Department for Environment Food & Rural Affairs

Report on measures for 2014 exceedance of the Target Value for Nickel in Sheffield Urban Area agglomeration zone (UK0007)

November 2016

This publication is available at www.gov.uk/government/publications

Any enquiries regarding this publication should be sent to us at

Air Quality
Department for Environment, Food and Rural Affairs
Area 2C
Nobel House
Smith Square
London
SW1P 3JR

Email: air.quality@defra.gsi.gov.uk

With technical input from Ricardo Energy & Environment and National Physical Laboratory

www.gov.uk/defra

Contents

Contents 3

1. Introduction 5

1.1 Context 5

1.2 Status of zone 5

2. Exceedance situation Sheffield [Ni_UK0007_2014_1] related to industrial emissions .7

2.1 Description of exceedance 7

2.2 Source apportionment 10

2.3 Measures 13

2.4 Modelling 14

2.5 Monitoring 14

3. Industrial Sources of Nickel 14

3.1 Environment Agency Regulated Plant Part A 14

3.2 Local Authority Regulated Plant Part B 15

3.3 Unregulated plant – Local Authority 15

A1: Local scale modelling of the industrial point sources 18

1. Industrial sources of Ni 18

2. Modelling approach 24

3. Model results 25

4. Conclusions 27

A2: Monitoring studies 28

1. Monitoring Site: Sheffield Tinsley AURN 28

2. Sample Analysis Methodology 28

3. Metals Concentrations 29

3.1 Correlations 30

3.2 Time Series 31

4. Wind Analysis 36

5. Pollution roses 37

6. Local Emission Sources 44

7. Part B processes regulated by Sheffield City Council 45

8. Part A processes regulated by the Environment Agency 45

9. Conclusions 47

Annex 1 - Mean and Median Metals Concentrations by Day of the Week 49

Annex 2 - Pollution Roses for Metal Concentrations and Ratio of Nickel Concentration to other Metals Concentrations 55

Annex 3 - Daily Metals Concentrations 67

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 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.

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 2014 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. Preliminary 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[2] on attainment and Air Pollution in the UK[3].

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

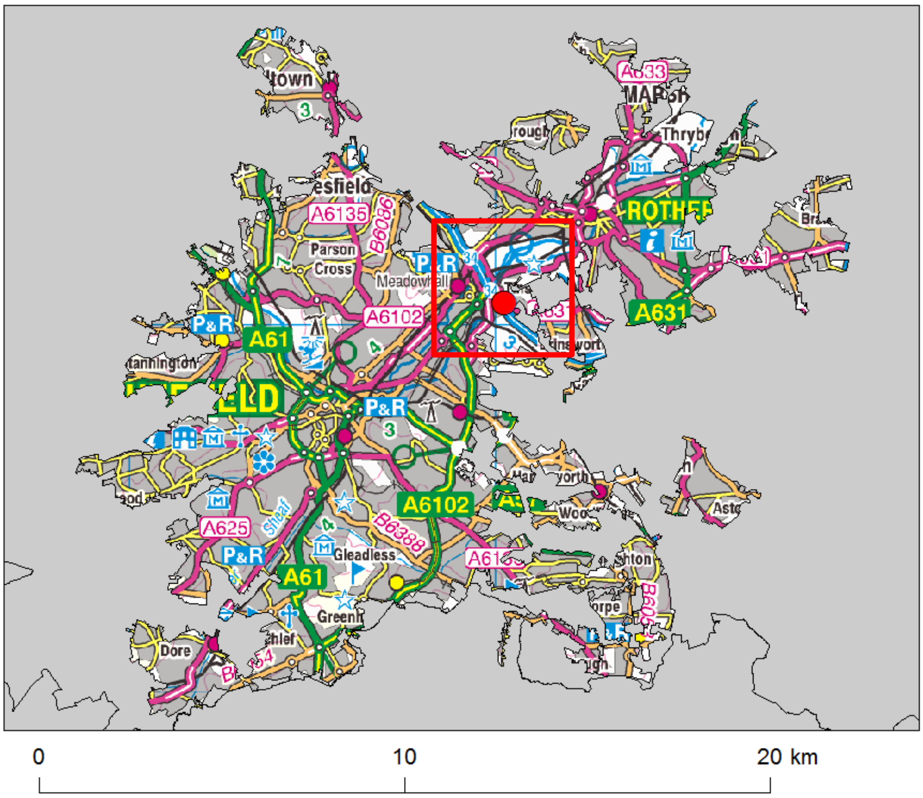
Table 1. Area exceeding Ni target value in 2014 and associated resident population for exceeding areas within Sheffield Urban Area zone UK0007.

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.

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

Figure 1. Location of exceedance of the Ni target value in 2014 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_2014_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_2014_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 2006-2015, and Figure 2 indicates the location of measurement sites. There is one measured exceedance at Sheffield Tinsley (GB0538A) in 2014 for which this report relates. Figure 3 shows the location of the exceedance situation in detail. This map also shows the locations of identified local industrial sources in the vicinity. The concentration of Ni at the other monitoring station within the Sheffield Urban Area agglomeration zone was below the TV in 2014 and no other exceedances have been reported during the 2006-2015 period.

Figure 3 shows in detail the exceedance situation Ni_UK0007_2014_1. 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 Sheffield Urban Area in 2014. 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 2015 was 18 ngm^{-3} (94% data capture). This is below the Ni TV and therefore this exceedance situation does not persist in 2015.

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

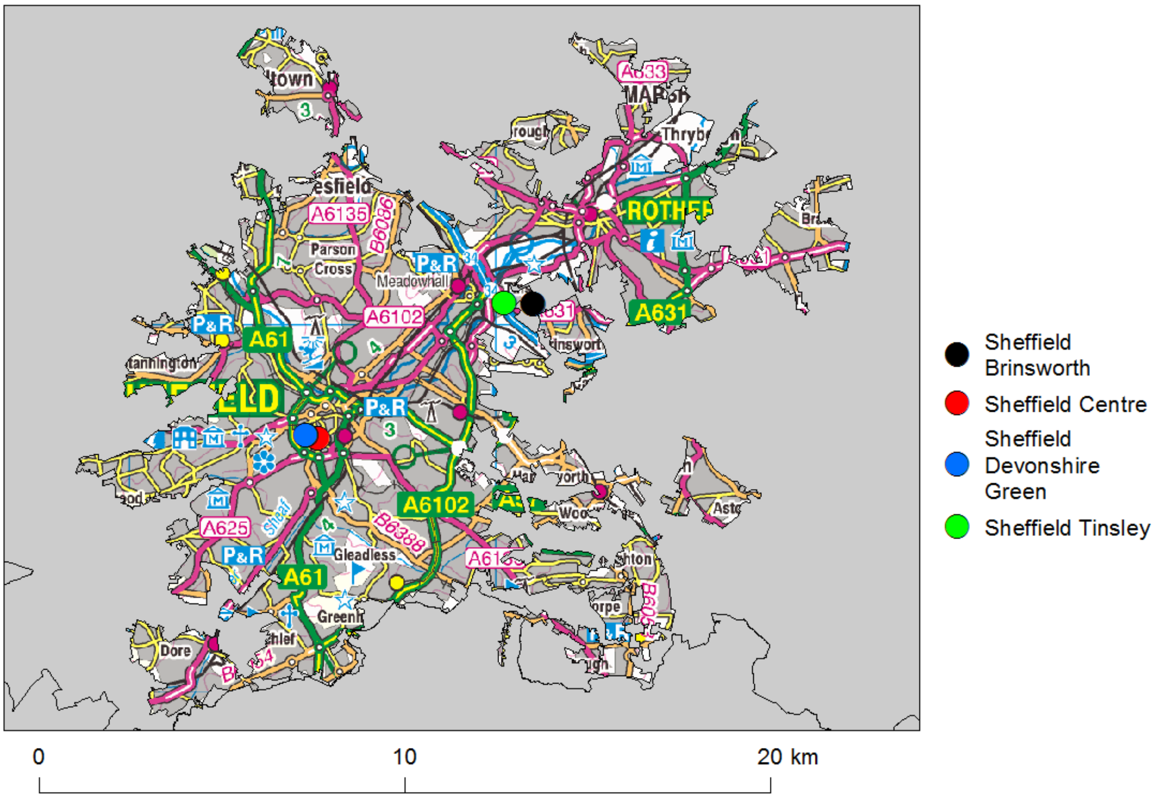
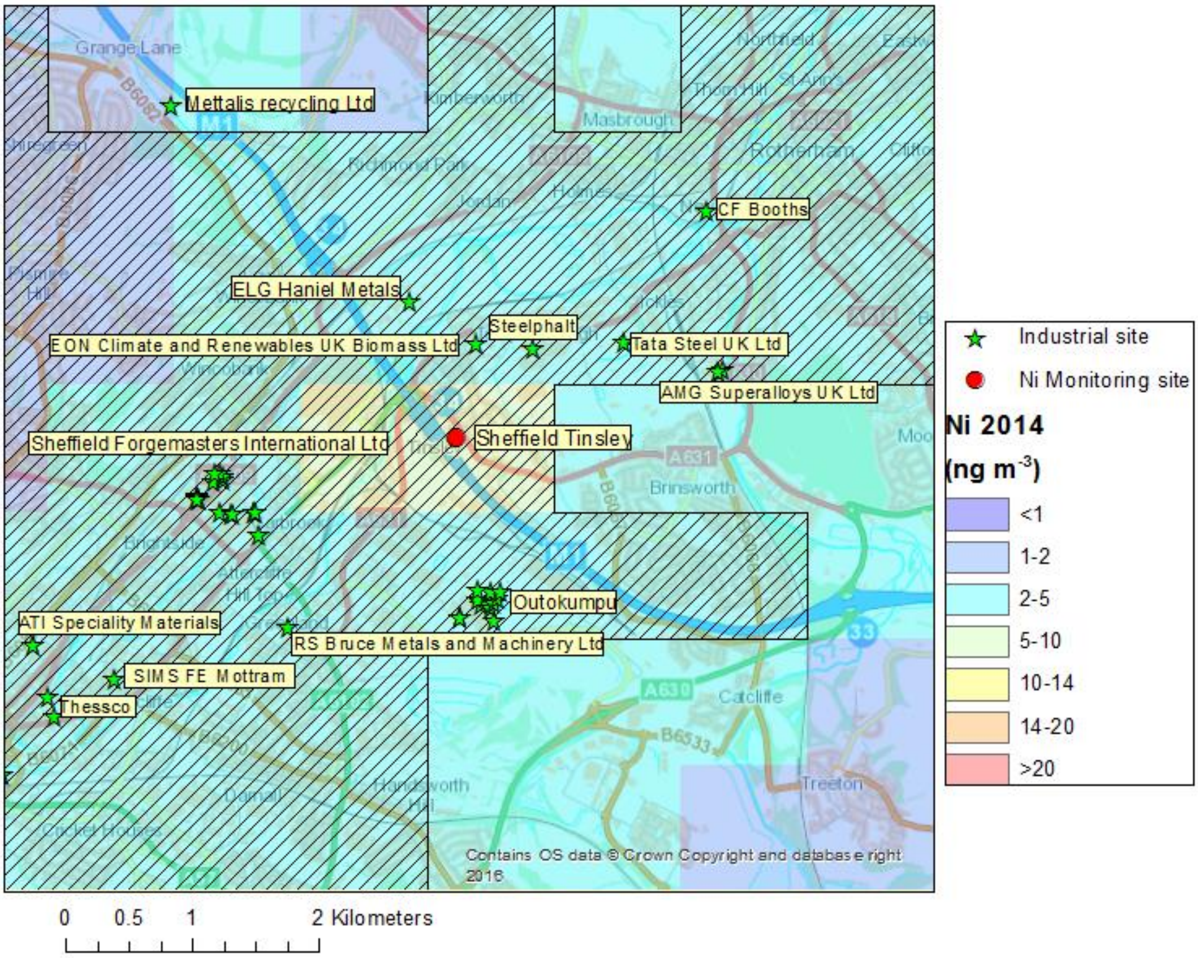


Table 2 Measured annual mean Ni concentrations in Sheffield Urban Area agglomeration zone UK0007 from 2004 to 2015 (ngm^{-3}). (Percentage data capture is shown in brackets).

Station (EoI code)	2004	2005	2006	2007	2008	2009	2010	2011	2012	2013	2014	2015
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)
Sheffield Tinsley (GB0538A)										14 (81)	21 (96)	18 (94)

* Data capture not available

Figure 3 Exceedance situation Sheffield [Ni_UK0007_2014_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 and Thessco).



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 preliminary 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 A.1.

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 emissions from all emissions sources and is equal to the annual Ni concentrations 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 preliminary fine scale modelling study presented in Appendix A. This shows local stack emissions contribute 3.53 ngm^{-3} Ni to the annual mean concentration measured at the Tinsley monitoring site. This study also shows that emissions from the Outokumpu site is the most significant local stack emissions source contributing 3.45 ngm^{-3}, as indicated in Table 4. The main source associated with this exceedance situation is attributed to local unidentified activities.

The source apportionment presented here has been informed by the preliminary 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_2014_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	Urban background increment: commercial and	Urban background increment: Shipping	Urban background increment: Off road mobile	Urban background increment: Other	c) Local increment: Total	Local increment: Industry including heat and power production	Total emissions for all sources (a+b+c)	Resident population
440500	390500	7	1.38	1.38	2.53	0.02	2.18	0.24	0.00	0.08	0.02	17.09	17.09	21	2422

Table 4. Detailed source apportionment for industrial sources only for exceedance situation Sheffield [Ni_UK0007_2014_1]. Annual mean Ni concentration (ngm^{-3}).

OS easting (m)	OS Northing (m)	Zone	Outokumpu	Sheffield Forgemasters	Other identified industry sources*	Unidentified sources	Local increment: Industry including heat and power production
272500	204500	41	3.45	0.05	0.03	13.55	17.09

* Other industry sources identified as contributing <0.01 ngm^{-3} each were TATA steel UK Ltd., AMG Superalloys UK Ltd, E.ON Climate and Renewables UK Biomass Ltd, Veolia ES (Sheffield) Ltd. and SIMS FE Mottram.

2.3 Measures

Improving air quality is a high priority for the Government, including the attainment of EU target values. The exceedence in this zone is just above the TV (and is below the TV for the 2015 reporting period). The Government takes any exceedence 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. Regular 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 2010/75/EU (IED);

- 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 of the identification of the unidentified 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 a daily monitoring campaign at the

Tinsley Monitoring station to obtain greater temporal resolution as regards the measurements made at the site (Appendix 2)

2.4 Modelling

Appendix A1 presents fine scale modelling that has identified the emissions sources as potential contributors to the concentrations measured at Tinsley Monitoring station. These have been established as:

- Outokumpu – Part A process with the highest reported Ni emissions in the area
- Modelling of contributions of other industrial sites in the area.
- Identification of additional sites that may have further contributions but are not regulated.
- Roadworks to the North East of the Tinsley monitoring station as part of the Bus Rapid Transport North scheme has been identified as a potential source of Ni dust re-suspension from Ni contaminated land.

2.5 Monitoring

Appendix A2 presents the outputs of a daily monitoring campaign whereby daily measurements are compared to meteorological data to provide measurement based indications of the likely key source directions. This study identifies some contribution to the Tinsley monitored concentrations from similar sources to the fine scale modelling study in Appendix 1 with additional unknown source contributions from locations to the North East of Tinsley. When these measurements are excluded from the analysis it is shown that the main contribution is from the direction of the Outokumpu site.

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 at section 5.2 of Appendix A2. From the industrial sites identified to date Outokumpu has been identified as making a significant contribution to the levels of Ni measured at Tinsley monitoring site. Outokumpu is regulated by the Environment Agency and is declared as being at BAT. As such there are currently no specific future measures affecting emissions of nickel. Further analysis of emissions samples from the area is being undertaken, in conjunction with Outukumpu to assist in identification of other potential sources of fugitive emissions that are currently unidentified.

3.2 Local Authority Regulated Plant Part B

Further information about operating processes at individual sites can be found at section 5.1 of Appendix 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.

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

Measure code	Measure Description	Classification	Implementation dates		Other information		Comment
Sheffield_1	Fine scale modelling to identify emissions sources that are potential contributors to the concentrations measured at Tinsley Monitoring station.	Air Quality Planning and Policy Guidance	Start:	2015	Source affected:	Industry including heat and power production	Modelling undertaken for 2014 establishes potential contributors as Outokumpu plant and small contributions from other local industrial sources. Modelling identified a shortfall in known emissions.
			Expected end:	2016	Spatial scale:	Local	
			Status:	Implementation	Status:	Implementation	
Sheffield_2	Daily monitoring campaign undertaken whereby daily measurements of Ni recorded at Tinsley monitoring station are compared to meteorological data to provide measurement	Air Quality Planning and Policy Guidance	Start:	2016	Source affected:	Industry including heat and power production	Daily monitoring undertaken from 25th February - 9th August 2016 identified an unknown source of contributions from locations to the North East of Sheffield Tinsley. When these measurements are excluded from the
			Expected end:	2016			

	based indication of the likely key source directions		Status:	Implementation			analysis it is shown that the main contribution is from the direction of the Outokumpu site.

A1: Local scale modelling of the industrial point sources

Supplementary modelling work was carried out to investigate the source of the measured exceedance of the annual mean TV for nickel at the Sheffield Tinsley monitoring station and is described here. Work undertaken to identify potential industrial sources of Ni in the area is presented in Section 1. Detailed fine scale modelling of identified industrial sources for which sufficient information was available was then carried out in ADMS 5.1. A description of the modelling methodology is presented in Section 2 and the model results are discussed in Section 3. Conclusions are presented in Section 4.

1. Industrial sources of Ni

Potential sources of Ni were investigated from a review of known industrial sites in the vicinity of the exceedance. Data sources included:

- National Atmospheric Emissions Inventory 2013 (NAEI2013)
- Environment Agency (EA) permitted sites
- Local Authority (LA) permitted sites, specifically information provided by Sheffield City Council (SCC) and Rotherham Metropolitan Borough Council (RMBC)

Annual emissions of Ni in 2014 and source release characteristics were collected for each identified industrial site. For a small number of sites, 2014 emissions data were either indicated but unspecified, or low levels of Ni emissions were reported without information on the source release characteristics. Therefore these sites were not modelled (see table 1). Those sites that were modelled in this study are listed in Table 2, including a description of where emissions were treated as a line (e.g. along a roof vent) or point releases (e.g. from a chimney stack). Figure 1 shows the locations of identified industrial sites.

