factor Ni/Mo solution (2), 13 factor Ni/Cr solution (3) and 14 factor Ni/Cr solution (4)

Table 7: Source contribution identified by each cluster / source direction

Source Direction	13 Factors						14 Factors						Mean					
	Ni/Mo source		Ni/Cr Source		Total		Ni/Mo source		Ni/Cr Source		Total		Ni/Mo source		Ni/Cr Source		Total	
	µg m^{-3}	% Ni	µg m^{-3}	% Ni	µg m^{-3}	% Ni	µg m^{-3}	% Ni	µg m^{-3}	% Ni	µg m^{-3}	% Ni	µg m^{-3}	% Ni	µg m^{-3}	% Ni	µg m^{-3}	% Ni
South	7.2	32.2	3.4	15.1	10.6	47.3	6.9	30.7	3.6	15.9	10.4	46.6	7.0	31.4	3.5	15.5	10.5	46.9
West	2.4	10.7	0.7	3.0	3.1	13.8	2.4	10.6	0.6	2.7	3.0	13.4	2.4	10.7	0.6	2.9	3.0	13.6
East	7.8	34.8	1.1	4.8	8.9	39.6	7.7	34.4	1.2	5.3	8.9	39.7	7.8	34.6	1.1	5.0	8.9	39.6

The clustering algorithm allocated each measurement to one of these 3 source directions and the mean concentration of each is shown in Table 7 and provides a quantification of the contribution of each source type (Ni/Mo or Ni/Cr) to the total Ni concentration measured at Sheffield Tinsley. Both the 13 and 14 factor solutions are shown and provide similar estimates for the Ni contributions from the different source types and directions. These can therefore be robustly combined to provide a mean contribution from each. The dominant source direction was from the South which contributed 46.9% to the Ni concentrations measured; this was made up of 31.4% Ni/Mo and 15.5% Ni/Cr. Given that the Outokumpu facility lays in this direction and accepted to be the largest emitter of Ni in the area, this can confidently be associated with this facility. The West source direction made the smallest contribution (13.6%) and was dominated by the Ni/Mo source type (10.7%) while the Ni/Cr source type contributed 2.9%. This cluster represents the emissions from over half of the Ni emitting industries in Sheffield, which lie in that direction. The East source direction contributed 39.6% which was dominated by the Ni/Mo source type (34.6%) with a more minor contribution from the Ni/Cr source type (5%). There are two facilities to the east, closely aligned with the peak concentrations identifiable in the bivariate polar plots – Darwin Holdings and Trefoil Industries – either or both could be responsible for the emissions from this cluster.

Conclusions

This study analysed the data from MARPL deployment at the Tinsley site between 19th January and the 26th March 2017. The aim of the project was to provide a source attribution of the measured nickel concentrations at this site.

The instrumentation deployed delivered a high time resolution dataset containing a range of elements and chemical constituents of PM_{10} which were used to directly apportion PM mass or infer source characteristics. In particular the range of different components measured was capable of distinguishing between different sources of nickel as they have different chemical composition.

The source apportionment was undertaken in a two-step process:

1. Positive Matrix Factorisation (PMF) – this method used the XRF measurements to apportion the nickel sources around Sheffield Tinsley. PMF yielded two types of Ni sources – one associated with high Mo concentrations (Ni/Mo) and one with high Cr (Ni/Cr). These describe different processes used in the industries around Sheffield and they were observed to be emitted at different times of days and consequentially had different diurnal profiles. However, they had similar weekday to weekend cycles suggesting both were driven by anthropogenic rather than meteorology. The Ni/Mo source contributed 72% of the overall Ni concentrations; and the Ni/Cr contributed 22%. The remaining 6% could not be assigned to a specific source.
The Ni/Mo source type also contained some Cu and Fe and was observed to peak in the early morning; this was consistent with local point sources influenced by a lack of dispersion. It was also elevated at the increased wind speeds necessary to either transport emissions from the industrial source to the measurement location although a role of wind driven resuspension cannot be ruled out.

The Ni/Cr source type also contained significant amounts of Mn, Cu, Ca and some Fe. It had no obvious diurnal pattern and was shown to peak when wind directions were from the south and increased with wind speed; this indicates that it was at least partially a wind-driven source. The type of activity which led to these emissions was therefore likely to be related to fugitive emissions from stockpiles, vehicle movements or material handling. The presence of Ca in the elemental signature for this source may help to identify the source as it is used in the steel making process and is a component of the slag produced as a by-product.

2. Clustering of conditional probability function bivariate polar plots – this method relies upon the combination of high time resolution measurements and meteorological measurement combined into bivariate polar plots; from where they can be grouped into clusters based on the influencing meteorological variables. The resulting factors from the PMF results were then cluster to be segregated into sources based on the direction and wind speed and calculated their contribution to Ni concentrations.

There were 3 source directions – East, West and South. The source was from the south, which contributed 46.9% to the Ni concentrations measured during this study, can confidently be associated with the Outokumpu facility as there were no other significant sources of Ni in that direction. This contribution can be viewed as 31.4% from the Ni/Mo source type, most likely related to point sources, and 15.5% from the Ni/Cr source type most likely related to fugitive emissions from stockpiles, vehicle movements or material handling.

The source from the West made the smallest contribution (13.6%) and represented the emissions from over half of the industries in Sheffield, which lie in that direction and was dominated by the Ni/Mo source.