Table 1. Identified Ni emitters which were not modelled

Operator	Address	Postcode	Process Type	Data provider
Mettalis Recycling Limited	Blackburn Grange	S9 1HW	Fragmentiser - Metal Shredding (Cars)	EA
ATI Specialty Materials	Carlisle Street East Works (FKA Atlas Site)	S47UR	Electro slag remelt furnace	SCC
R.S Bruce Metals and Machinery Limited	March Street	S9 5DQ	Stainless Steel Cutting. Processing of sludges.	EA
CF Booths	Armer Street	S60 1AF	Asbestos stripping from railway vehicles	RMBC
ELG Haniel Metals	Sheffield Road	S9 1RT	Started Operating in 2012 - Shredding of Metal	EA
Steelphalt	Sheffield Road	S60 1DR	Asphalt Production. Slag Handling - Potential to emit low level Nickel	EA

Table 2. Identified Ni emitters included in the modelling study

Operator	Site Name	Stack Name	Stack Location (description)	Ni emissions in 2014 (kg/year)	Source type	Data provider
Thessco		A1	Melting Shop Bag Filter	0.0003	Point	EA
Thessco		A2	Water Atomiser Bag Filter	0.0007	Point	EA
Sheffield Forgemasters International Ltd Sheffield	Sheffield Forgemasters Brightside	A1	Melting Shop, Bag Filter Plant Roof Vents	1.6800	Line	EA
		A2	Snow Grinder and Melt Shop Flame Cutting Facility	1.1200	Point	EA
		A3	Forge Ingot Burning, Bag Filter and Plant Stack	2.2600	Point	EA
		A4	Gas Fired Boiler Plant Stack	0.0001	Point	EA
		A5	Gas Fired Boiler Plant Stack	0.0001	Point	EA
		A6	Gas Fired Boiler Plant Stack	0.0001	Point	EA
		A7	Gas Fired Boiler Plant Stack	0.0001	Point	EA
		A8	Forge Heating Furnace No.1 Stack	0.0002	Point	EA

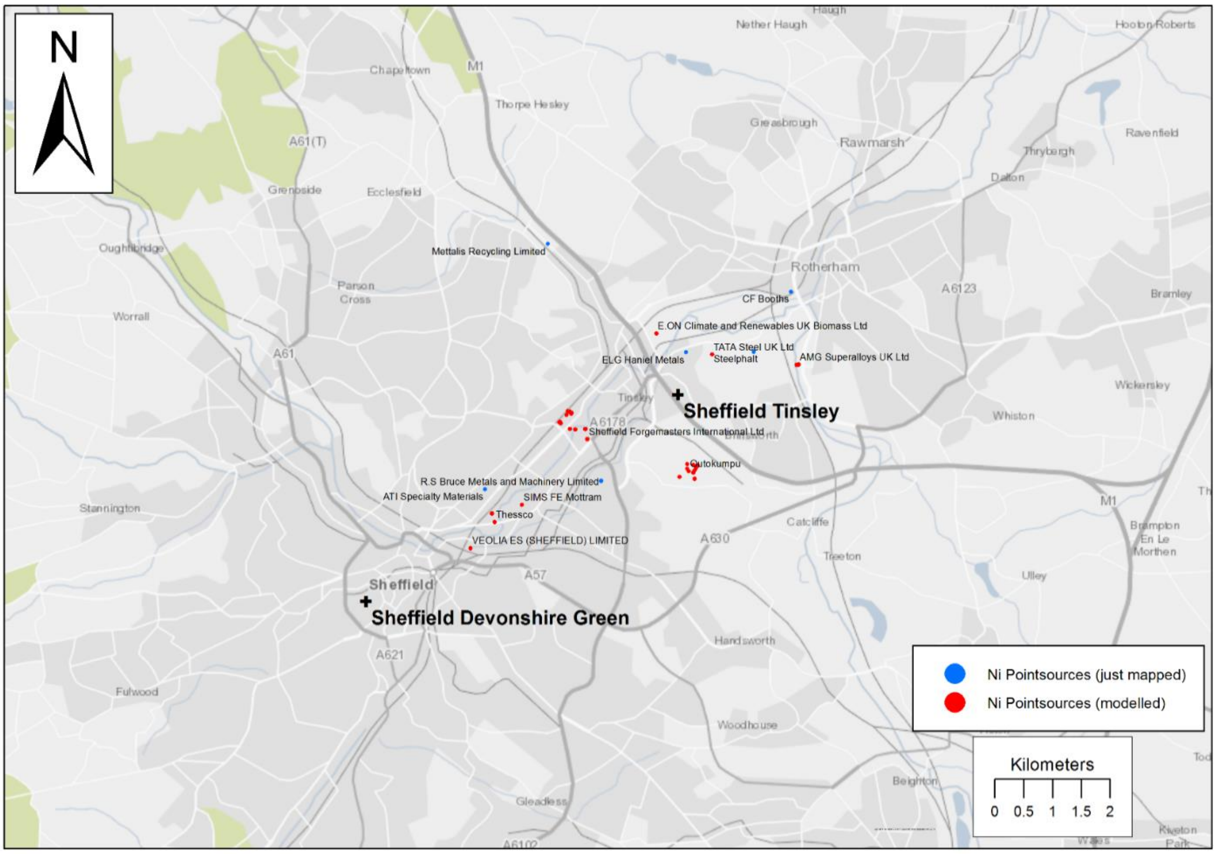
		A9	Forge Heating Furnace No.7 Stack	0.0015	Point	EA
		A11	Heavy Forge Roof Vents (exhausts from forge furnaces2, 14, 17, 28, selas furnace and heat treatment furnaces NTP1 to 16, 18 and 20a/b)	0.0035	Line	EA
		A13	Foundry Shot Blast Stack	0.4600	Point	EA
		A15	Foundry Burning Booth Stack	8.3500	Point	EA
		A20	Foundry Heat Treatment Furnace Stacks	0.0003	Point	EA
		A21	Foundry Heat Treatment Furnace Stacks	0.0005	Point	EA
		A22	Foundry Heat Treatment Furnace Stacks	0.0003	Point	EA
		A28 (251-255)	Melting Shop Low Casting Bay Roof Vents (Furnaces 251-255)	4.3000	Line	EA
		A31	Forge Heating Furnace No.3 stack	0.0007	Point	EA
Outokumpu	Stainless Melting and Continuous Casting	A1	Melt Shop Bag Filter	161.0000	Line	EA
		A2	DC Arc Furnace	4.0000	Point	EA

		A3	Grinder Bag Filter	39.0000	Point	EA
		A4	Grinder Bag Filter	2.0000	Point	EA
		A5	Grinder Bag Filter	5.0000	Point	EA
		A6	Radial Saw Bag Filter	0.0000	Point	EA
		A13	Cast Product cut-off Bag Filter	6.0000	Point	EA
		A14	Grinder Bag Filter	3.0000	Point	EA
		A15	Melting Shop Scavenging Filter (West)	1.0000	Point	EA
		A16	Melting Shop Scavenging Filter (East)	1.0000	Point	EA
		A17	EAF Dust Storage Silo Filter	0.0000	Point	EA
		N/A	West vent melt shop roof	90.0000	Line	EA
		N/A	East vent melt shop roof	148.0000	Line	EA
TATA Steel UK Ltd	Brinsworth Strip Mill	A1	Reheat furnace	0.0200	Point	EA

Appendix A1: Local Scale Modelling

AMG Superalloys UK Ltd	Fullerton Road	A1	Arc Furnace	3.4824	Point	EA
		A2	Arc Furnace	15.0904	Point	EA
E.ON Climate and Renewables UK Biomass Ltd	Blackburn Meadows Renewable Energy Plant	Release Point A1	Main Stack	8.7400	Point	EA
VEOLIA ES (SHEFFIELD) LIMITED	Sheffield Energy Recovery Facility	Release Point A1	Main Stack	28.5400	Point	EA
SIMS FE Mottram	Oakes Green, Stevenson Road, Sheffield	FEM 2	Furnace extraction - Cyclone and dry bag filter	0.0155	Point	SCC

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



2. Modelling approach

Modelling of each of the identified Ni sources listed in Table A.2 was carried out at a spatial resolution of 50 m x 50 m over an area of 10 km x 10 km that includes both Sheffield Tinsley and Sheffield Devonshire Green monitoring stations. A 10 km by 10 km area was extracted from OS Terrain 50 dataset to allow the effect of topographical features of the valley to be included in the model. The height of the terrain was specified at the centre of each 50 m x 50 m grid square.

Meteorological data was sourced from Sheffield Doncaster Airport, with additional data from RAF Waddington and Western Park Weather Station (Museums Sheffield) used to gap fill missing data. The protocol for gap filling[4] was as follows: 1 hour gaps were filled based upon the previous hour, gaps up to 3 hours were based upon interpolation, and larger gaps (>3 hours) were filled with measurements from RAF Waddington, except for relative humidity, where Weston Park museum was used preferentially and otherwise RAF Waddington.

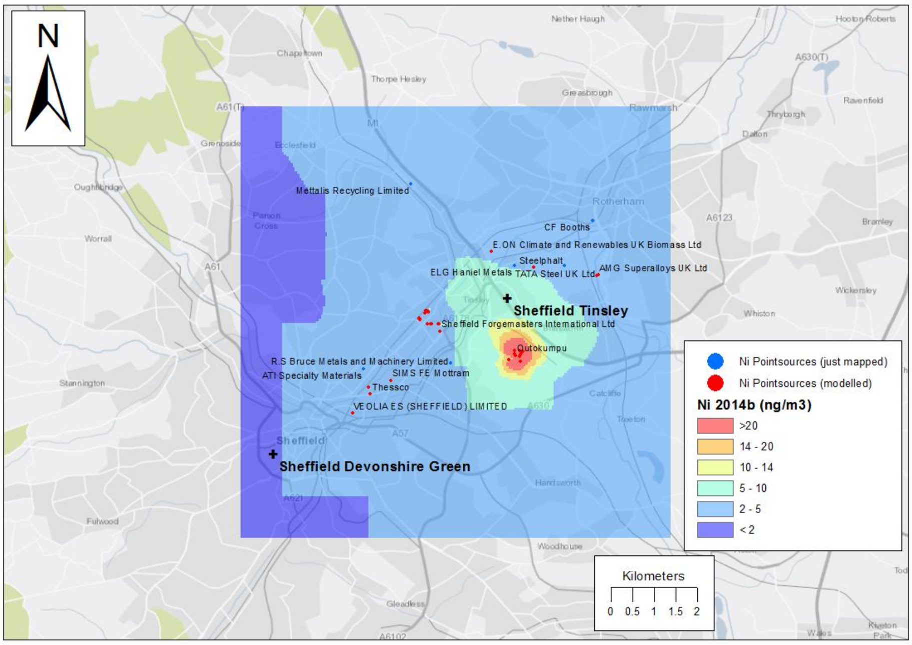
The national model at a 1 km x 1 km resolution provided a background component for the Ni concentrations. The results of the fine scale modelling of industrial sources were added to this background component. To avoid double counting of industrial source contributions, the contribution from any sites that were included in both the national and local fine-scale models were subtracted from the background model.

3. Model results

The output of the local fine-scale modelling is presented in Figure A.2. The highest modelled concentrations are located around the Outokumpu site and the modelling suggests an exceedance of the Ni TV at this location which may extend over a spatial area of relevance to the directive (at least 250 m x 250 m for industrial locations). The footprint of the modelled exceedance does not extend to 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 no population exposure within the exceedance area. However public access within the exceedance area was identified to the south (pavement along the Europa Link road).

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

Figure 2. Annual mean Ni concentrations for 2014 from local fine-scale modelling of industrial sources added to the nickel background concentrations from the national model. The locations of modelled industrial sources and additional industrial sources not modelled (just mapped) are also shown.

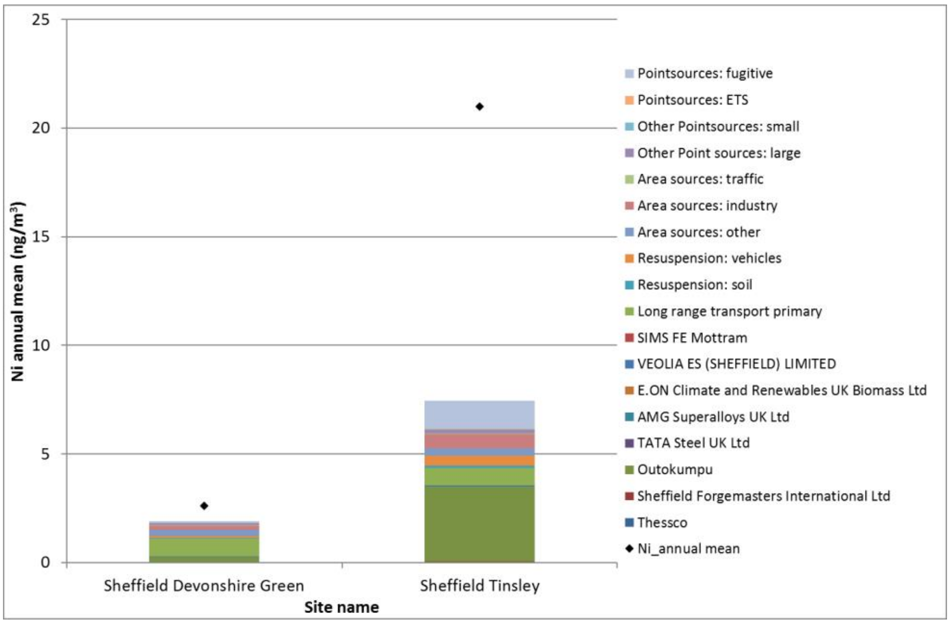


Contains OS data © Crown copyright and database right (2015)

The model results were assessed at the locations of the two nearby monitoring stations: Sheffield Tinsley and Sheffield Devonshire Green. Figure A.3 presents the modelled concentrations from different sources at the monitoring stations compared with the measured concentrations.

This analysis suggests that the main industrial source of Ni at both the Sheffield Tinsley and Sheffield Devonshire Green monitoring stations is Outokumpu. The combined modelling output represents 73% of the observed concentration at Sheffield Devonshire Green. However, the combined modelling represents 35% of the observed concentrations at Sheffield Tinsley indicating other significant Ni sources have not been captured.

Figure 3. Annual mean Ni source apportionment at Sheffield monitoring sites in 2014 (combined detailed and national modelling output)



4. Conclusions

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

- The detailed modelling indicates localised exceedances of the Ni TV (20 ngm^{-3}) associated with the Outokumpu site.
- The footprint of the modelled exceedance does not extend to the location of the Sheffield Tinsley monitoring station and inspection of the area of modelled exceedance compared to 1 km gridded population (2011 census) indicates no resident population exposure although there is public access within the exceedance area to the south with pavement along the Europa Link road.
- The source apportionment analysis suggests that the main identified industrial source of Ni at both the Sheffield Tinsley and Sheffield Devonshire Green monitoring stations is Outokumpu, although this only accounts for a small proportion of the measured exceedence.
- The combined modelling output represents 73% of the observed concentration at Sheffield Devonshire Green.
- The combined modelling represents 35% of the observed concentrations at Sheffield Tinsley indicating other Ni sources have not been captured. The magnitude of emissions from Outokumpu are an order of magnitude higher than all the other local industrial sites included in the current study (Table 2). This is suggestive of an unknown source of emissions. This could be a smaller source very close to the Sheffield Tinsley monitoring station or a more distant source with a greater magnitude of emissions.

A2: Monitoring studies

Summary of Daily Metals Concentrations measured at Sheffield Tinsley 25th February 2016 to 9th August 2016

David Butterfield & Sharon Goddard
National Physical Laboratory
November 2016

1. Monitoring Site: Sheffield Tinsley AURN

In February 2016 the Partisol 2000 sampler taking weekly PM_{10} metals samples was replaced with a Partisol 2025 to enabling daily sampling to take place. Daily sampling took place from 25th February 2016 to 9th August 2016. From 10th August the Partisol 2025 was reprogrammed and the sampling reverted to weekly. During the daily sampling there were a few malfunctions with the Partisol 2025 which resulted in the loss of samples between:

10th March to 15th March Power cut caused sampler to stop sampling and the sampler failed to restart when power was restored;
17th June to 20th June Earth problems with Partisol caused sampler to freeze;
13th July to 26th July Sampler freezing and returned to service agent for repair.

2. Sample Analysis Methodology

The heavy metals analysed were vanadium (V), chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), arsenic (As), selenium (Se), cadmium (Cd), and lead (Pb).

Analysis for particulate-phase metals took place at NPL using PerkinElmer Elan DRC II and Elan 9000 ICP-MS following NPL's procedure, accredited by UKAS to ISO 17025, which is fully compliant with the requirements of EN 14902[5].

5 CEN (2005) Ambient air quality – Standard method for the measurement of Pb, Cd, As and Ni in the

One of two ICP-MS instruments in the NPL metals laboratorv.

Upon arrival at NPL, the filters were cut accurately into half portions. Each portion was digested at temperatures up to 220°C using an Anton Parr Multiwave 3000 microwave. The digestion mixture used was 8 ml of nitric acid and 2 ml hydrogen peroxide.

ICP-MS analysis of the digested solutions involved an instrument calibration using at least four gravimetrically-prepared calibration standard solutions. A quality assurance (QA) standard was repeatedly analysed (after every two solutions), and the change in response of the QA standard was mathematically modelled to correct for the long-term drift of the instrument. The short-term drift of the ICP-MS was corrected for by use of an internal standards mixture (containing Y, In, Bi, Sc, Ga) continuously added to all the samples via a mixing block. Each sample was analysed in triplicate, each analysis consisting of five replicates.

The amount of each metal in solution (and its uncertainty) was then determined by a method of generalised least squares using XLGenline[6] (an NPL-developed program) to construct a calibration curve.

3. Metals Concentrations

The following sections provide the results of different data analysis methods to try and distinguish between local sources of heavy metals.

6 Smith, I.M. NPL Report MS 11, Software for determining polynomial calibration functions by generalised least squares: user manual; NPL: Teddington, 2010.

3.1 Correlations

Figure 1 shows a correlation matrix of the different metal concentrations measured, calculated by the OpenAir Package[7] in the statistical computing package "R":

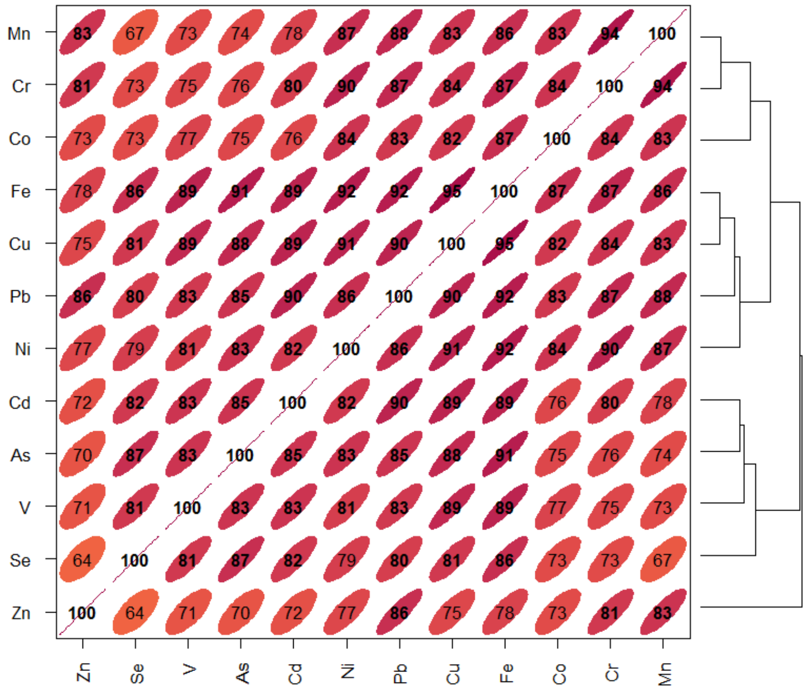


Figure 1 Correlation matrix of metal concentrations

It can be seen that there is good correlation between all of the metals (r >0.70) except between zinc and selenium (r=0.64). Cluster analysis of the correlations shows that nickel has very good correlation with iron, copper and lead concentrations. Iron is best correlated with all of the other metals, except zinc, indicating that nearly all of the sources are iron based. Although zinc regularly has the highest concentrations, it is not well correlated with other metals indicating that this source is unrelated to the other sources of metals emissions. However, it is still probably an industrial source due to the concentration distribution across the days of the week.

[7] Carslaw, D. C. and K. Ropkins, (2012) openair --- an R package for air quality data analysis, Environmental Modelling software, Volume 27-28, 52-61.

3.2 Time Series

Figures 2a &b and 3a & b show time series of all the metals over the monitoring period and the nickel concentrations on their own for comparison with the target value of 20 $ng.m^{-3}$.

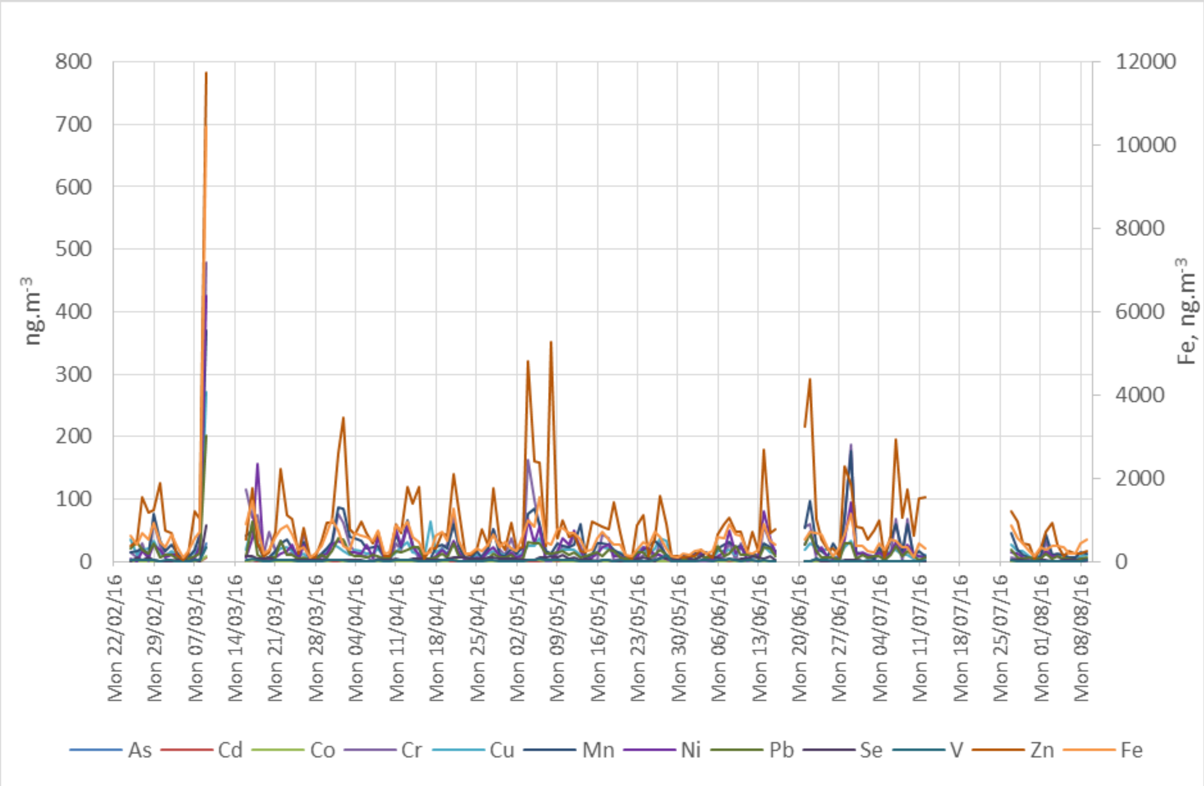


Figure 2a Time series of daily metal concentrations

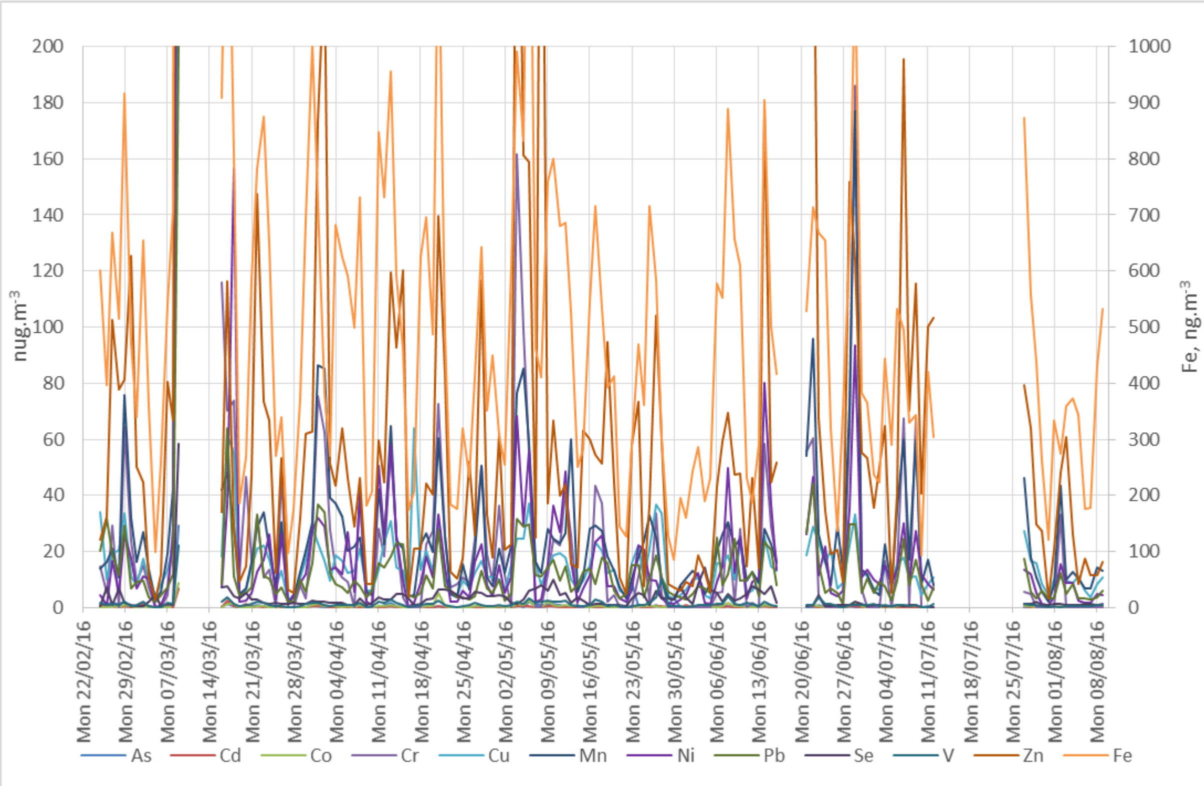


Figure 2b Time series of daily metal concentrations

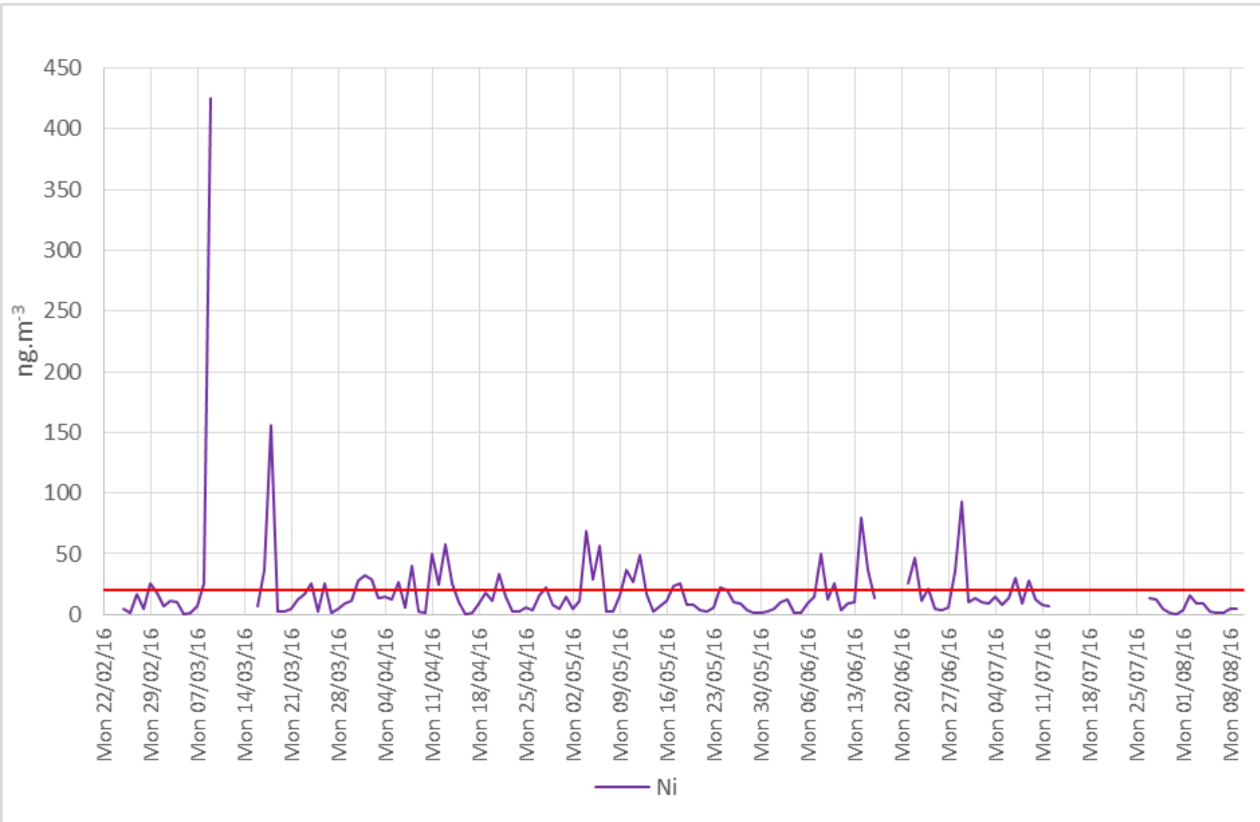


Figure 3a Time series of daily nickel concentrations

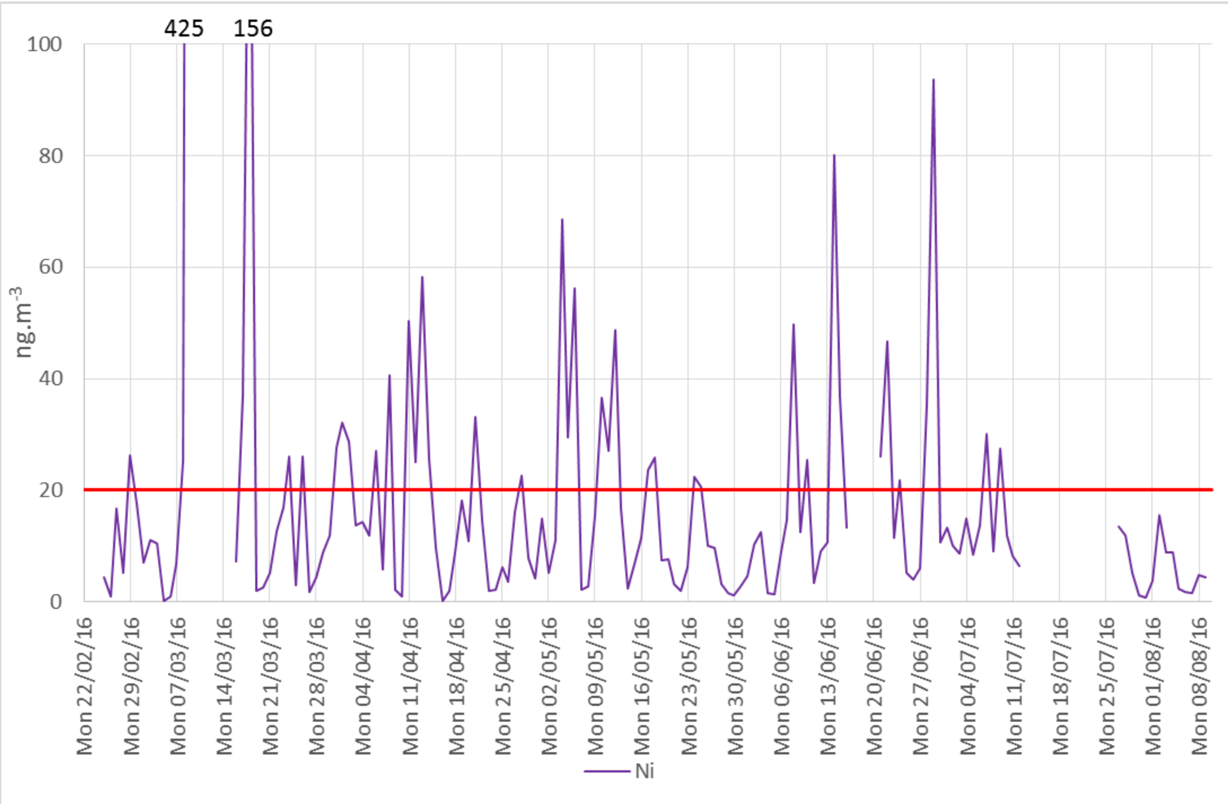
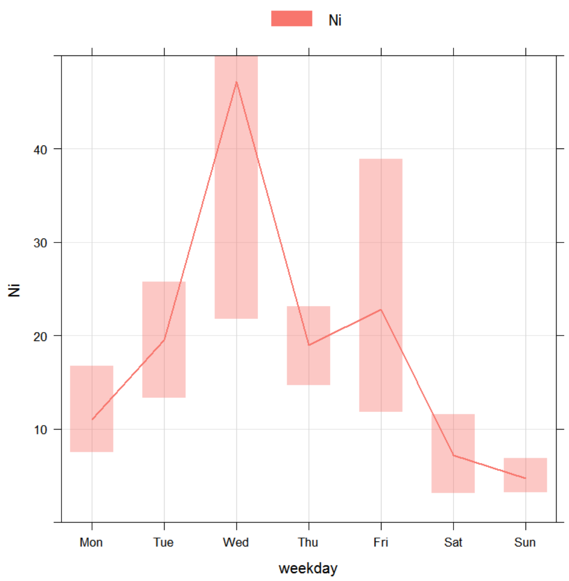


Figure 3b Time series of daily nickel concentrations

The mean nickel concentration over the period is 19.0 ng.m^{-3}, which is very close to the EU annual mean Target Value of 20 ng.m^{-3}.

Figure 4 shows how the nickel concentrations vary across the days of the week: (Plots produced by OpenAir).



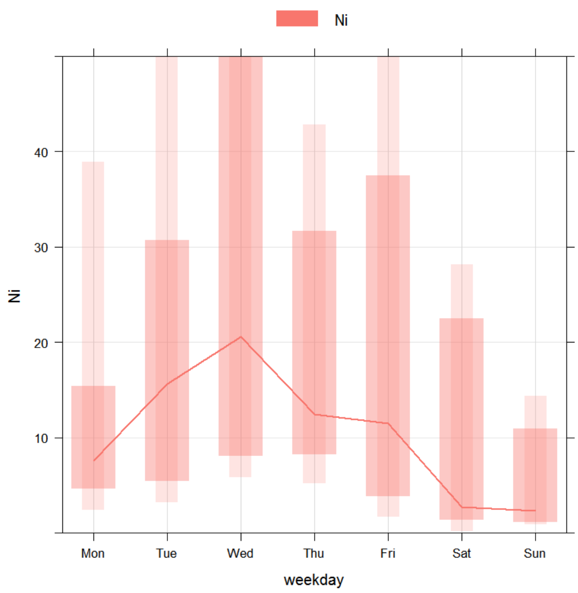
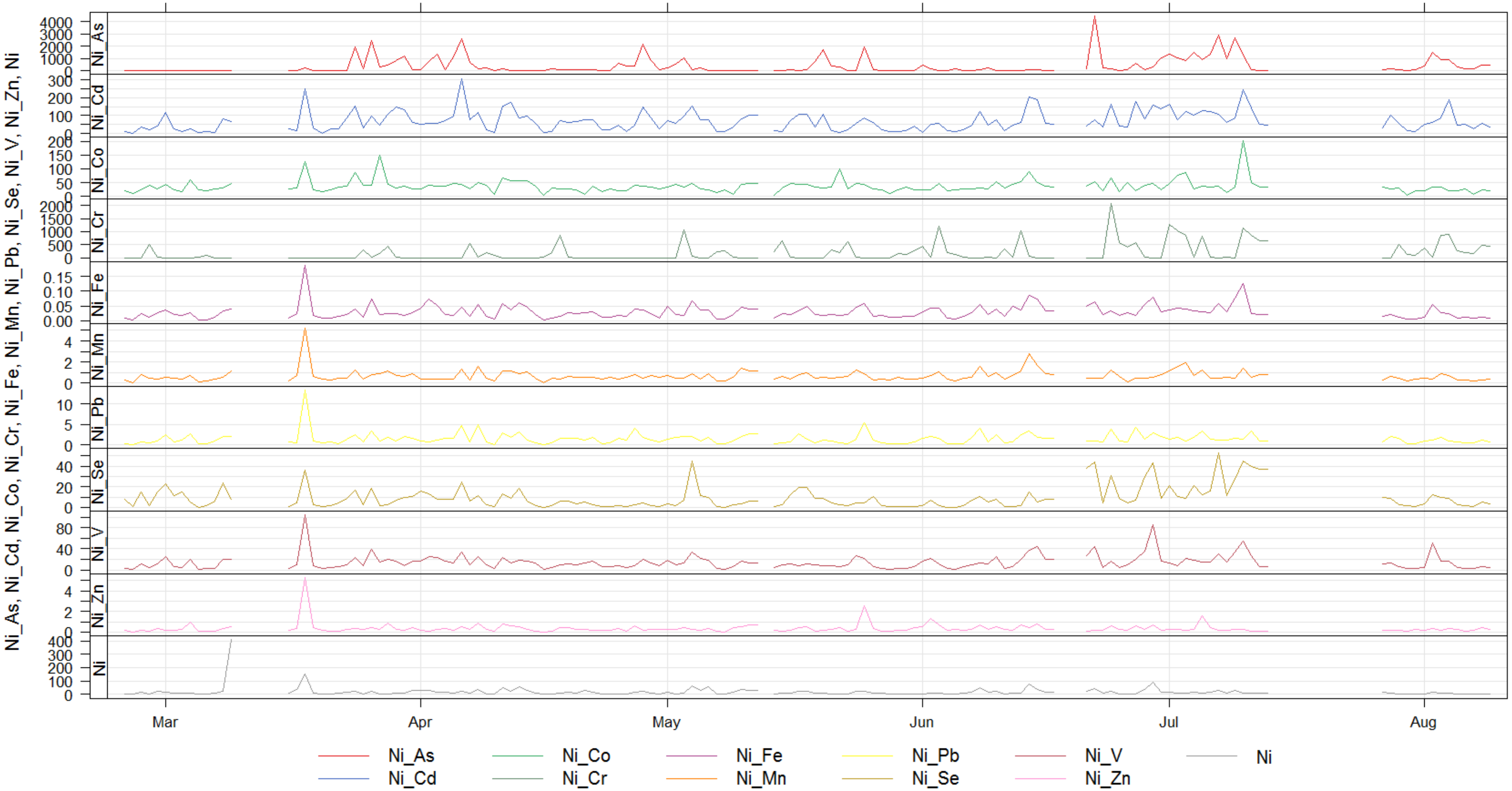


Figure 4 Mean nickel concentration **Median nickel concentrations**

The shaded area on the mean chart is the standard deviation of measurements made on that day. The darker shaded area on the median chart represents data within the 25-75% quartile range while the lighter shaded area represents data within the 5%-95% range.

Mean and median charts for all the metals are presented in Annex 1. These show that all mean metal concentrations are dominated by the high measurements experienced on Wednesday 9th March 2016, however the median concentrations shows there is very little working day dependence and that concentrations are normally lower on Saturday and significantly lower on Sunday, except for cadmium & selenium which has a weaker or no day dependence.

Figure 5 shows the ratio of nickel concentrations to the other metal concentrations, the actual concentration of nickel is plotted as the bottom trace for reference:



Note: strip charts are dimensionless apart from the bottom trace for nickel concentration, which is in ng.m^{-3}

Figure 5 Ratio of nickel concentration to other metal concentrations, nickel concentration plotted as reference

For the very high nickel concentration measured on 9th March (425 ng.m^{-3}) the ratios are relatively unchanged indicating that all metal concentrations rose on this day. For the nickel concentration of 156 ng.m^{-3} on 18th March, most of the metals ratios (except chromium and arsenic) significantly increased indicating that these concentrations did not rise in-line with the increased nickel concentration. This indicates that the emission source responsible for this nickel increase also emits chromium and arsenic. For the high nickel concentration on 29th June (93.6 ng.m^{-3}) all bar one of the ratios show that nickel increased at a greater rate than the other metals, with the exception of chromium, whose ratio was unchanged. The concentration ratios for the raised nickel concentration on 14th June (80.1 ng.m^{-3}) show similar behaviour as to those on the 29th June with chromium being the only metal whose concentration rose in-line with that of nickel.

4. Wind Analysis

Figure 6 shows the wind rose for the monitoring period, with wind data removed for days where no metals measurements were made. There are no onsite or local wind measurements made, so modelled wind speed and direction from the UK-AIR website for the Sheffield Tinsley AURN site have been used. This data is modelled on a 10km x 10km basis so is not fully representative of the Tinsley site.

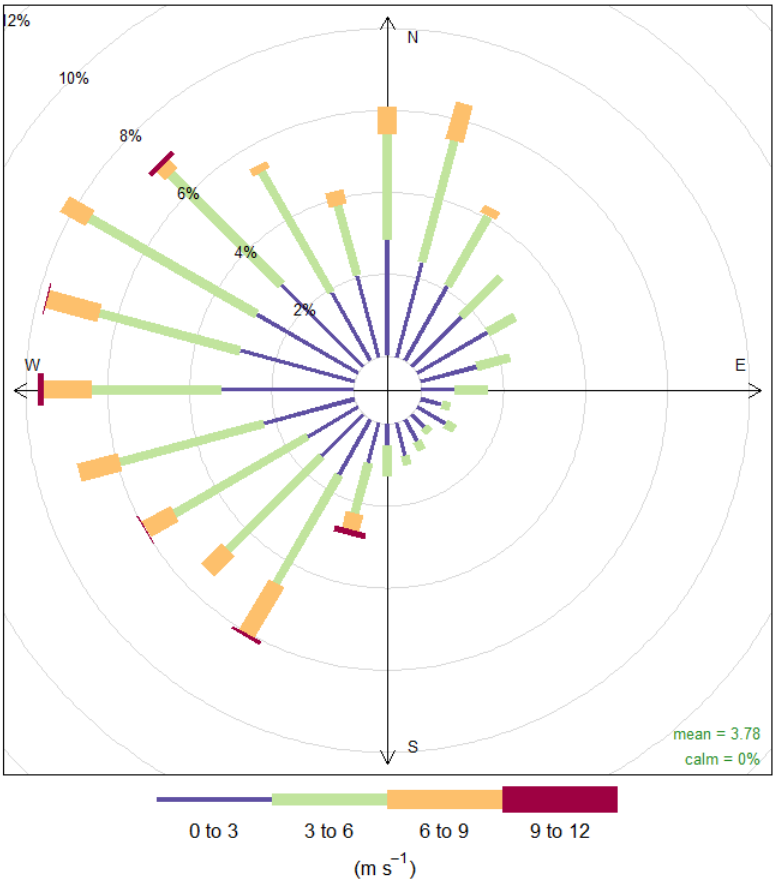
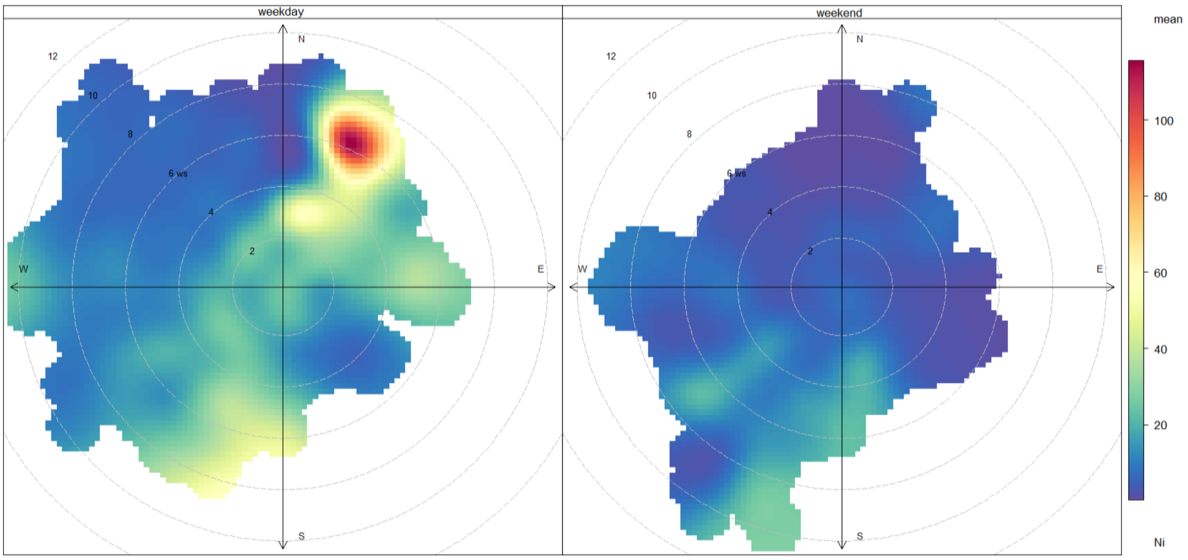


Figure 6 Wind rose for modelled wind speed and direction for the Sheffield Tinsley AURN site

The rose shows that the predominant wind directions are in the sector from NE through W to SW. Low wind speeds occur when the wind is coming from the sector S through SE to E.