The source to the East contributed 39.6%. Of this, 34.6% was related to the Ni/Mo source type most likely related to point sources, and 5% from the Ni/Cr source type most likely related to fugitive emissions from stockpiles, vehicle movements or material handling.

The widespread nature of the Ni/Mo point related source type across industries in Sheffield makes this challenging to tackle. However, focusing resources to identify specific processes from the identified industrial sources (Outokumpu, Darwin Holdings and Trefoil Industries) would be a useful initial step towards reducing Ni emissions. The Ni/Cr source type was clearly most influenced by the local Outokumpu activity and was responsible for 15.5% of the Ni measured at

the Tinsley measurement station. Further work with Outokumpu to identify the processes and / or activities which are leading to these emissions may be the most cost-effective way of ensuring that the measurements at the Sheffield Tinsley site remain below the annual mean EU Target Value for Ni of 20 ng m^{-3}.

The ongoing assessment of the Sheffield Tinsley site against the EU Target Value should clearly continue to be assessed using the standard measurement approach. However, if a further assessment of the contribution of the different sources is required, either during different seasonal conditions or following an intervention to reduce emissions from a specific source, then a repeat of the measurement strategy employed here should be considered.

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Appendix

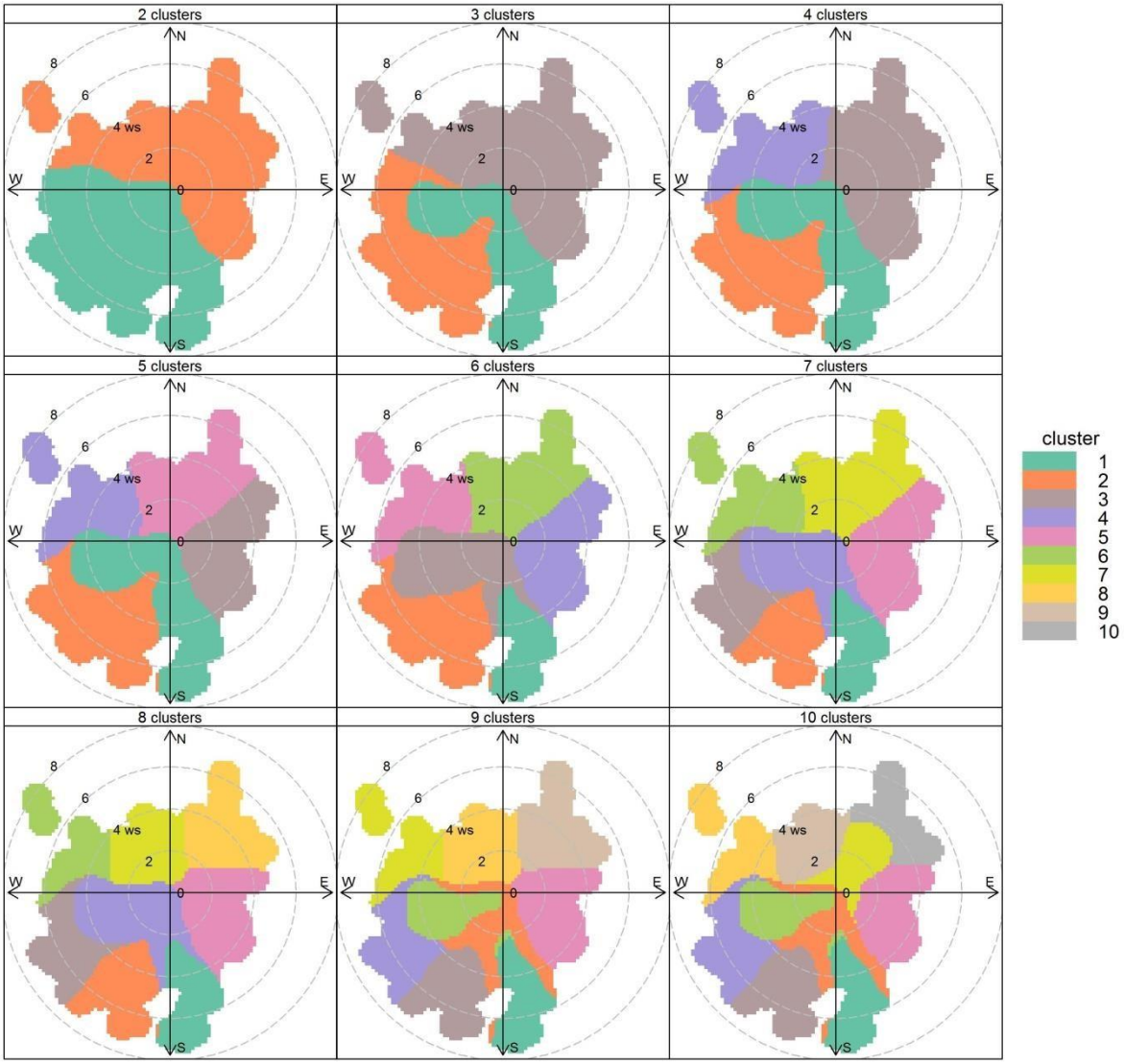

Figure 24: k-means clustering between 2 and 10 clusters on 13 Factor Ni/Mo source at 50th percentile CPF BPPs