5. Pollution roses

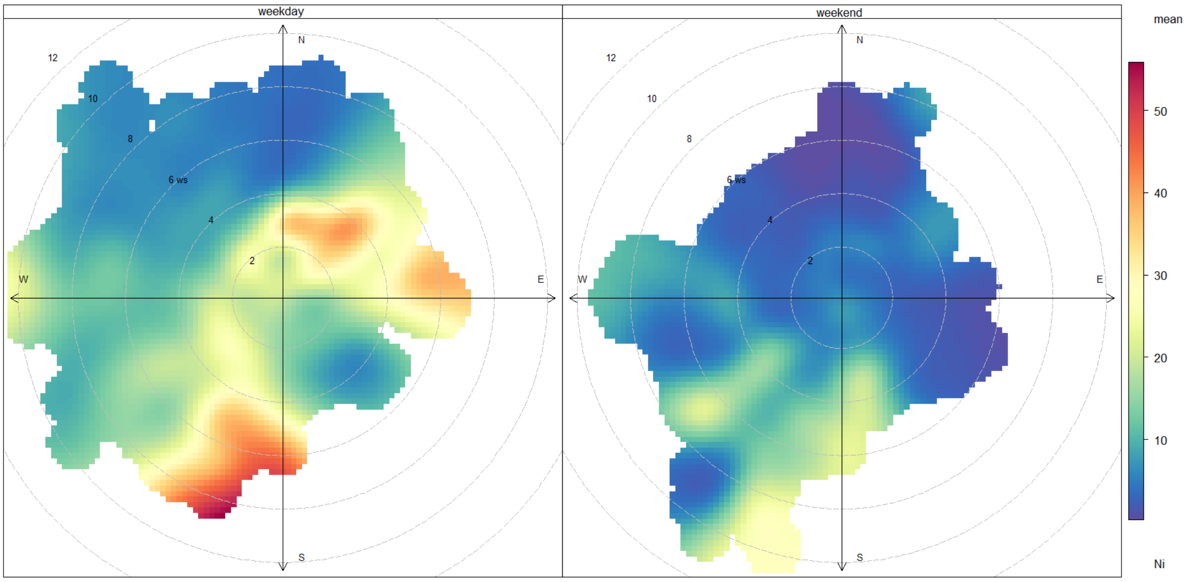
By combining the daily metals concentration data with the hourly wind data (single daily concentration used for each hourly wind data point) pollution roses have been generated using OpenAir, see Figures 7 to 13. The colour represents the measured mean concentration at a specific wind direction and speed, the distance from the centre of the plot corresponds to wind speed, i.e., colours close to the origin are concentrations measured at very low wind speeds whilst colours further from the origin represent concentrations measured at higher wind speeds. The angular position represents the wind direction. The white areas represent wind directions and speeds that did not occur during the measurement period.



Weekday **Weekend**

Figure 7 Nickel – all data

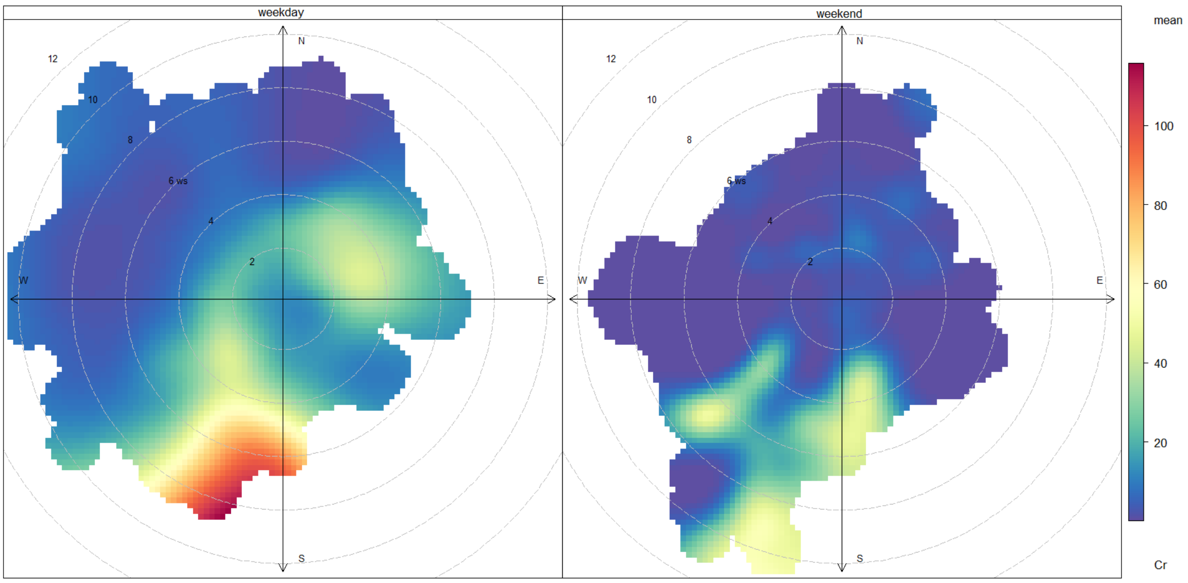
The concentrations of all the metals measured on 9th March are elevated and this high level dominates all of the plots, so has been removed for the remaining pollution roses.



Weekday **Weekend**

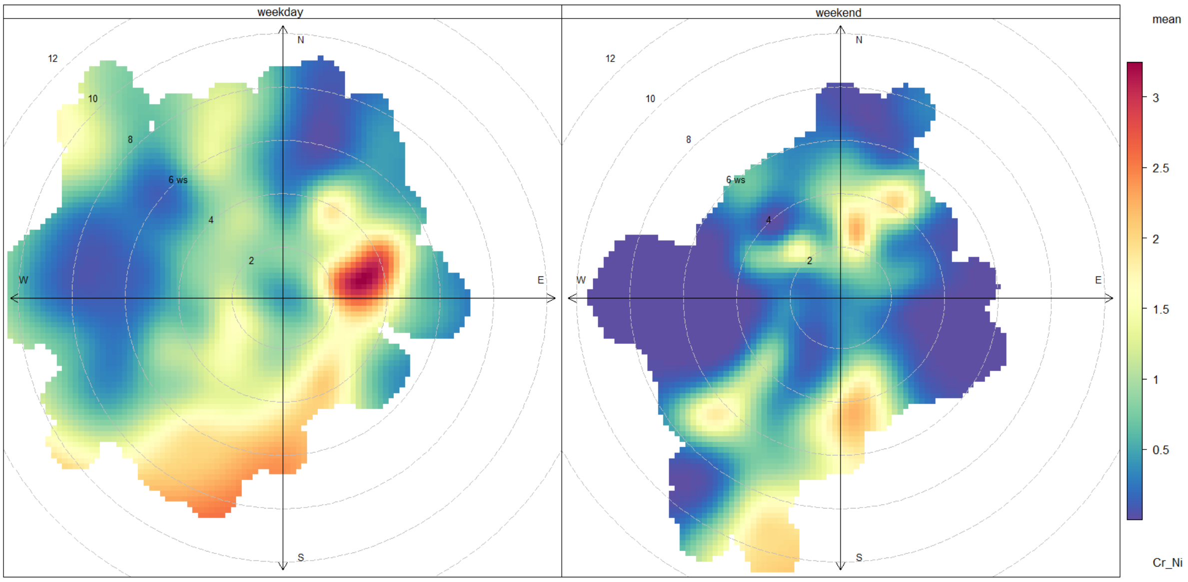
Figure 8 Nickel with 9th March removed

The following Figures show the mean metal concentration and the ratio of the metal versus that of nickel:



Weekday **Weekend**

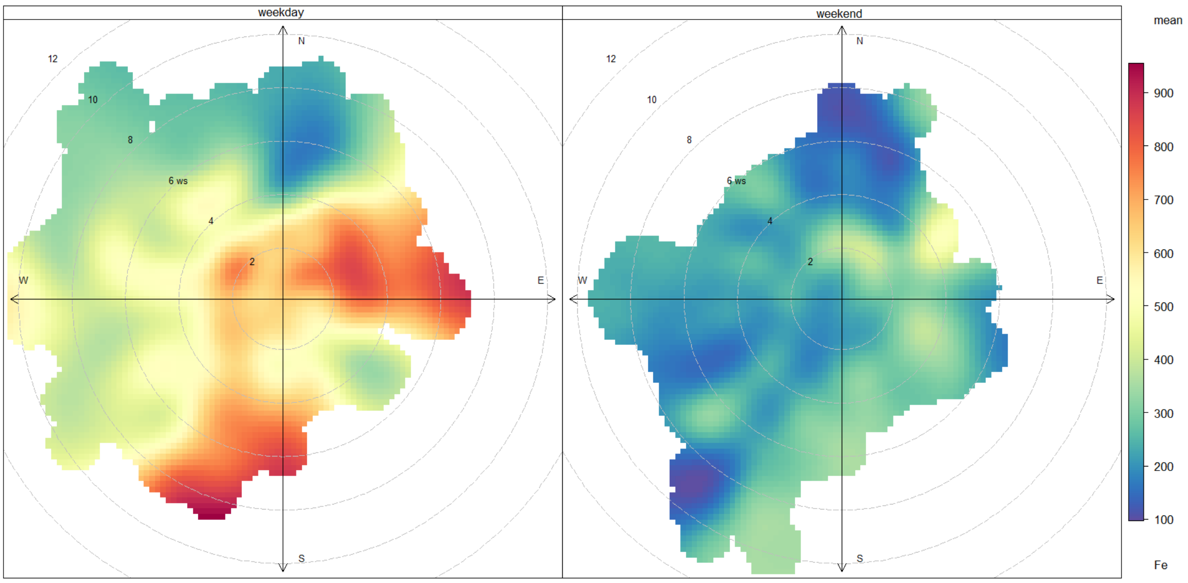
Figure 9a Chromium, ng.m^{-3}



Weekday **Weekend**

Figure 9b Chromium / Nickel

It can be seen that the chromium concentration pollution rose is similar in distribution to that of nickel, with both showing a significant source to the south to southwest of the monitoring site. Both show reduced concentrations at the weekend, but still with significant concentrations measured when the wind is coming from the southwest quadrant. When the wind comes from the southwest the chromium concentration rises more quickly than the nickel concentration.



Weekday **Weekend**

Figure 10a **Iron, ng.m^{-3}**

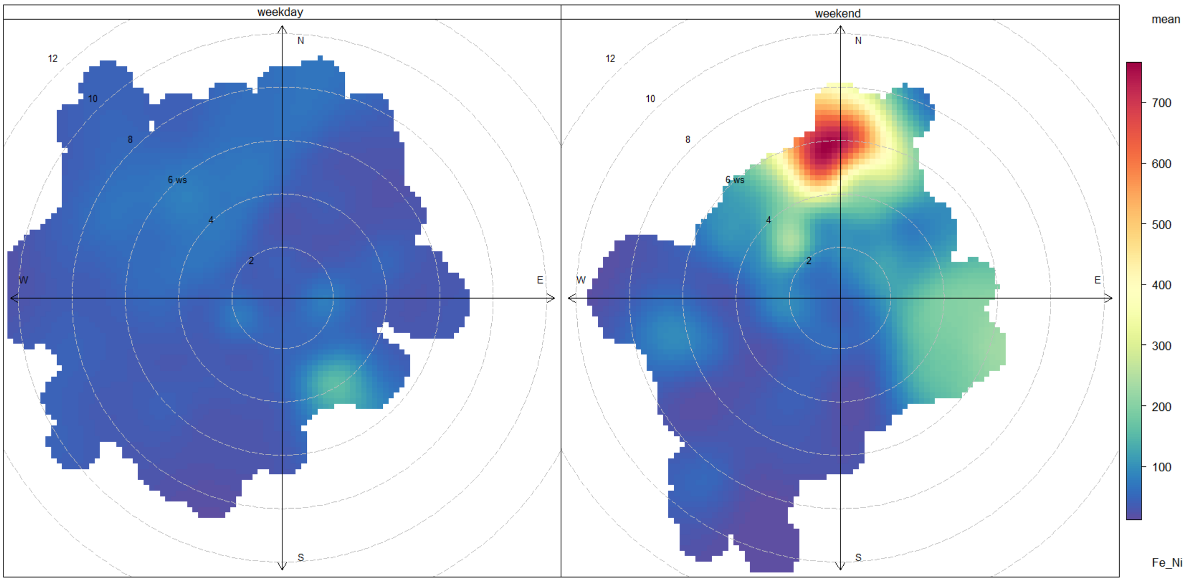


Figure 10b **Weekday Iron / Nickel** **Weekend**

The weekday iron concentrations show a similar distribution to the nickel and chromium concentrations, however, at the weekends the highest concentrations appear to come from the north. When the wind is from the southwest the ratio between iron and nickel is roughly constant.

Most of the metals show a similar behaviour to iron indicating a similar emission source. Selenium, vanadium and arsenic seem to show individual distributions in their pollution roses, which are shown in Figures 11 to 13.