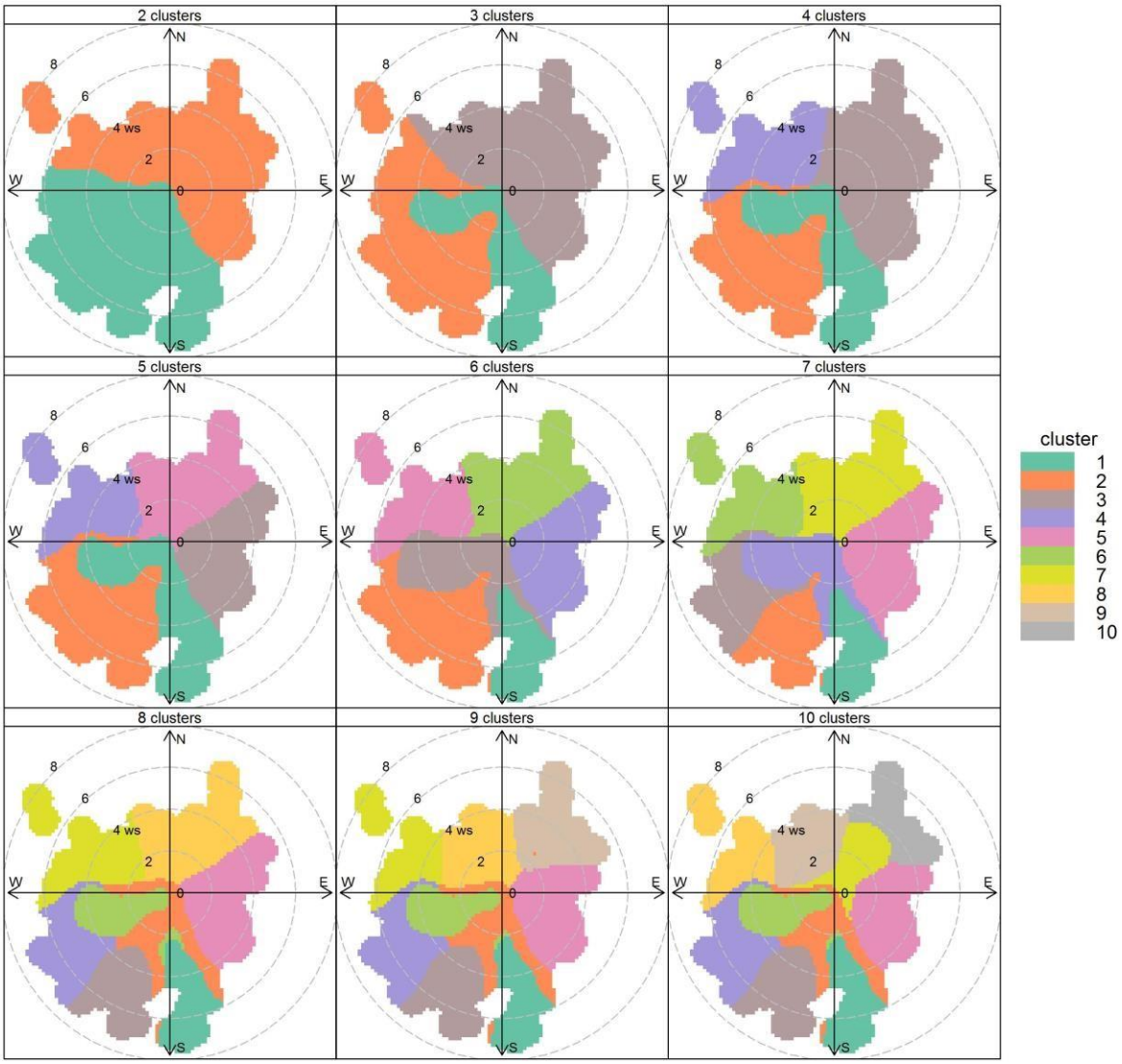

Figure 25: k-means clustering between 2 and 10 clusters on 13 Factor Ni/Mo source at 55th percentile CPF BPPs

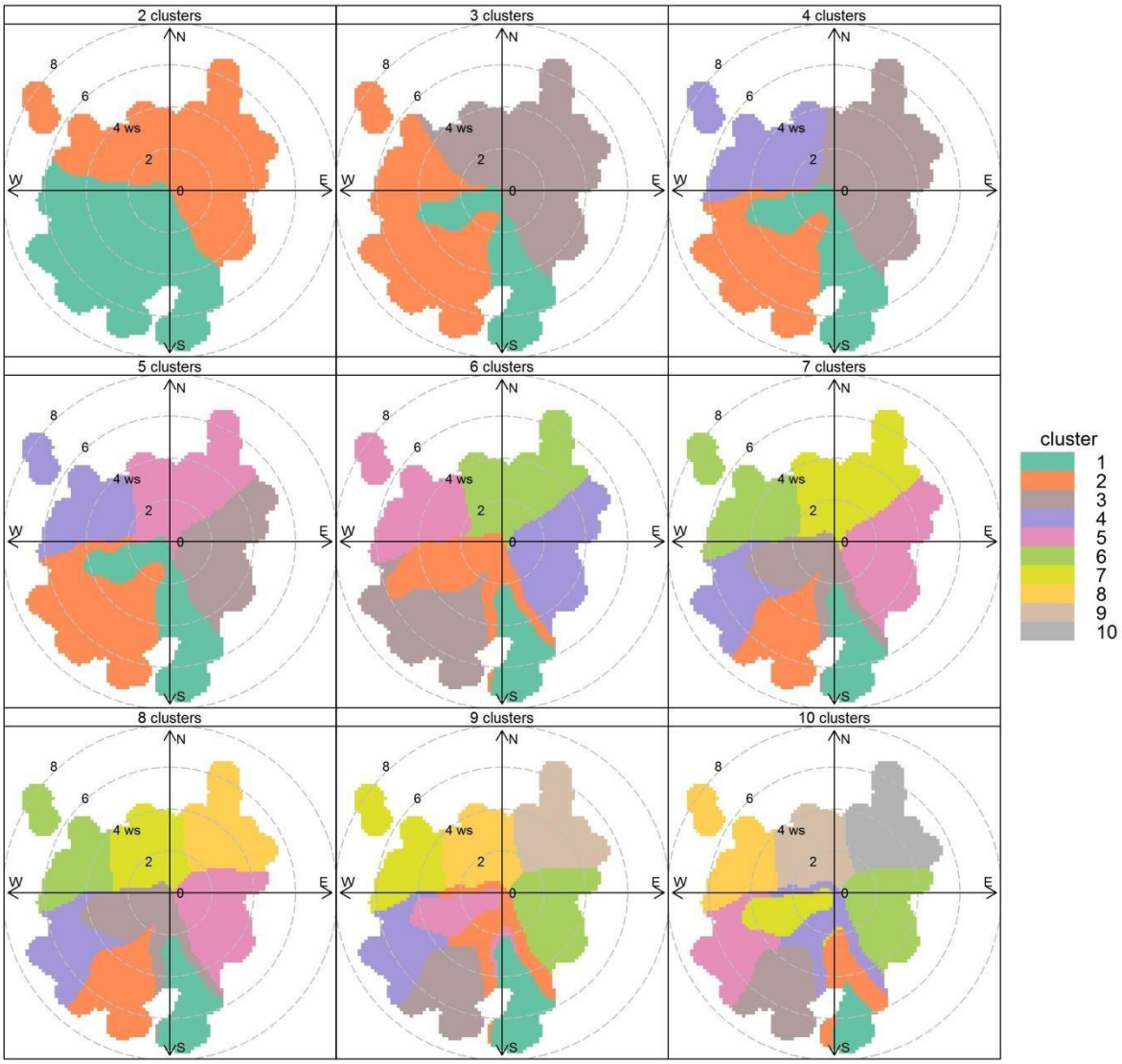

Figure 26: k-means clustering between 2 and 10 clusters on 13 Factor Ni/Mo source at 60th percentile CPF BPPs