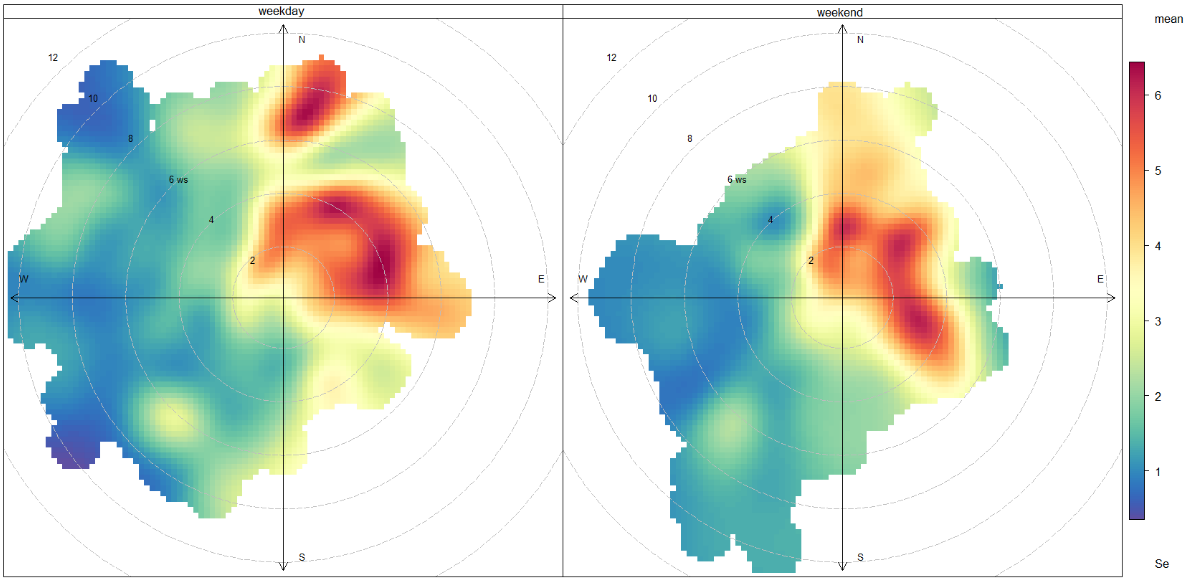


Figure 11a **Weekday Selenium, ng.m^{-3}** **Weekend**

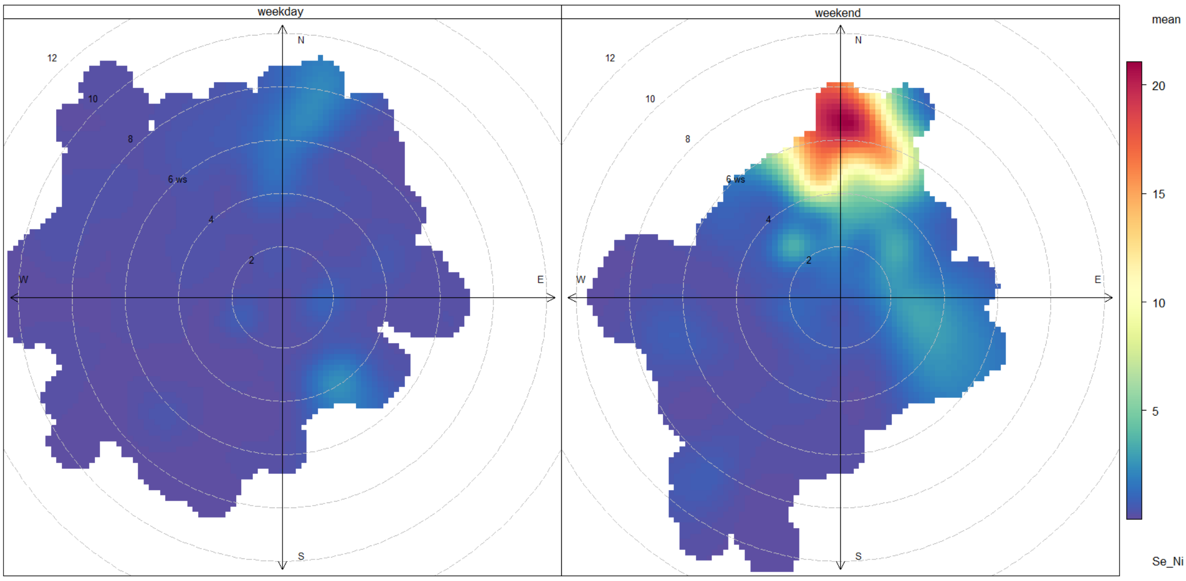


Figure 11b **Weekday Selenium / Nickel** **Weekend**

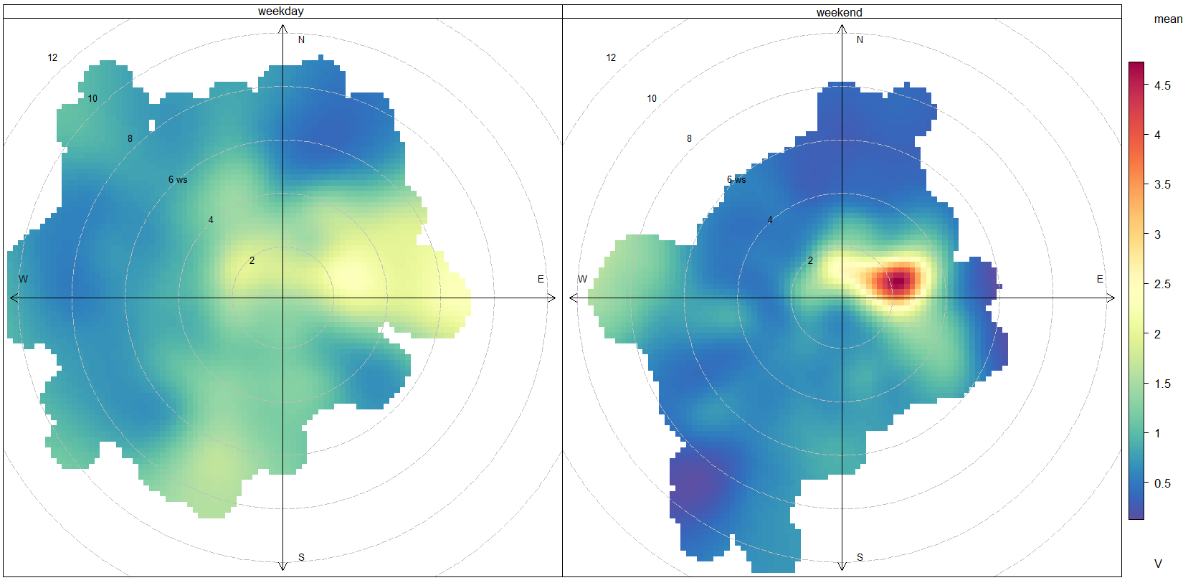


Figure 12a **Weekday Vanadium, ng.m^{-3}** **Weekend**

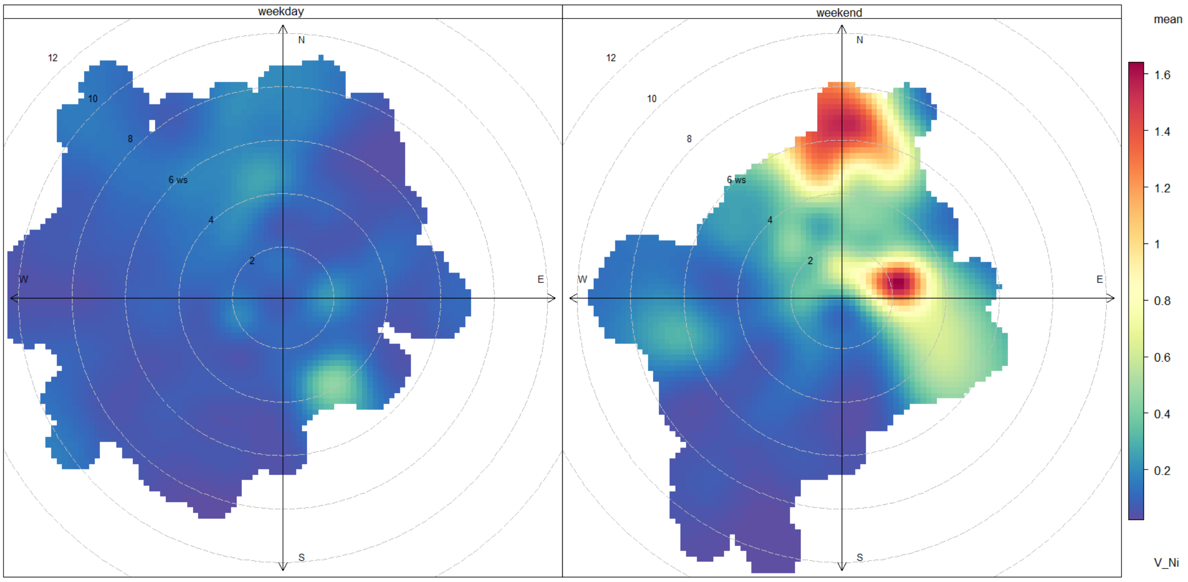
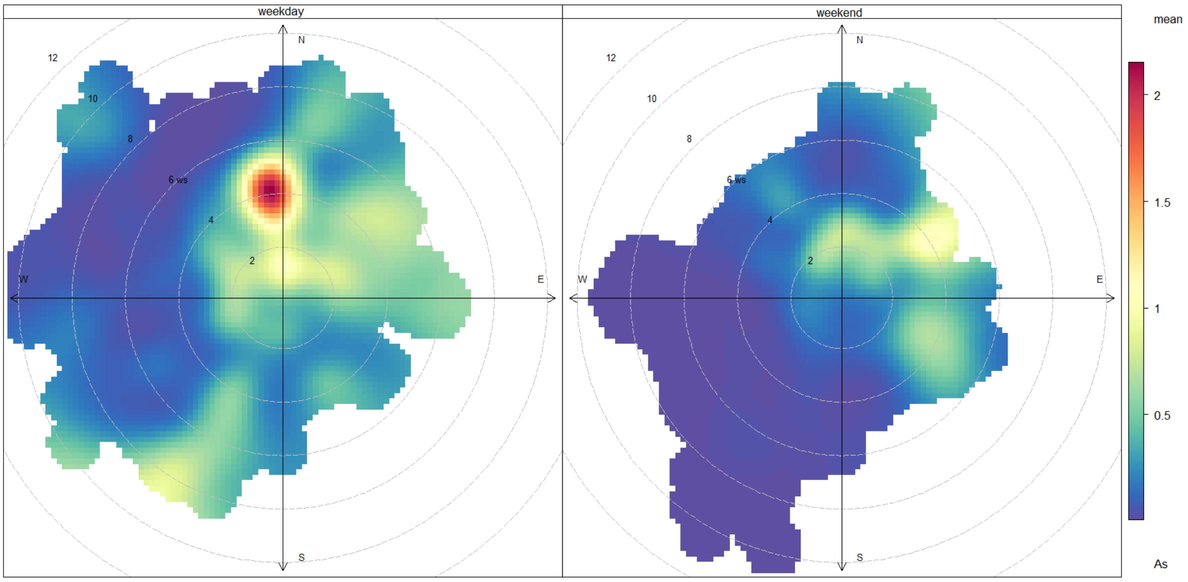
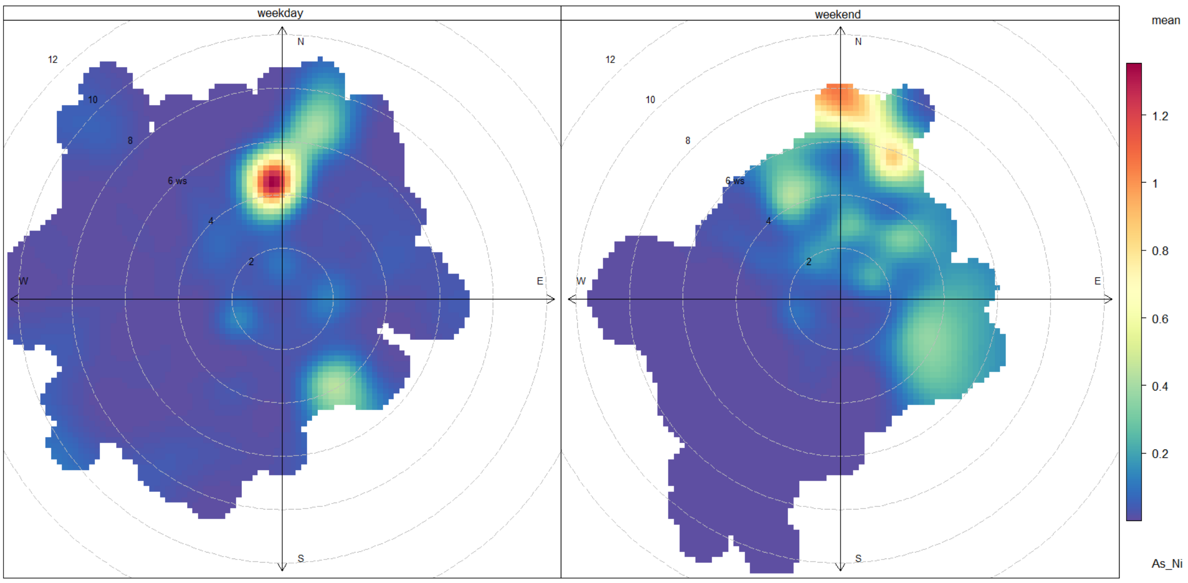


Figure 12b **Weekday Vanadium / Nickel** **Weekend**



Weekday **Weekend**

Figure 13a **Arsenic, ng.m^{-3}**



Weekday **Weekend**

Figure 13b **Arsenic / Nickel**

Pollution roses for all of the individual metals are presented in in Annex 2.

6. Local Emission Sources

There are numerous metals processing emission sources surrounding the Tinsley monitoring station as shown in Figure 14.

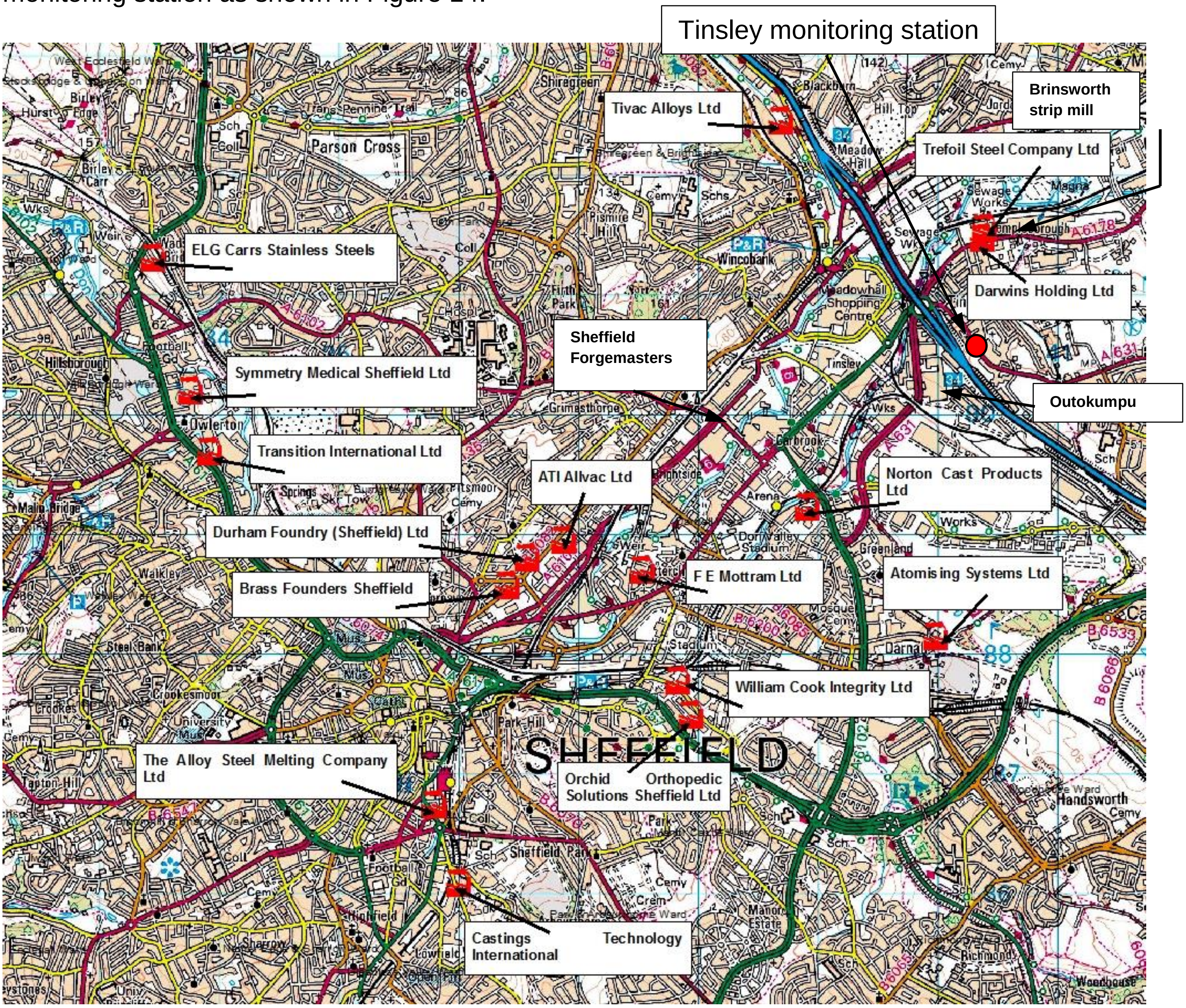


Figure 14 Local metals emission processes surrounding the Tinsley monitoring site

The following information describes the industrial metals sources close to the Tinsley monitoring site and was supplied by Sheffield Council's Environmental Protection Department and the Environment Agency.

7. Part B 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/shotblasting 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 600kg and 920kg. The furnaces vent internally to the foundry so emissions are fugitive. They have shotblasting and welding benches that vent internally but one arc air unit vents externally and is monitored annually for total particulates only.

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. These are monitored annually for total particulate matter only.

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.

8. Part A processes regulated by the Environment Agency

Sheffield Forgemasters International Limited: Steel scrap, other raw materials and alloys are melted in a 90 tonne (up to 100 tonne charge weight) Electric Arc Furnace

(EAF). 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 (VAD), a Vacuum Oxygen Decarburising unit (VOD) and depending on the process route being used, a Ladle Furnace (LF). 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 (EAF), 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 (AOD) for reducing the carbon content of the liquid steel and, depending on the process route being used, to a ladle arc furnace (LAF) or to an argon rinse station. Lime is added to the EAF and AOD 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 the EAF, AOD and LAF to achieve the correct steel analysis to meet specifications.

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. The Mill 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 copper shot using an electric arc furnace and the production of ferro boron, chrome boron and nickel boron in three smaller electric arc furnaces.

Some of these companies have supplied feed stock information for March 2016. Most of the breakdowns only gave the nickel content, however, three provided the chromium content as well and these are shown in Tables 1 & 2.

Company	Nickel, tonnes	Direction from monitoring site to emission source, degrees	Emissions Regulation, Part
Outokumpu	1636.66	160 to 220	A
Brinsworth Strip Mill	204.69	30 to 60	A
Sheffield Forgemasters	23.33	230 to 260	A
Atomiser Systems Ltd	5.46	200 to 220	B
Norton Cast Products	1.69	210 to 230	B

Table 1 Nickel feedstock used by surrounding industries in March 2016

Company	Chromium tonnes	Nickel tonnes	Chromium / nickel ratio	Direction from monitoring site to emission source, degrees
Outokumpu	3479.75	1636.66	2.1	160 to 220
Atomiser Systems Ltd	17.43	5.46	3.2	200 to 220
Norton Cast Products	0.83	1.69	0.5	210 to 230

Table 2 Nickel and chromium feedstock used by surrounding industries in March 2016

The use of chromium and nickel feedstocks is dominated by Outokumpu, which is consistent with the raised nickel and chromium concentrations measured when the wind is from the south and south west. Outokumpu is also the nearest industrial process to the monitoring site in the southwest quadrant, so its emissions are likely to be dominant.

9. Conclusions

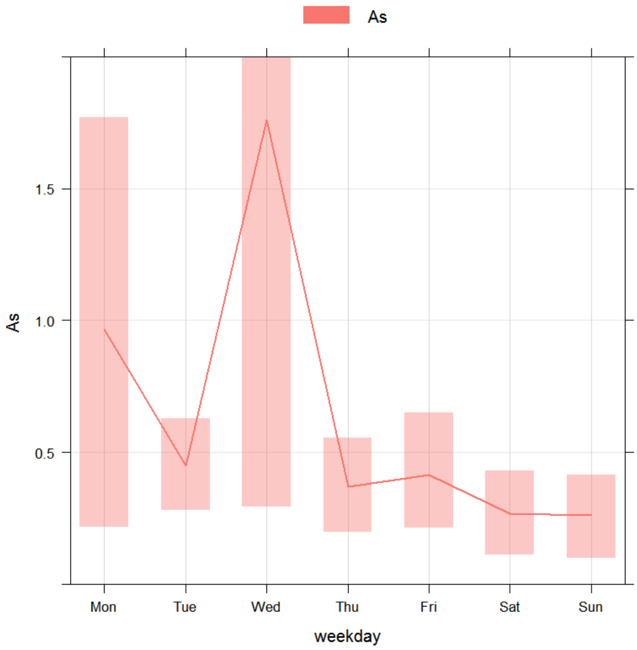
Moving from weekly to higher time resolution (daily) monitoring has demonstrated additional insight about the sources of Ni and other heavy metals impacting measurements at Tinsley.

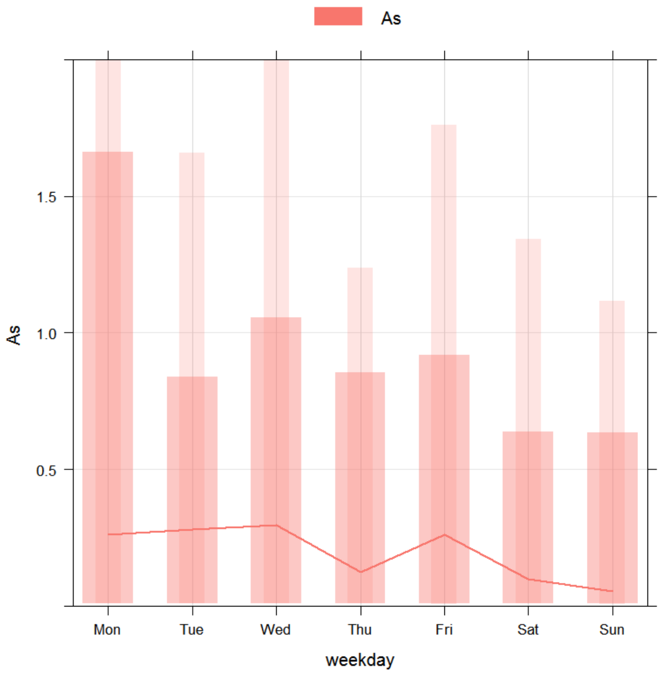
Further monitoring with an even higher time resolution (hourly) may provide even further insight into dominant sources. However, real-time wind monitoring would have to be installed to provide better quality wind data. The analysis in this report used the modelled wind speed and direction for Tinsley provided by UK-AIR. Wind measured on site will be much more representative of the local conditions than the forecast model, as this provides data on a 10km x 10km square. This would be essential to interpreting hourly data as well as aiding future dispersion modelling.

Conclusions of this work should be considered alongside localised dispersion modelling representing the known emissions in the vicinity of the monitoring station. Consideration should also be given to the likely emissions sources from this work to establish additional information as inputs to the model.

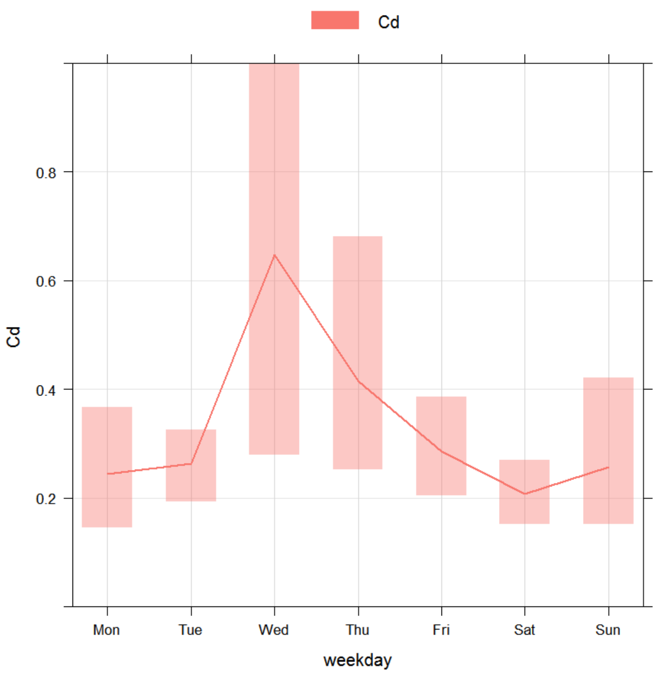
Annex 1 - Mean and Median Metals Concentrations by Day of the Week

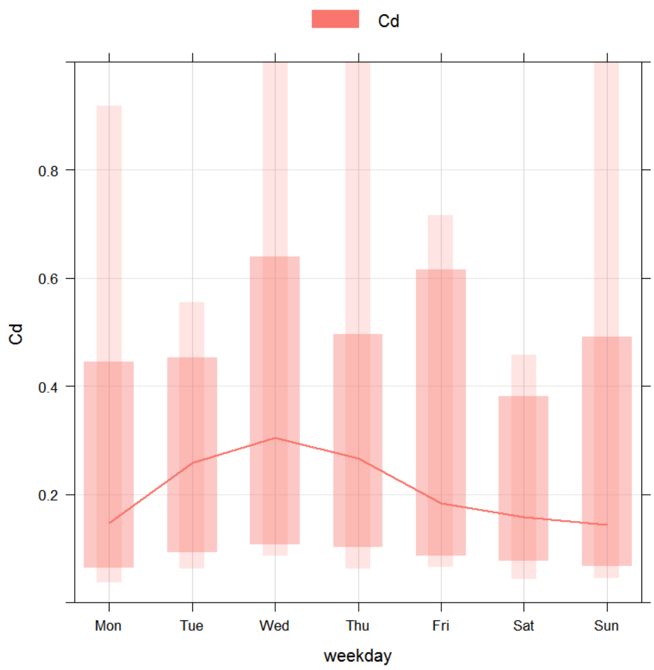
For all charts the Y-axis is in ng.m^{-3}