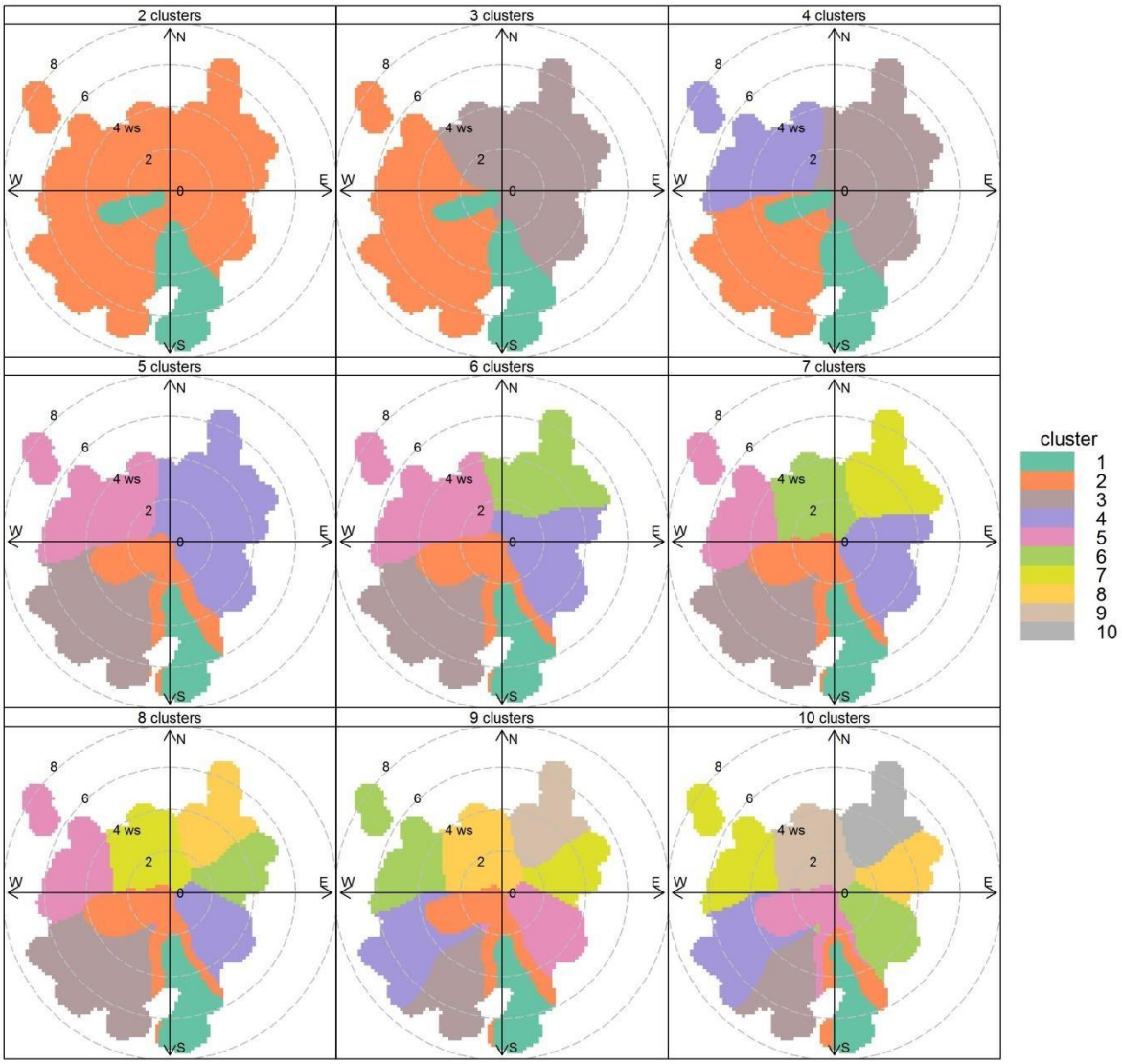

Figure 27: k-means clustering between 2 and 10 clusters on 13 Factor Ni/Mo source at 65th percentile CPF BPPs

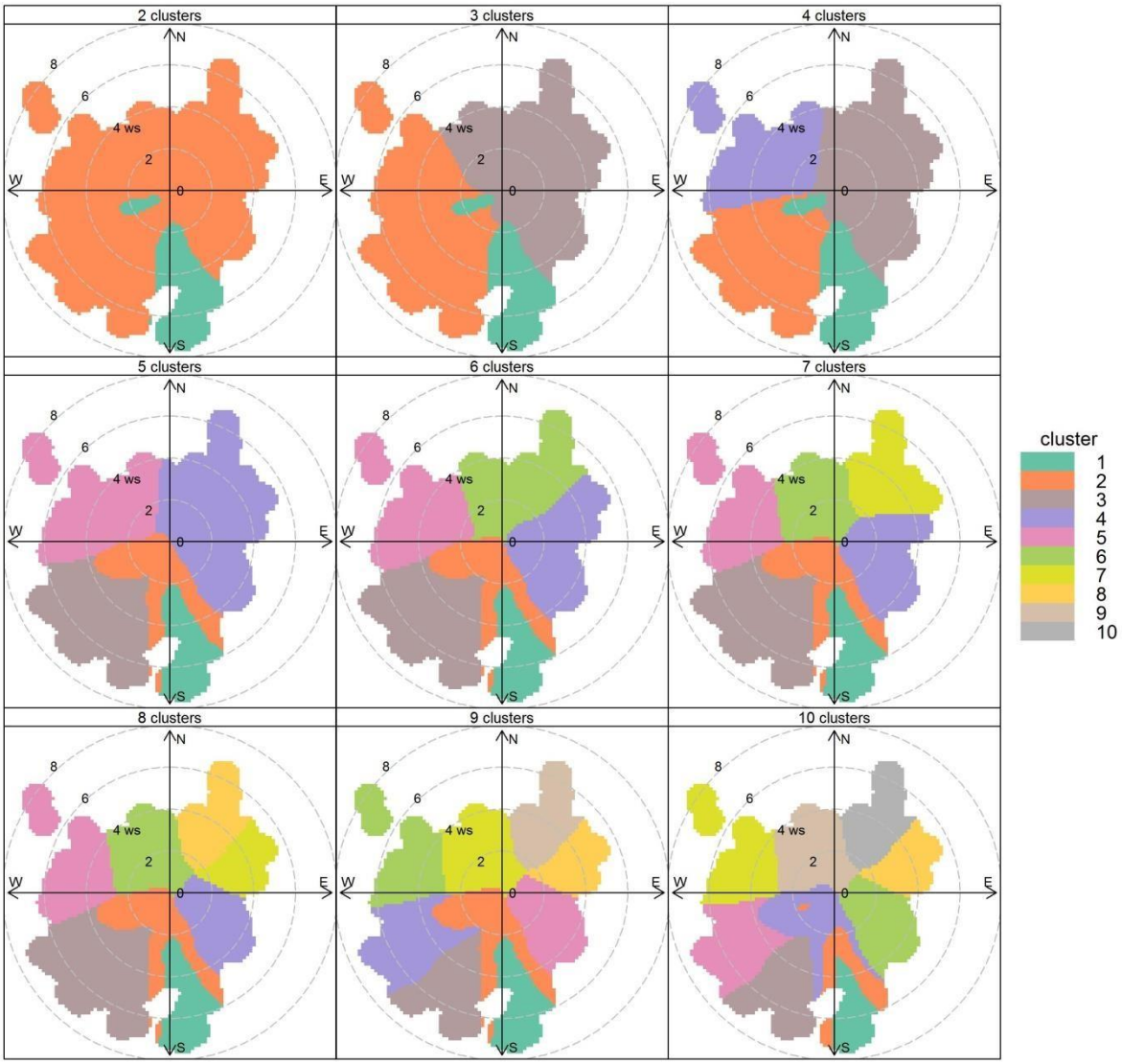

Figure 28: k-means clustering between 2 and 10 clusters on 13 Factor Ni/Mo source at 70th percentile CPF BPPs