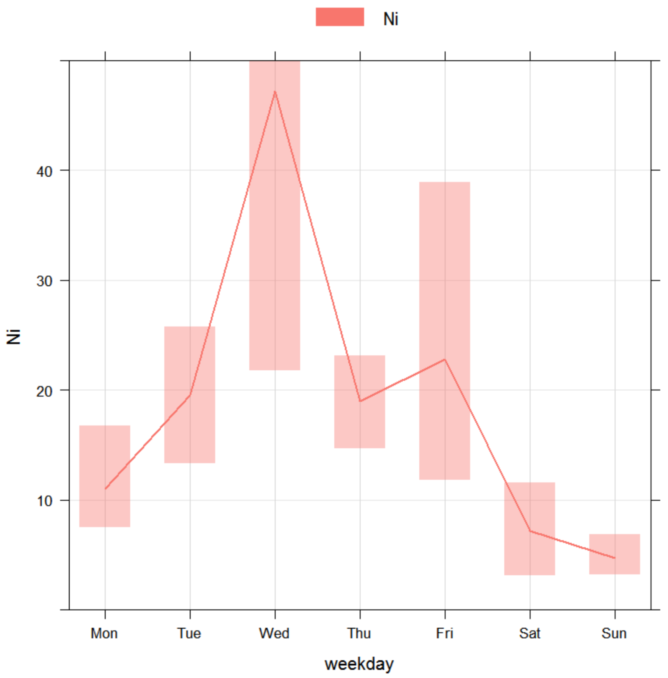


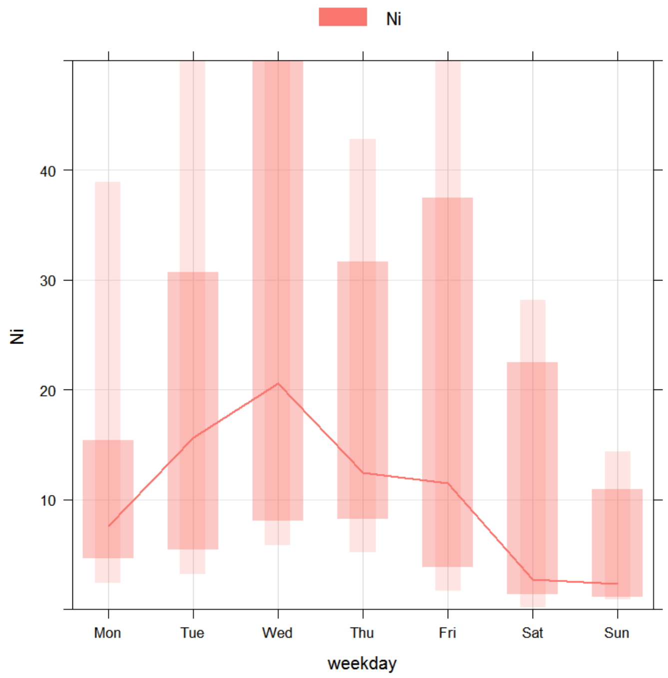
Arsenic



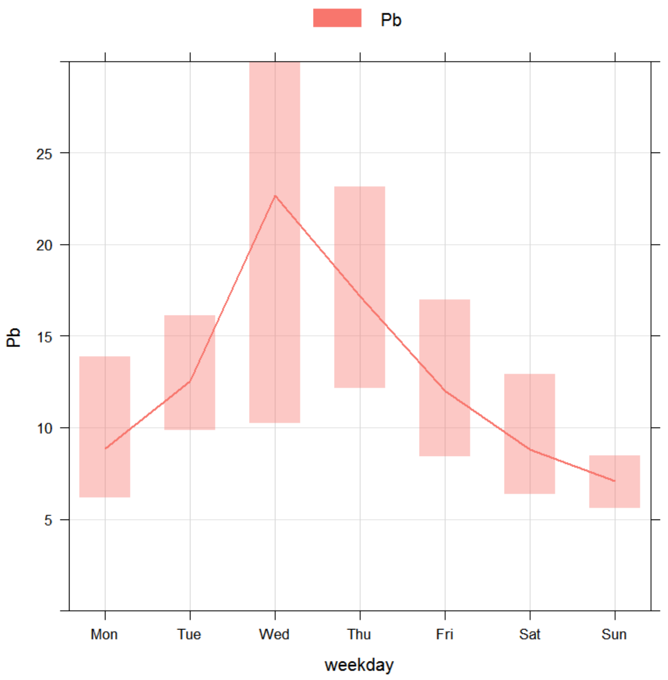


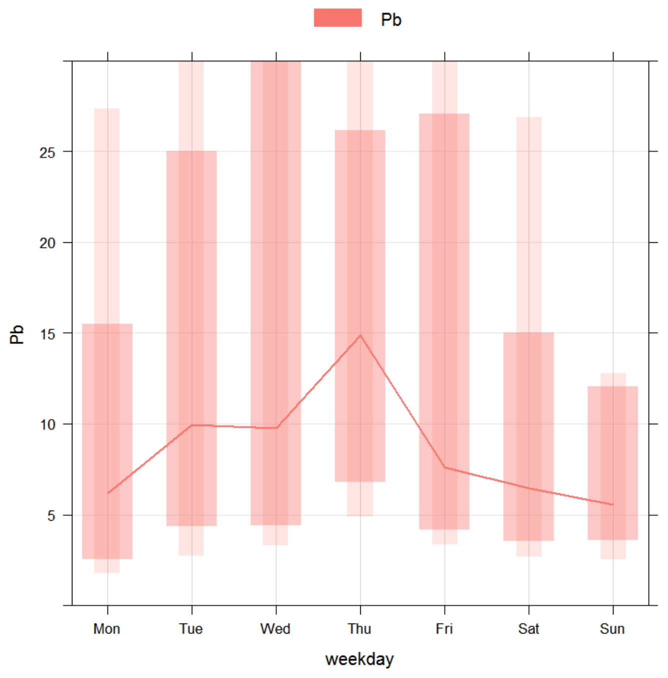
Cadmium


Ni
40
30
20
10
Ni
Mon
Tue
Wed
Thu
Fri
Sat
Sun
weekday

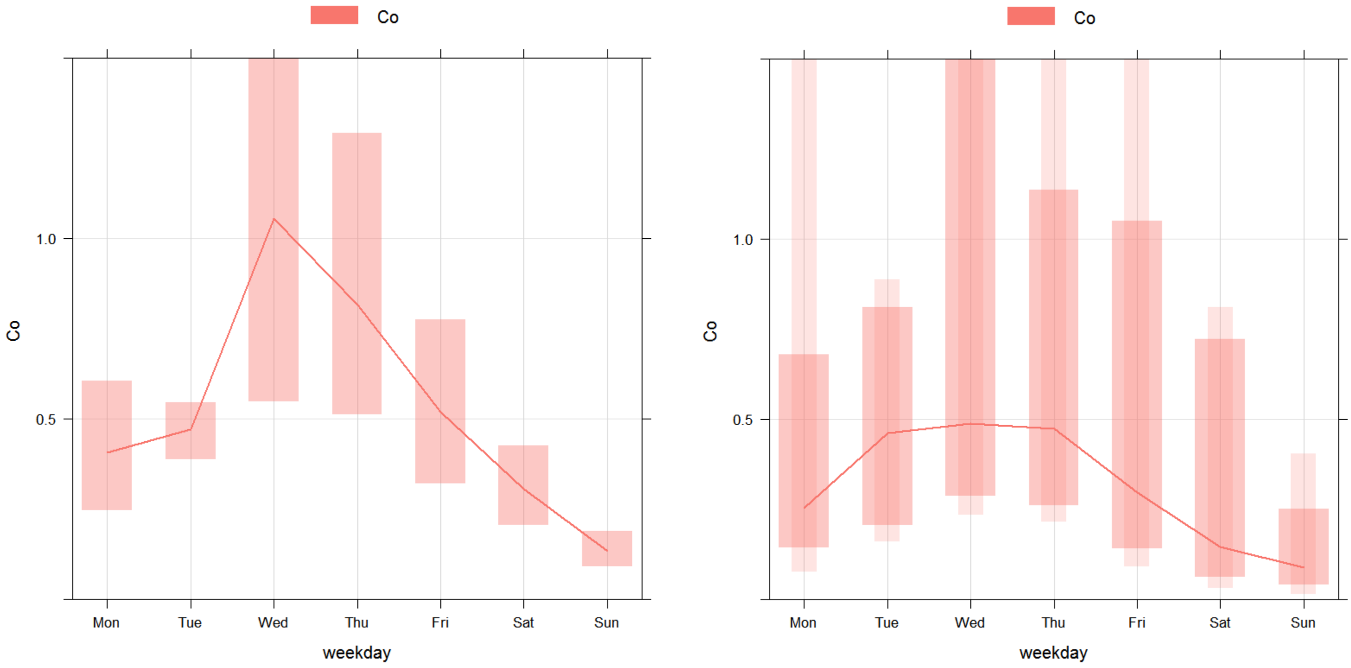

Ni
40
30
20
10
Ni
Mon
Tue
Wed
Thu
Fri
Sat
Sun
weekday

Nickel

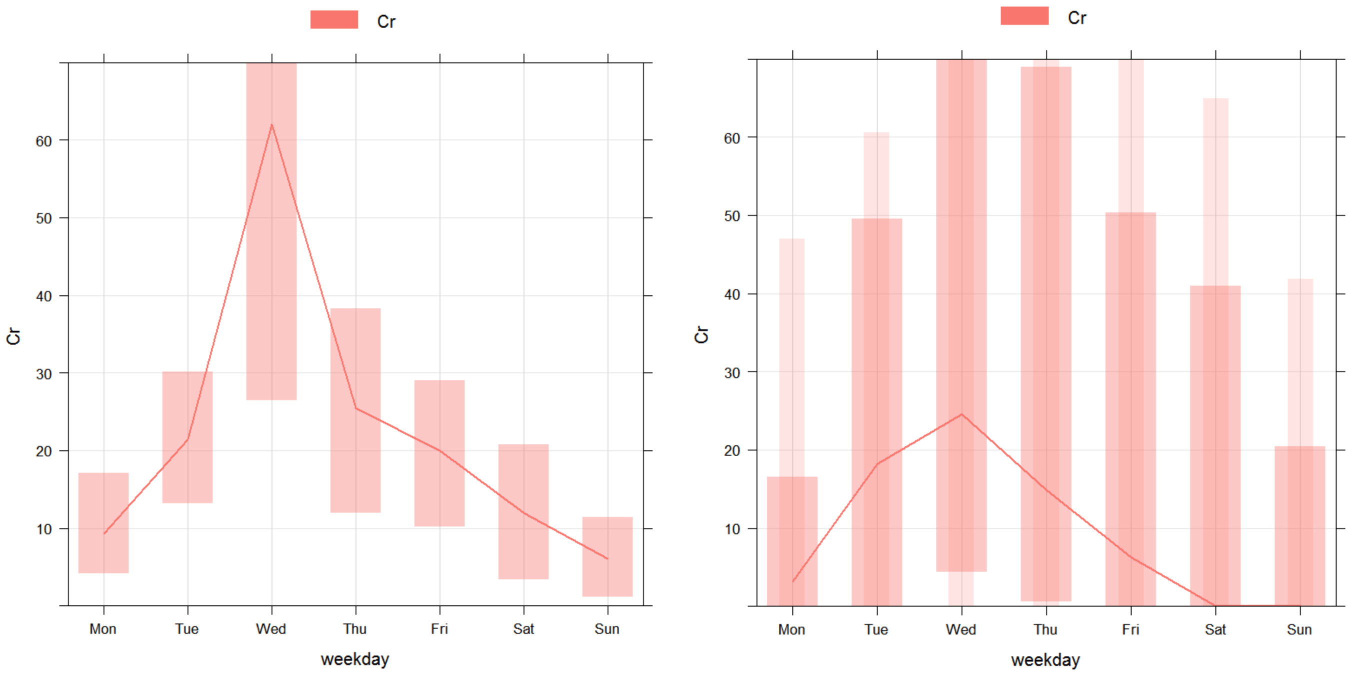

Pb
25
20
15
10
5
Pb
Mon
Tue
Wed
Thu
Fri
Sat
Sun
weekday


Pb
25
20
15
10
5
Pb
Mon
Tue
Wed
Thu
Fri
Sat
Sun
weekday

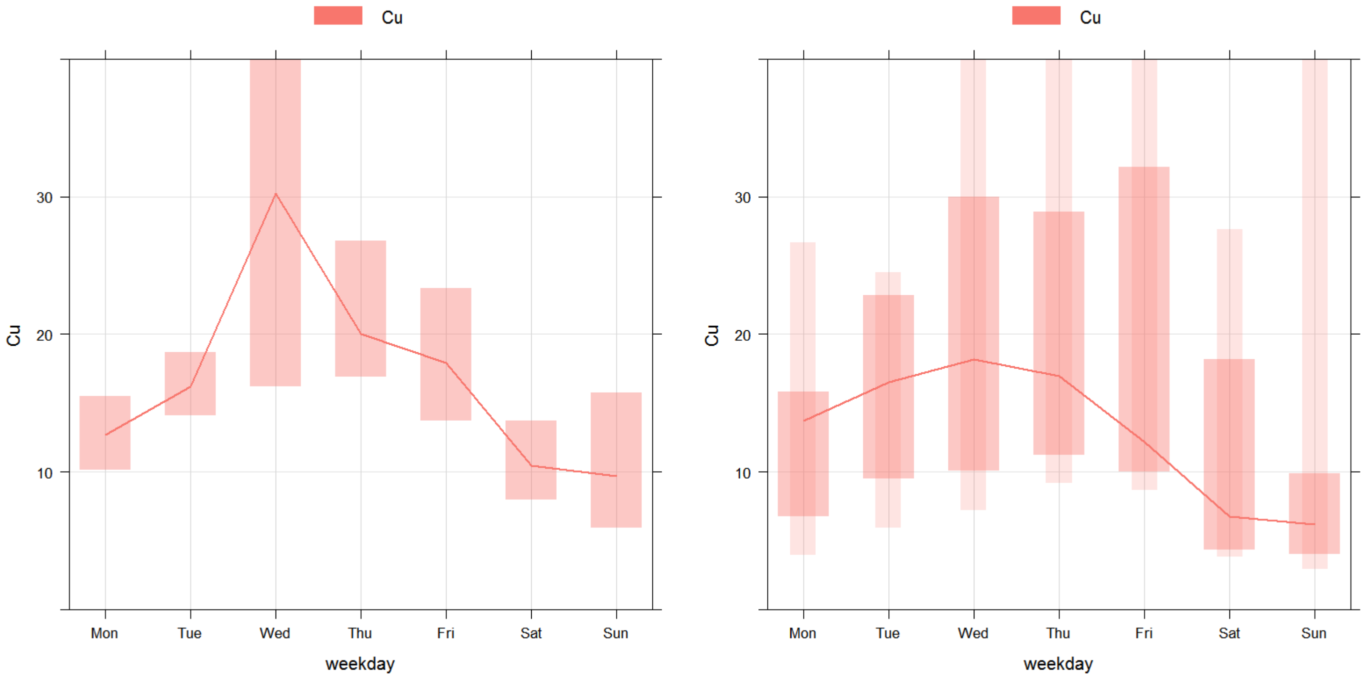
Lead



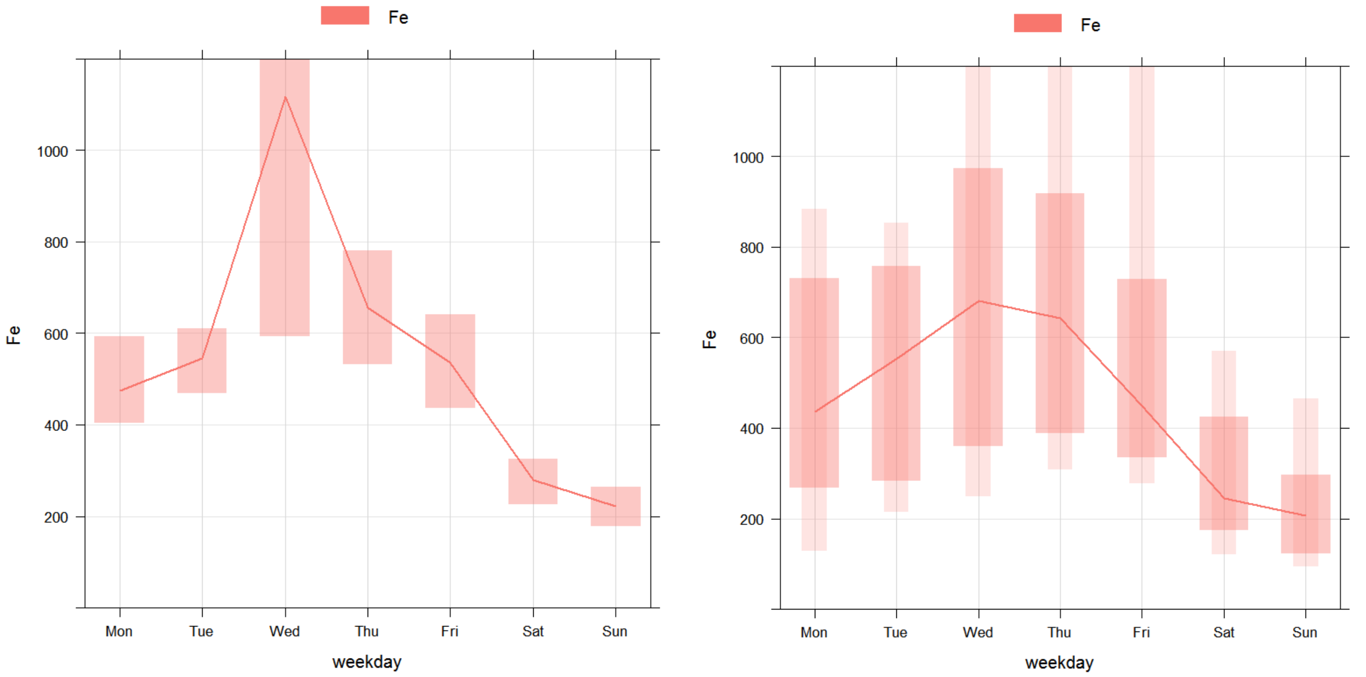
Cobalt



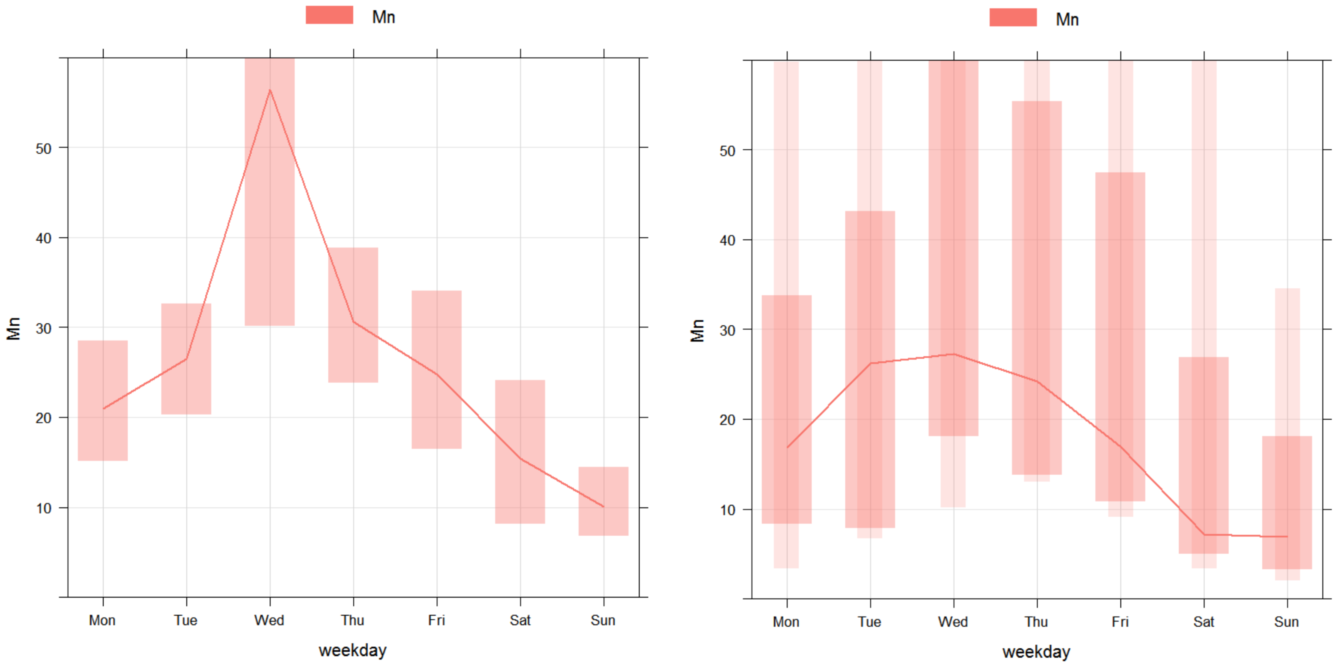
Chromium


Cu
30
20
10
Cu
Mon
Tue
Wed
Thu
Fri
Sat
Sun
weekday
Cu
30
20
10
Cu
Mon
Tue
Wed
Thu
Fri
Sat
Sun
weekday