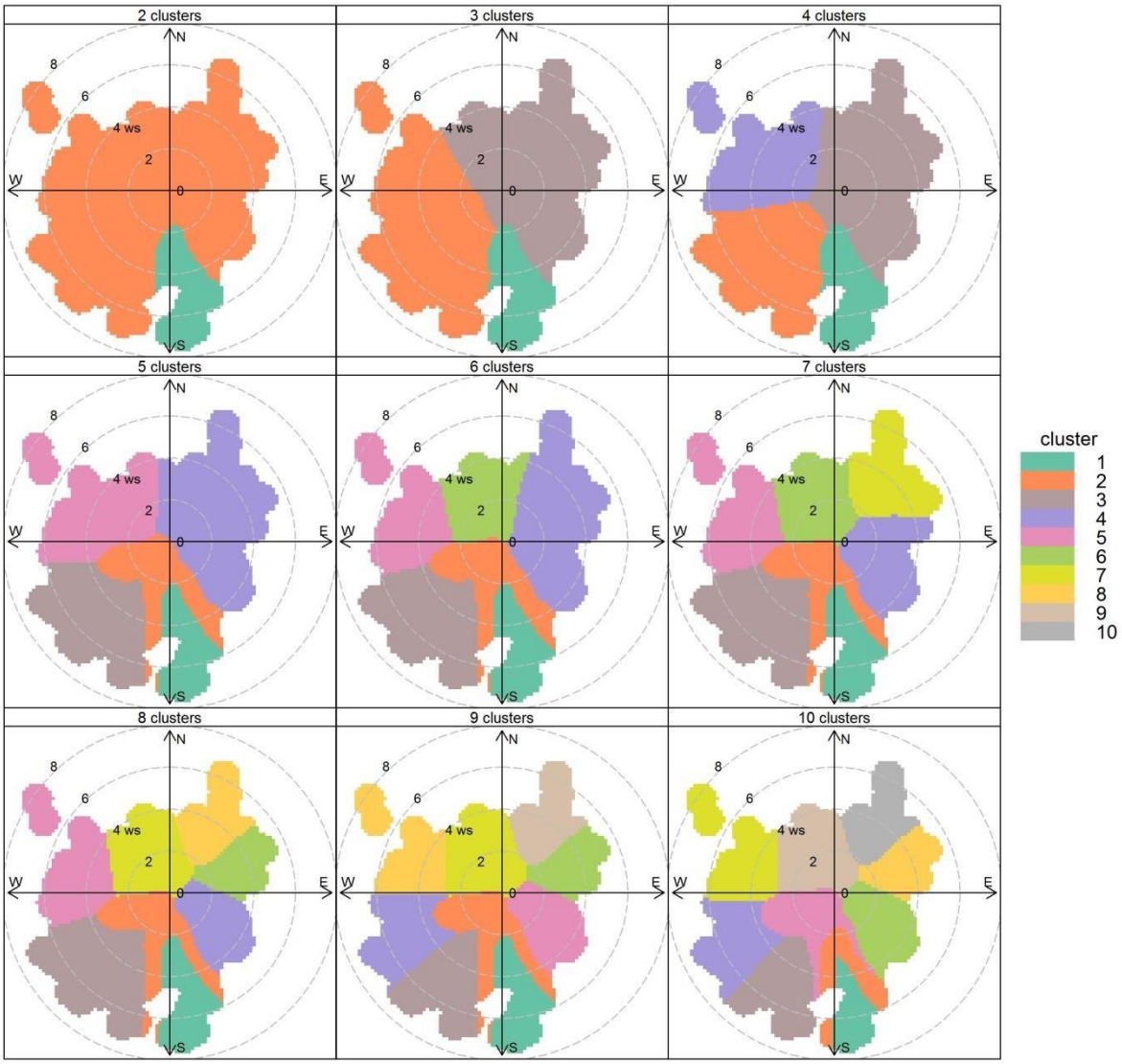

Figure 29: k-means clustering between 2 and 10 clusters on 13 Factor Ni/Mo source at 75th percentile CPF BPPs