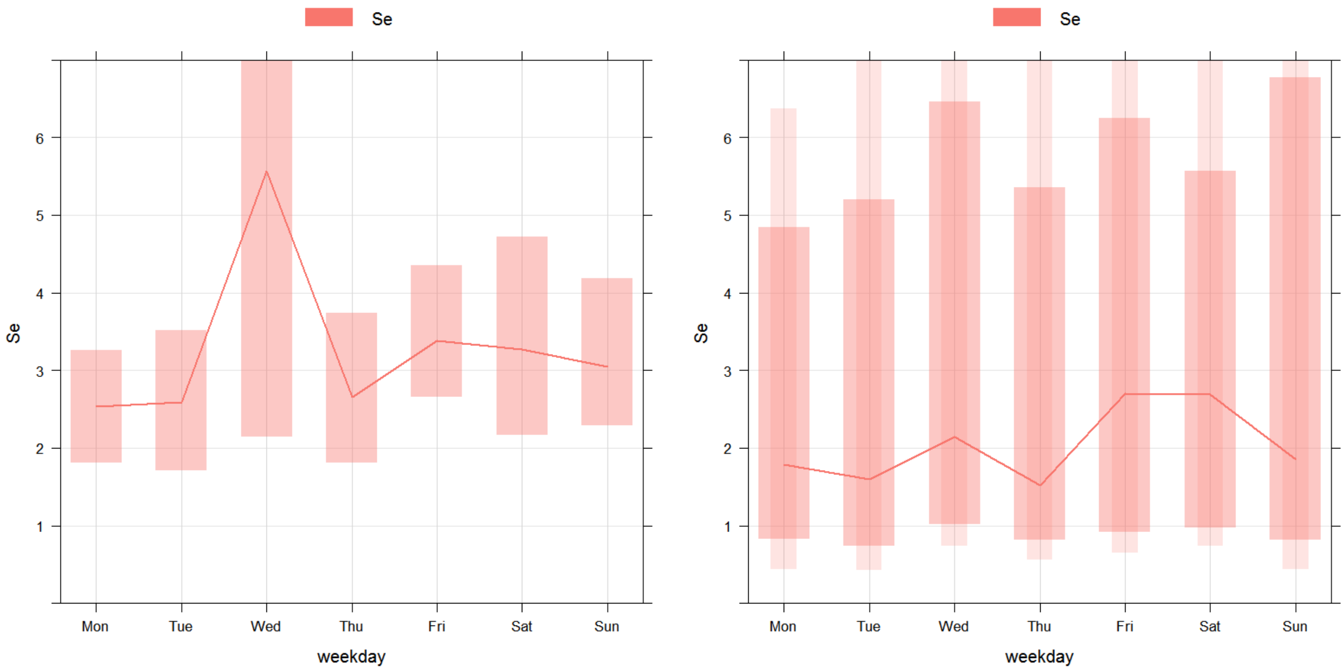
Copper


Fe
1000
800
600
400
200
Fe
Mon
Tue
Wed
Thu
Fri
Sat
Sun
weekday
Fe
1000
800
600
400
200
Fe
Mon
Tue
Wed
Thu
Fri
Sat
Sun
weekday

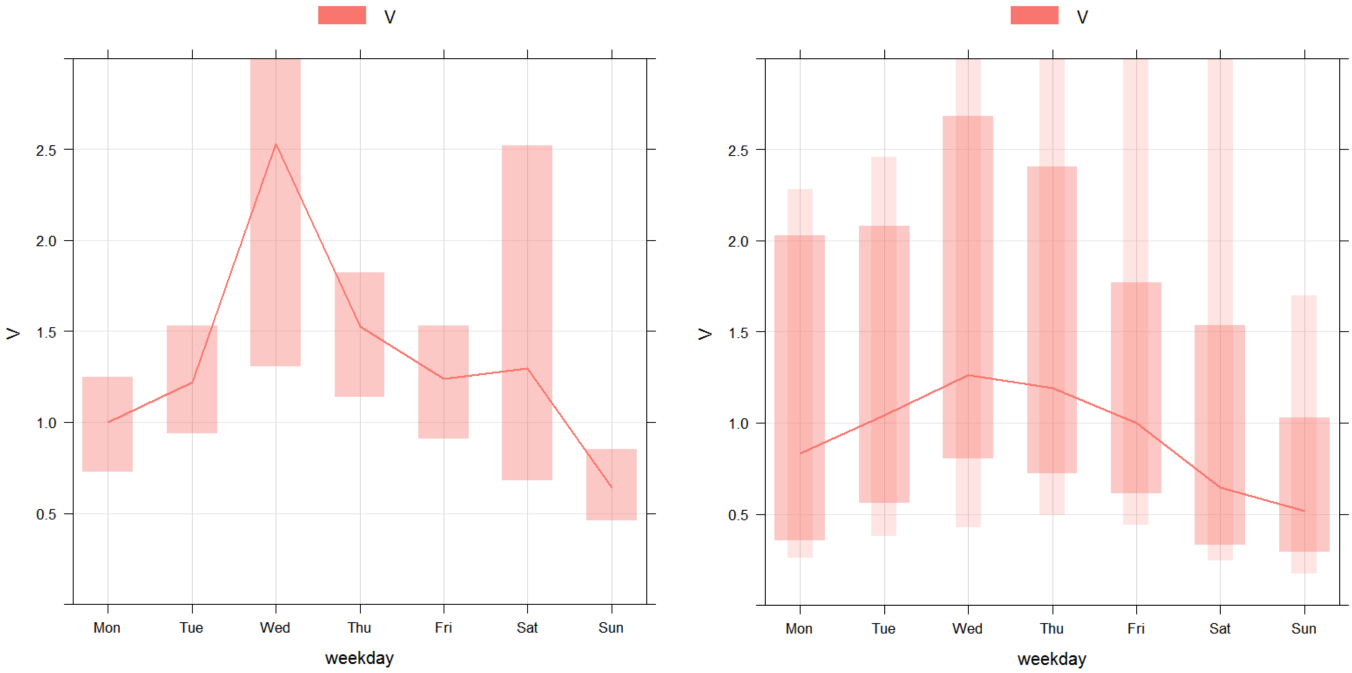
Iron



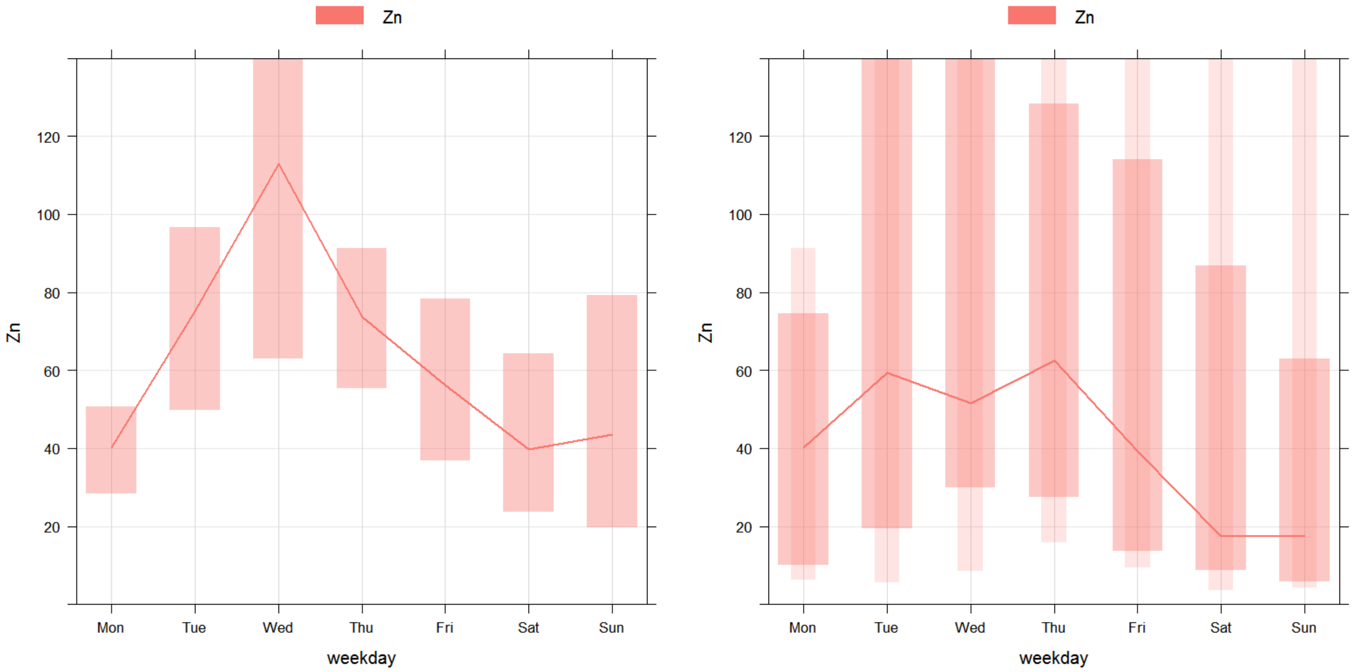
Manganese



Selenium



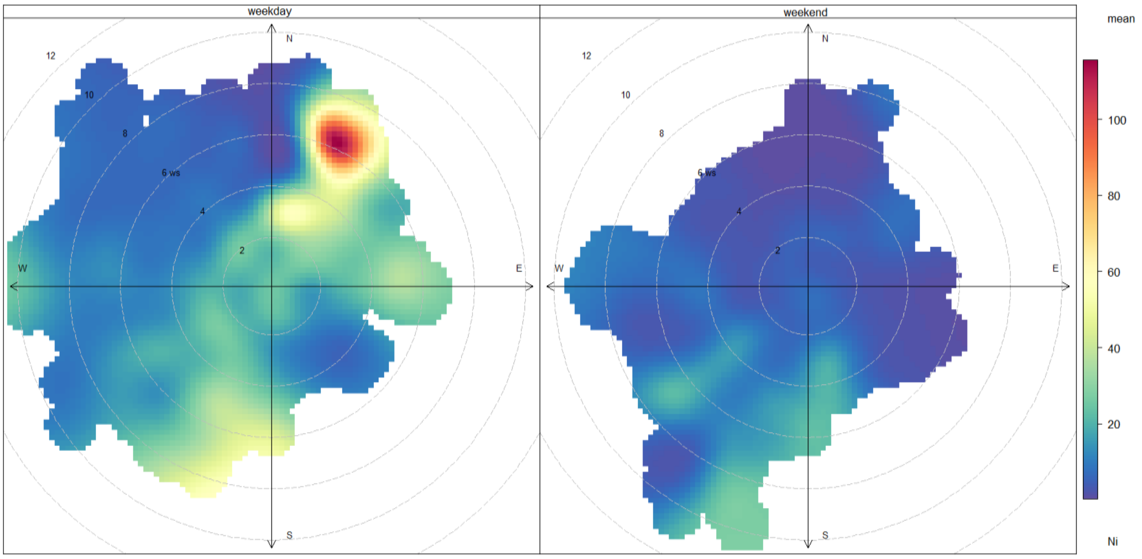
Vanadium



Zinc

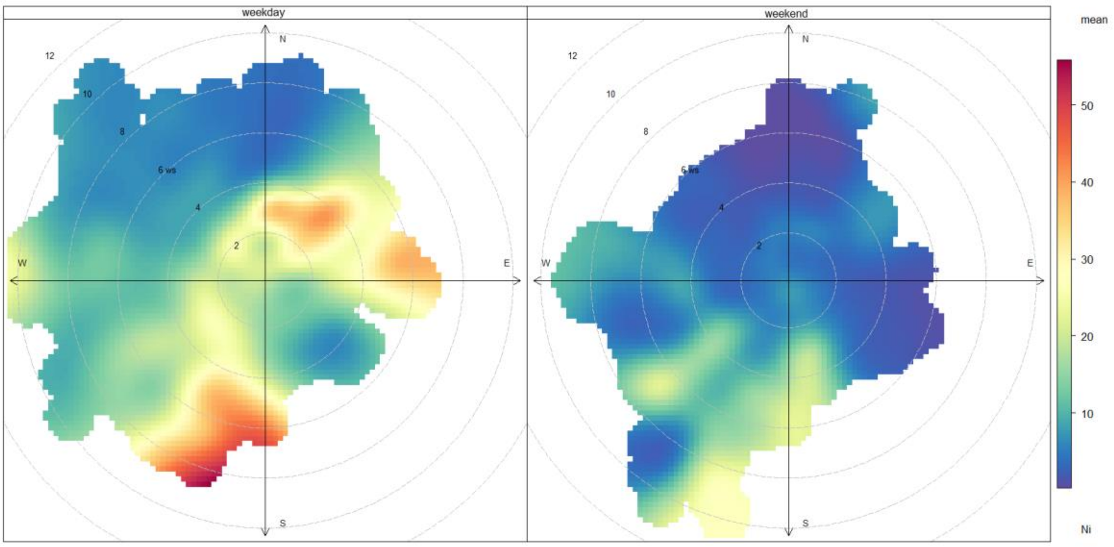
Annex 2 - Pollution Roses for Metal Concentrations and Ratio of Nickel Concentration to other Metals Concentrations

Colour scale units are in $ng.m^{-3}$ for the concentration plots and dimensionless for the ratio plots.



Weekday **Weekend**

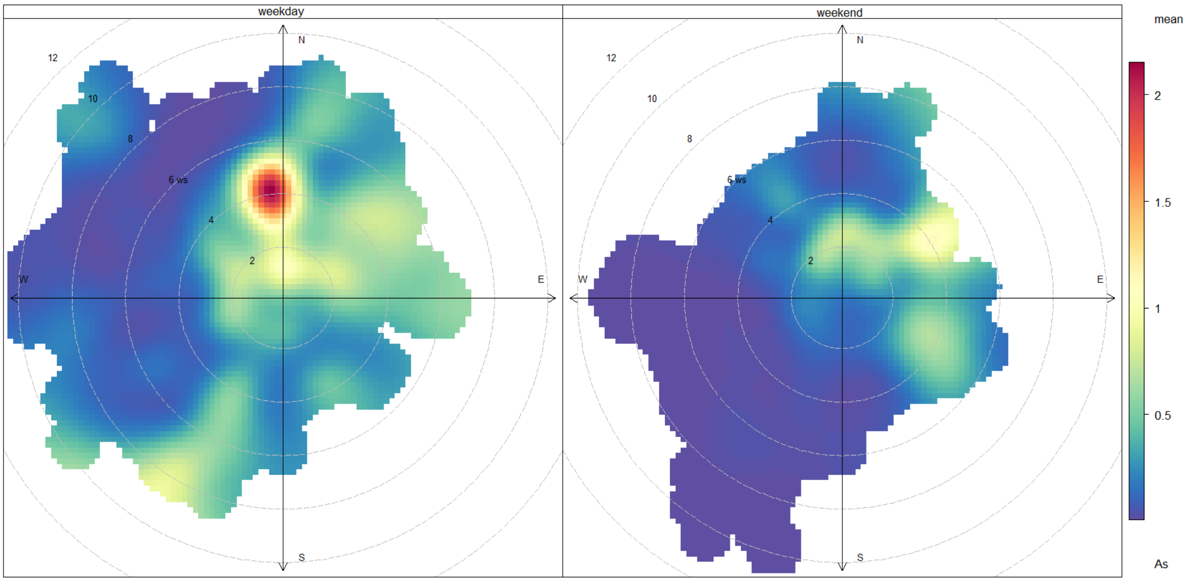
Nickel – all data



Weekday **Weekend**

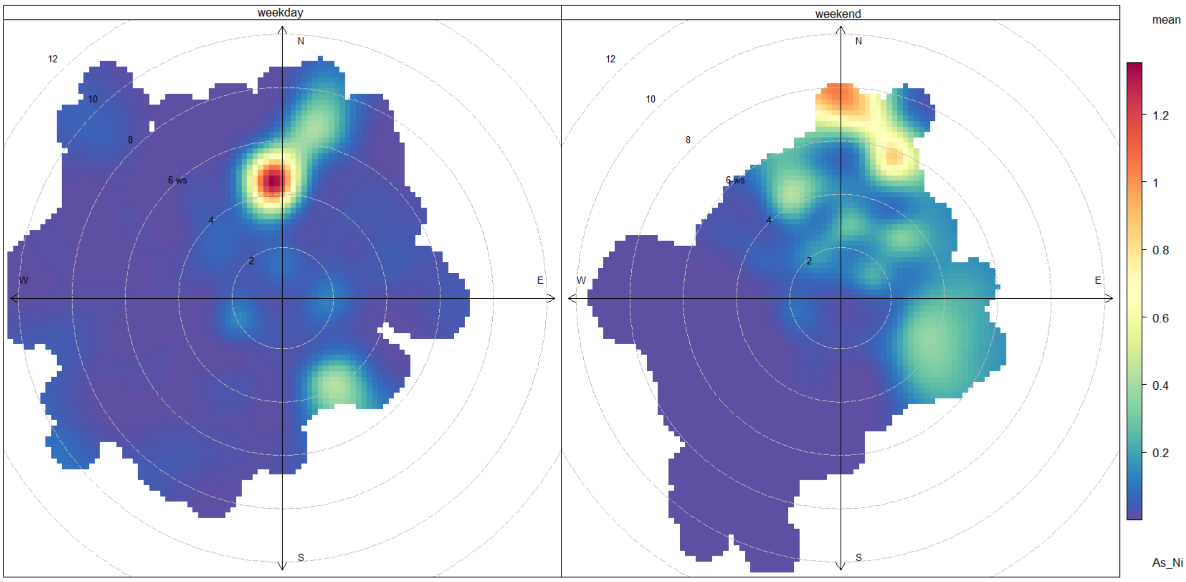
Nickel with 9th March removed

For all subsequent plots the concentrations on the 9th of March have been removed as all the metal concentrations are very high on this day.