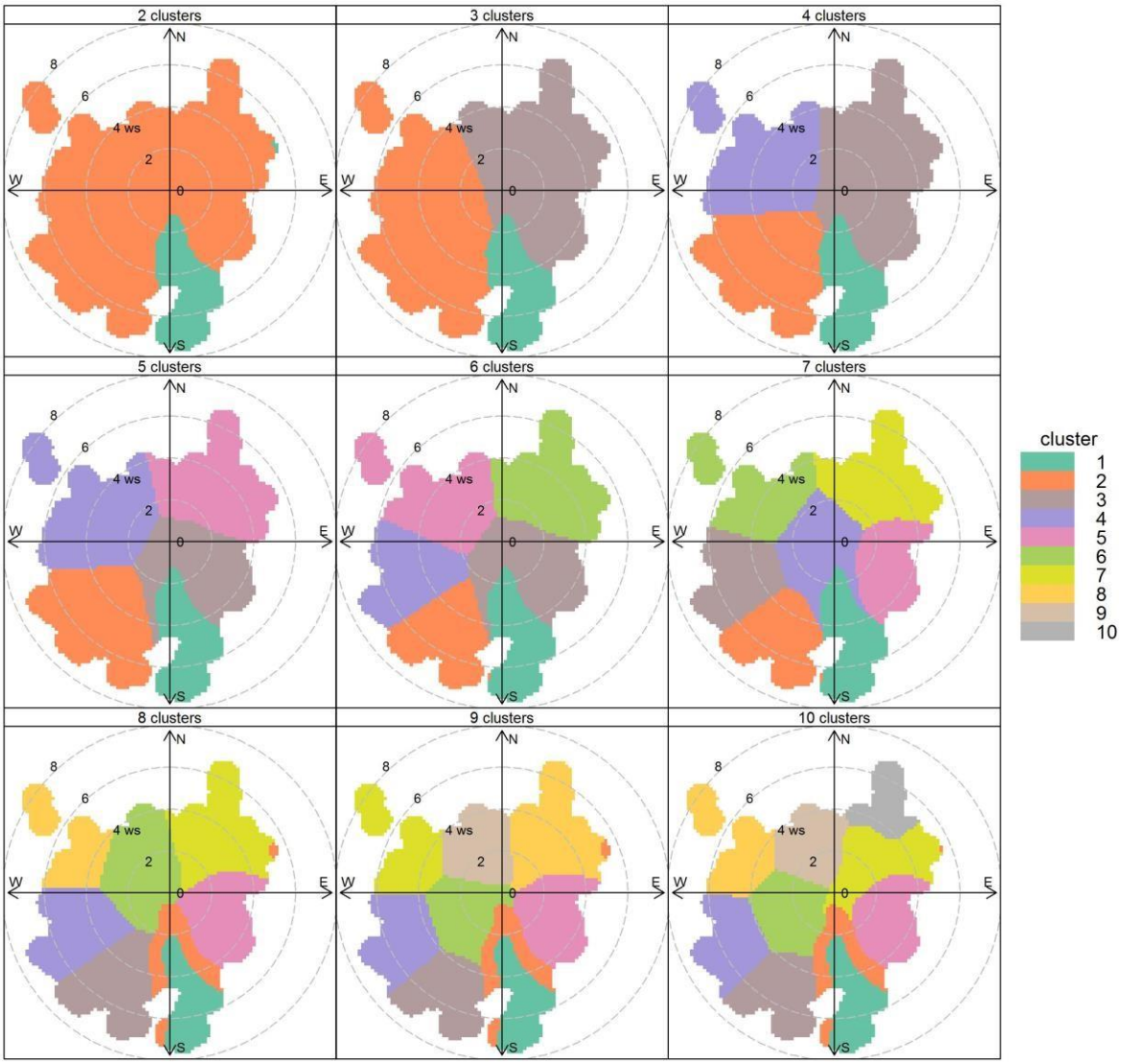

Figure 30: k-means clustering between 2 and 10 clusters on 13 Factor Ni/Cr source at 75th percentile CPF BPPs

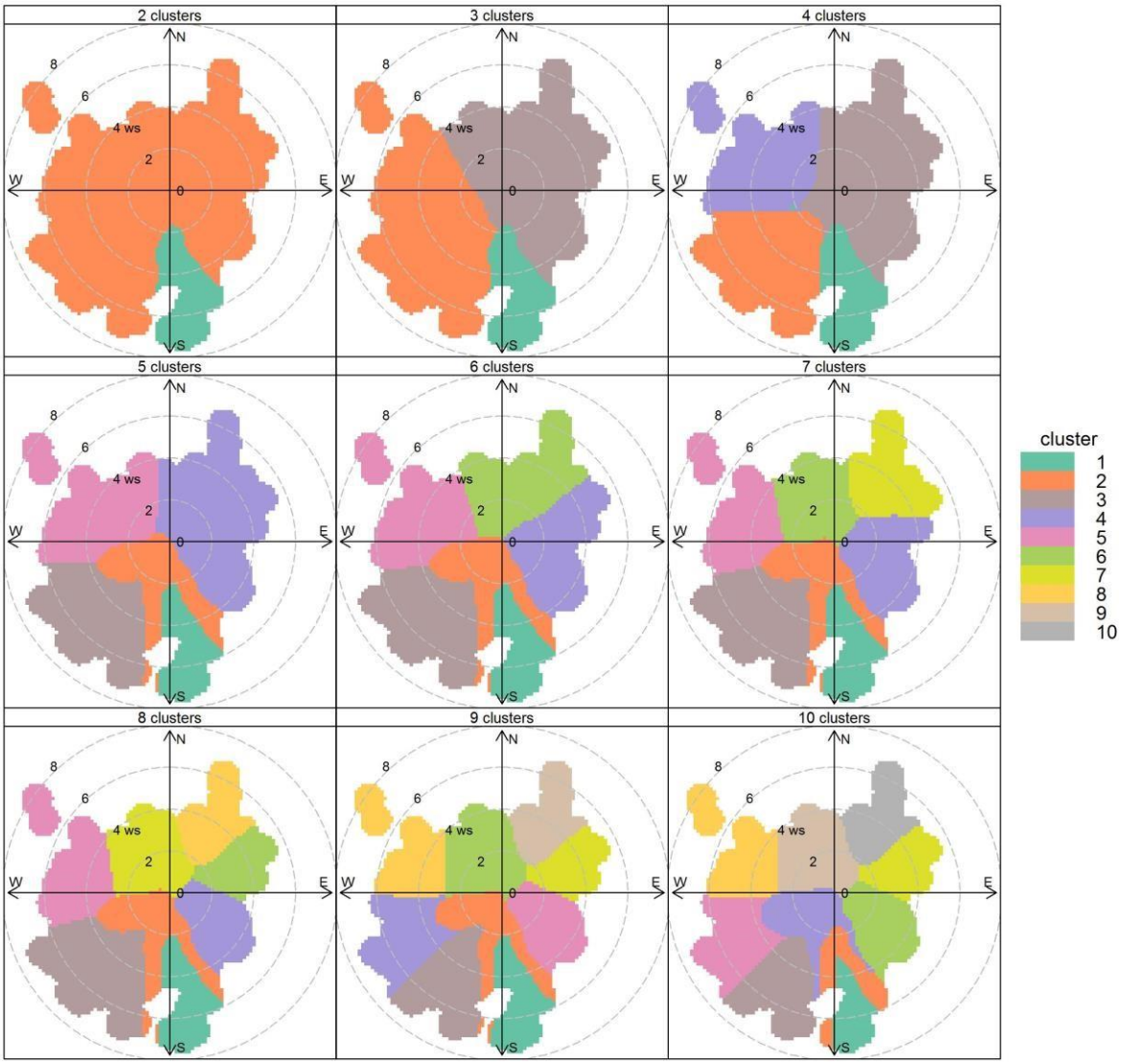

Figure 31: k-means clustering between 2 and 10 clusters on 14 Factor Ni/Mo source at 75th percentile CPF BPPs

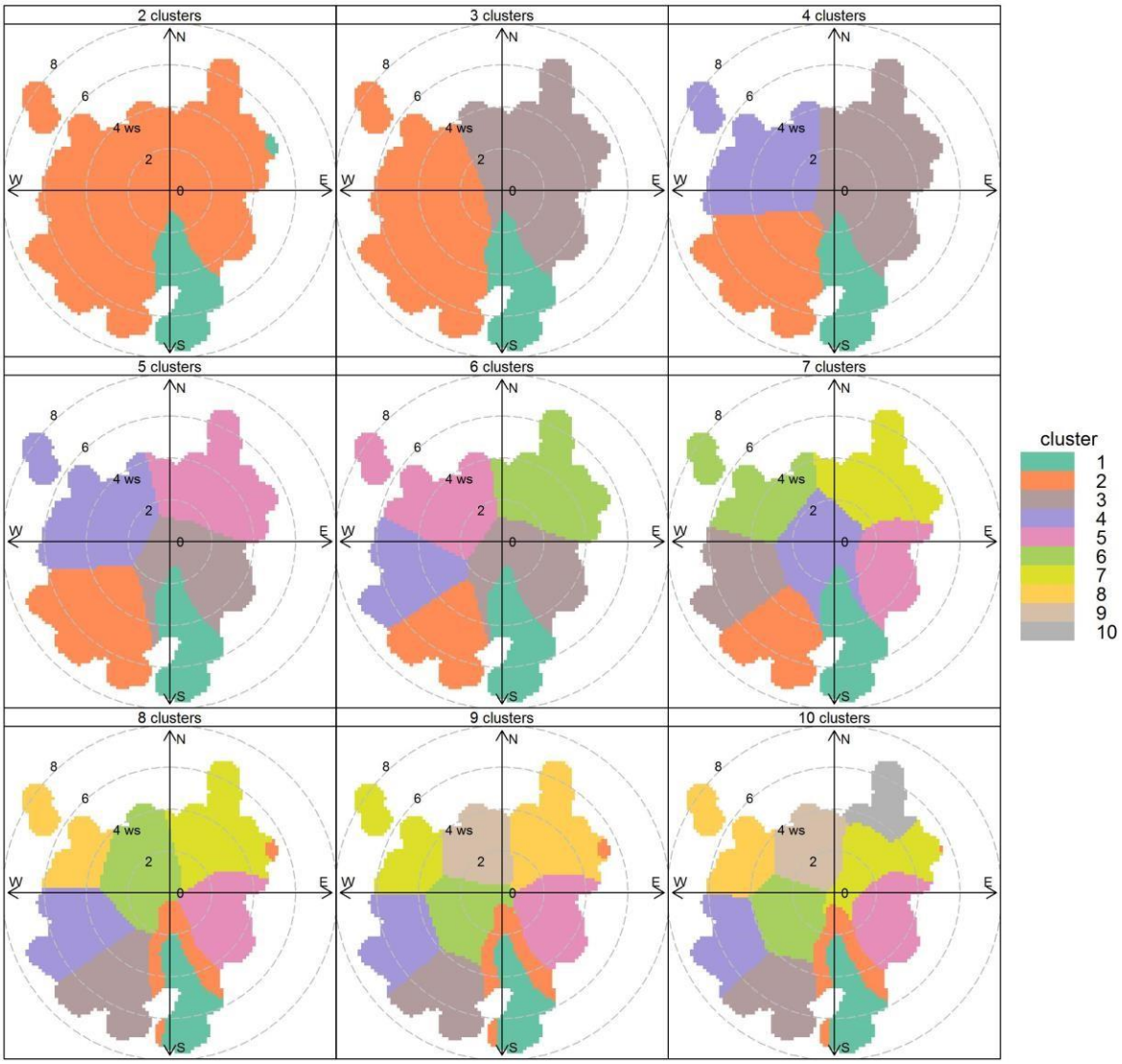

Figure 32: k-means clustering between 2 and 10 clusters on 14 Factor Ni/Cr source at 75th percentile CPF BPPs