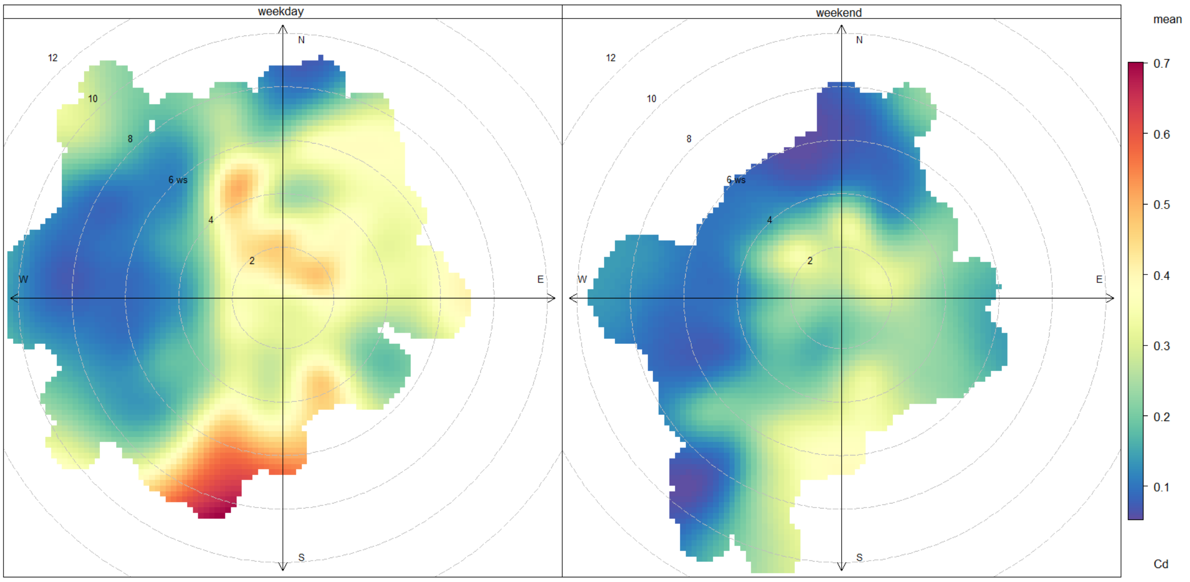
Weekday **Weekend**

Arsenic, ng.m^{-3}

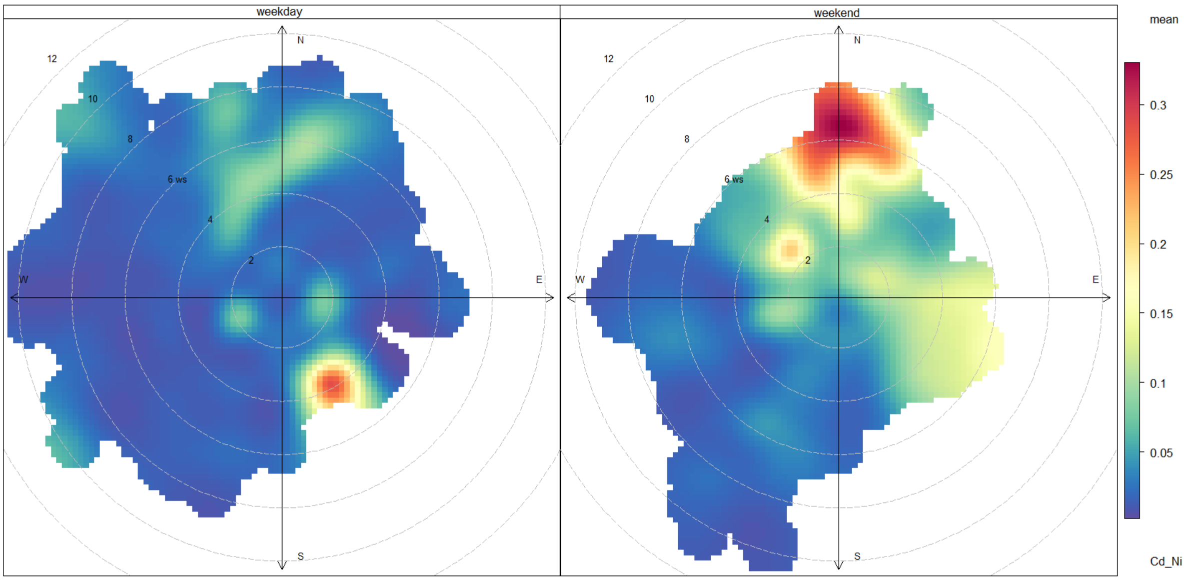


Weekday **Weekend**

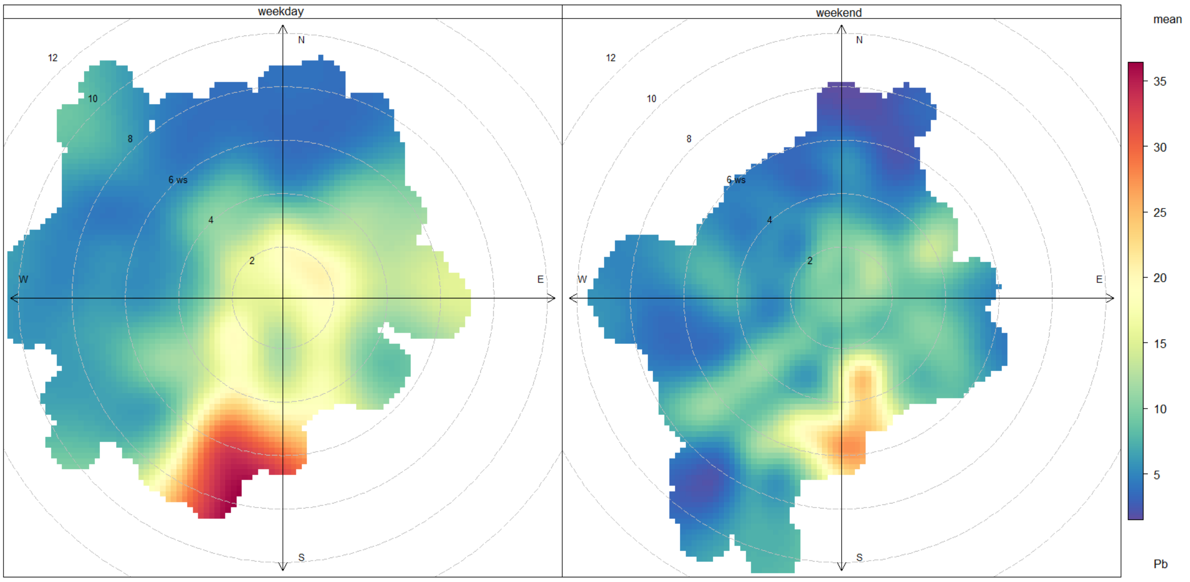
Arsenic / Nickel



Weekday **Weekend**
Cadmium, ng.m^{-3}

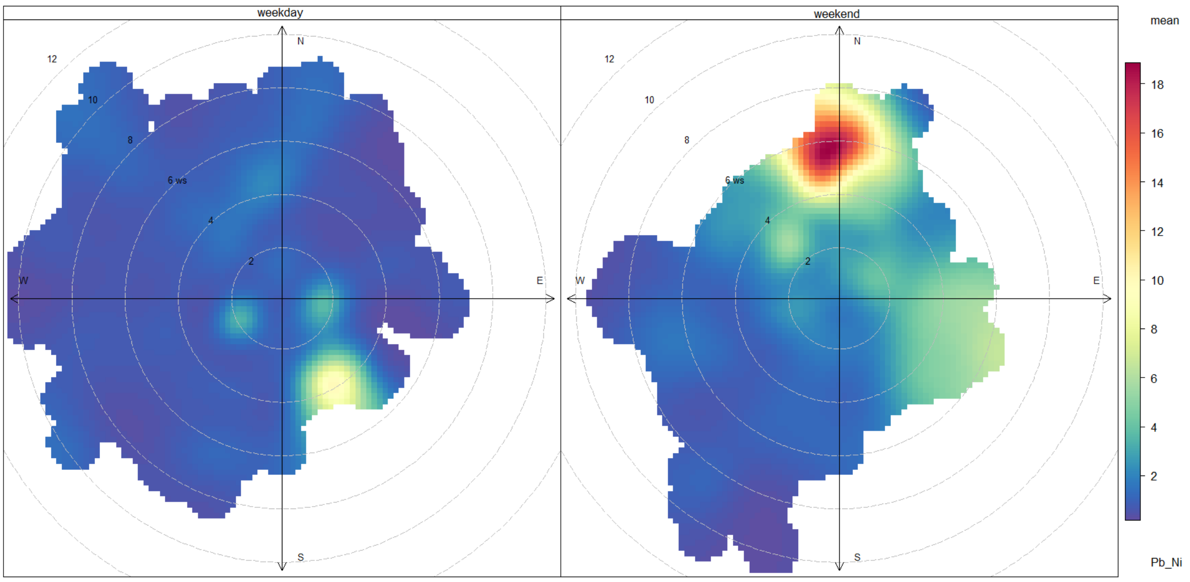


Weekday **Weekend**
Cadmium / Nickel



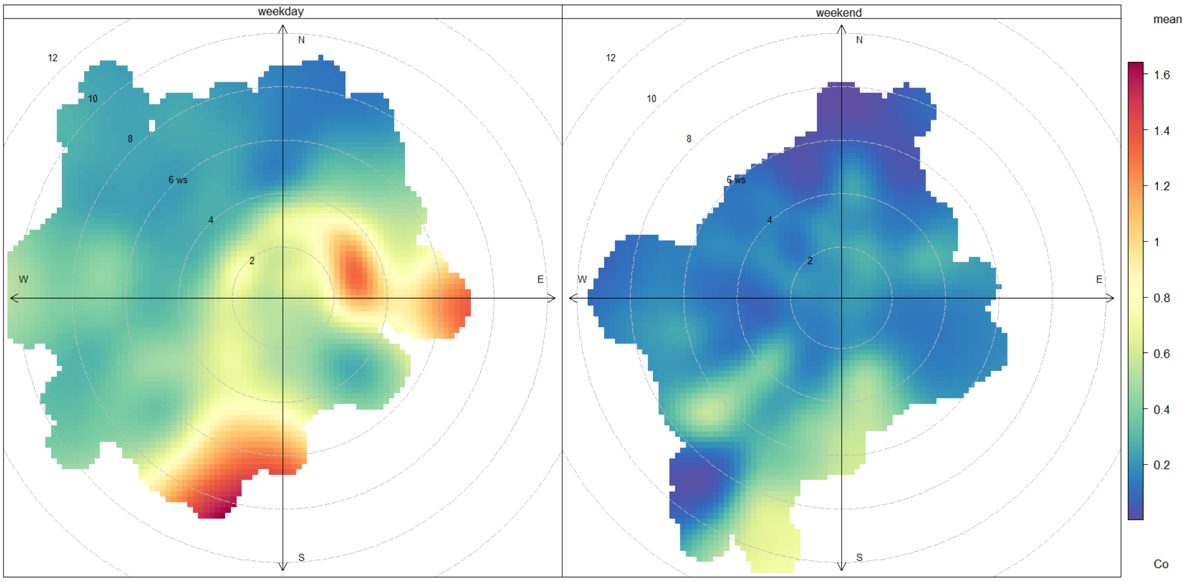
Weekday **Weekend**

Lead, ng.m^{-3}



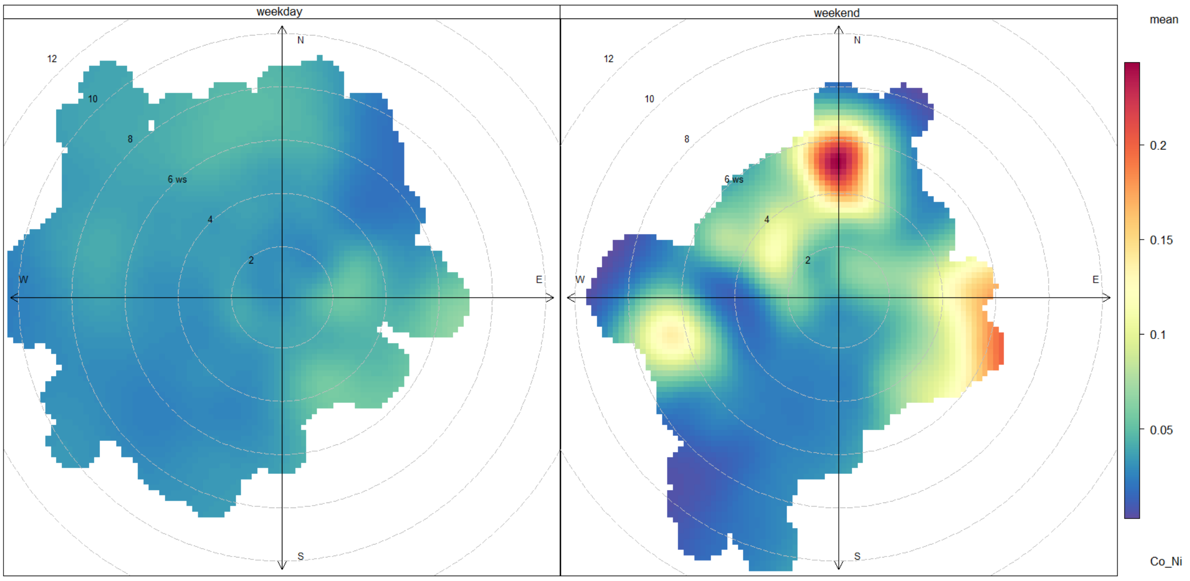
Weekday **Weekend**

Lead / Nickel



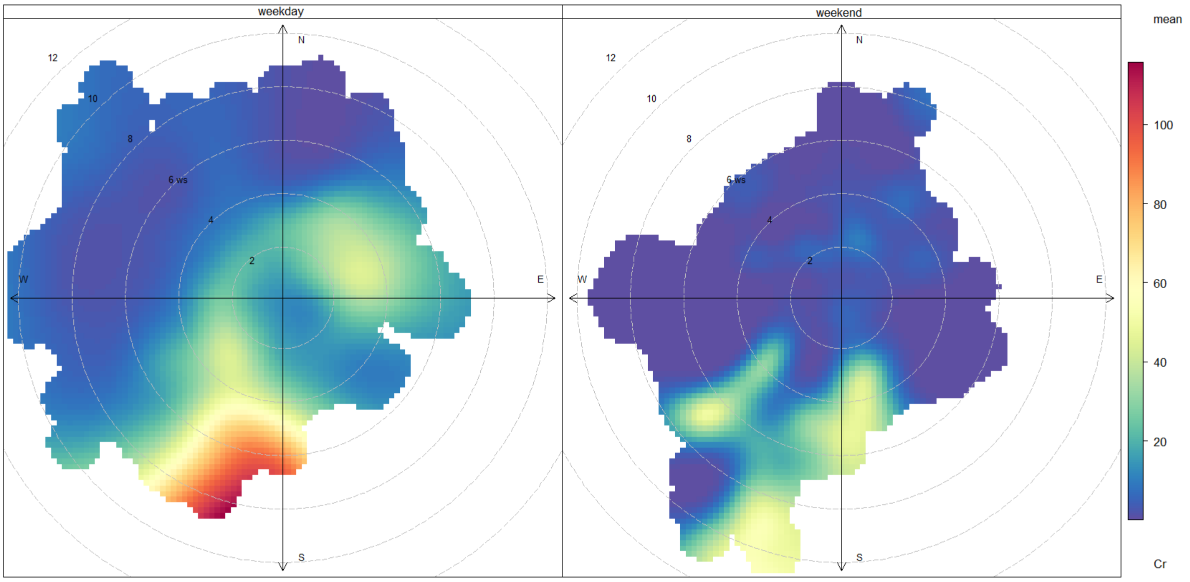
Weekday **Weekend**

Cobalt, ng.m^{-3}



Weekday **Weekend**

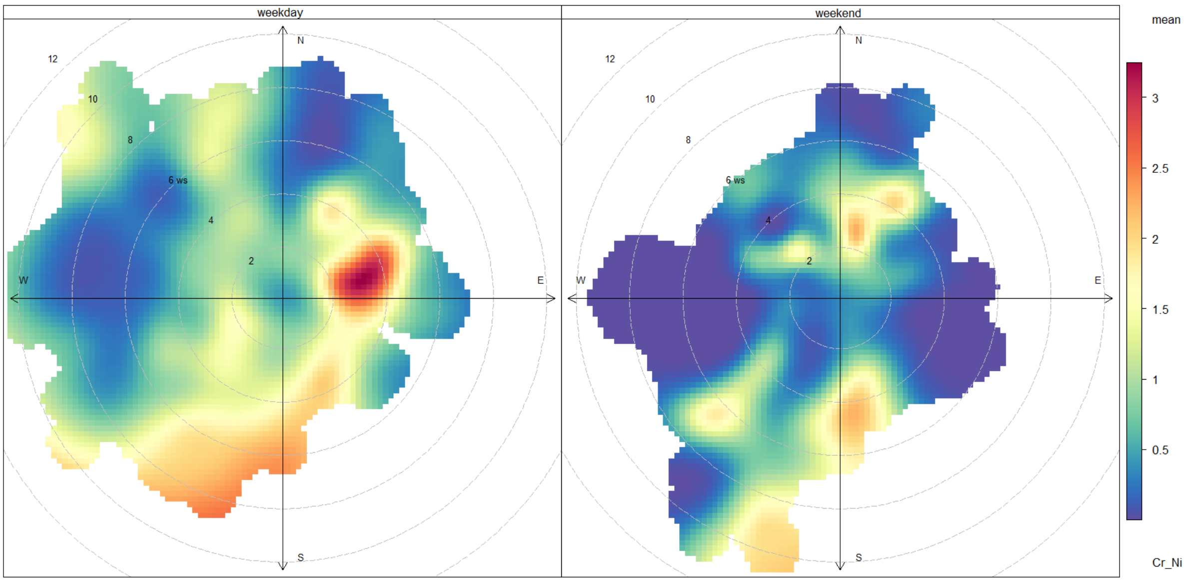
Cobalt / Nickel



Weekday

Chromium, ng.m^{-3}

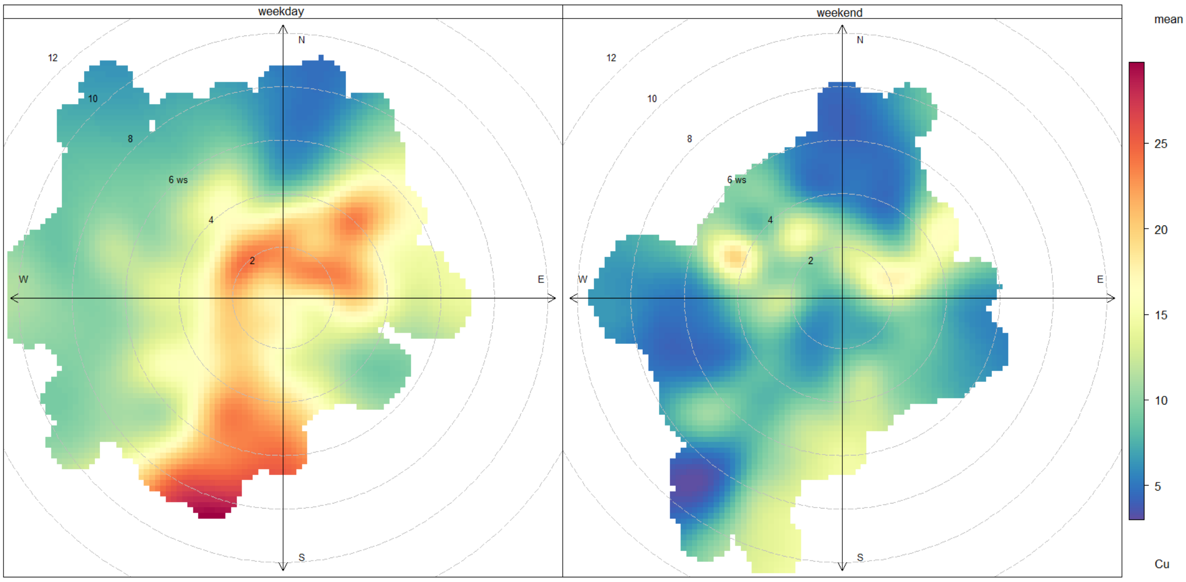
Weekend



Weekday

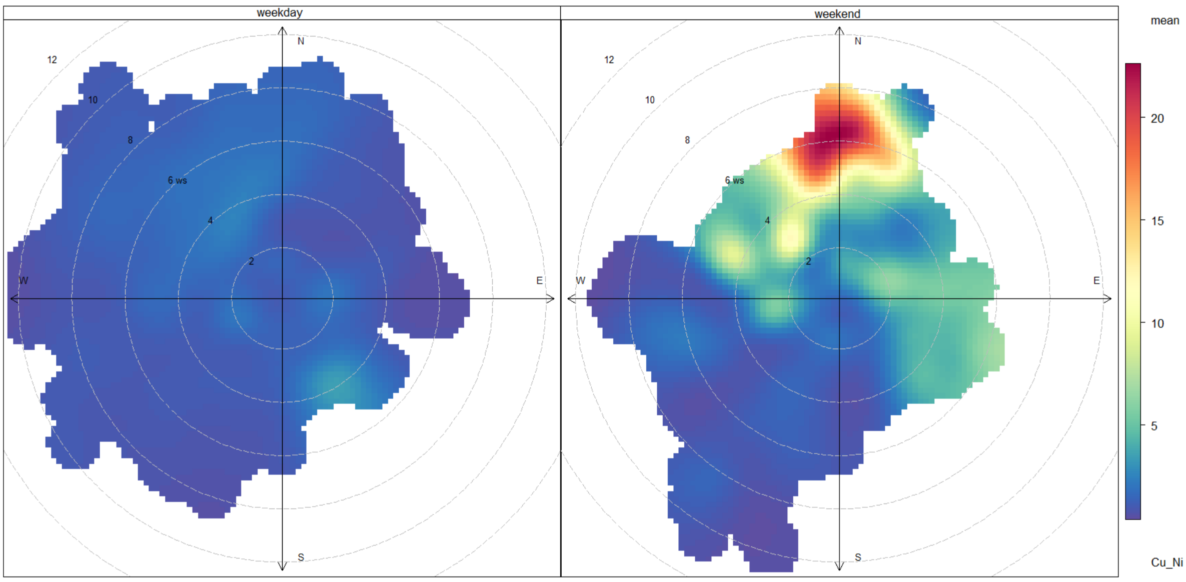
Chromium / Nickel

Weekend



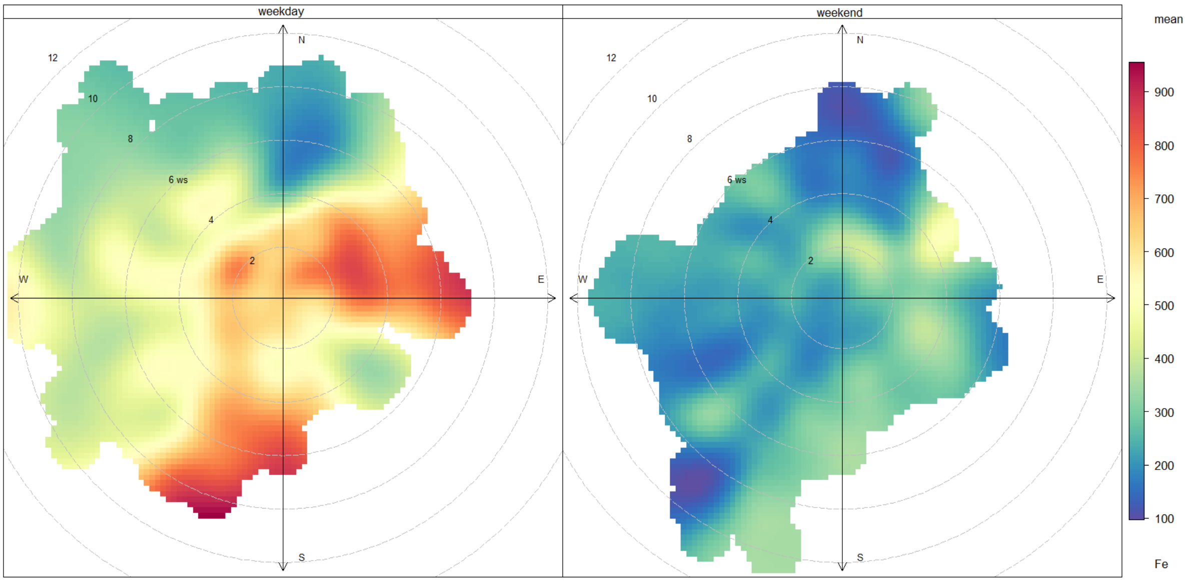
Weekday **Weekend**

Copper, ng.m^{-3}



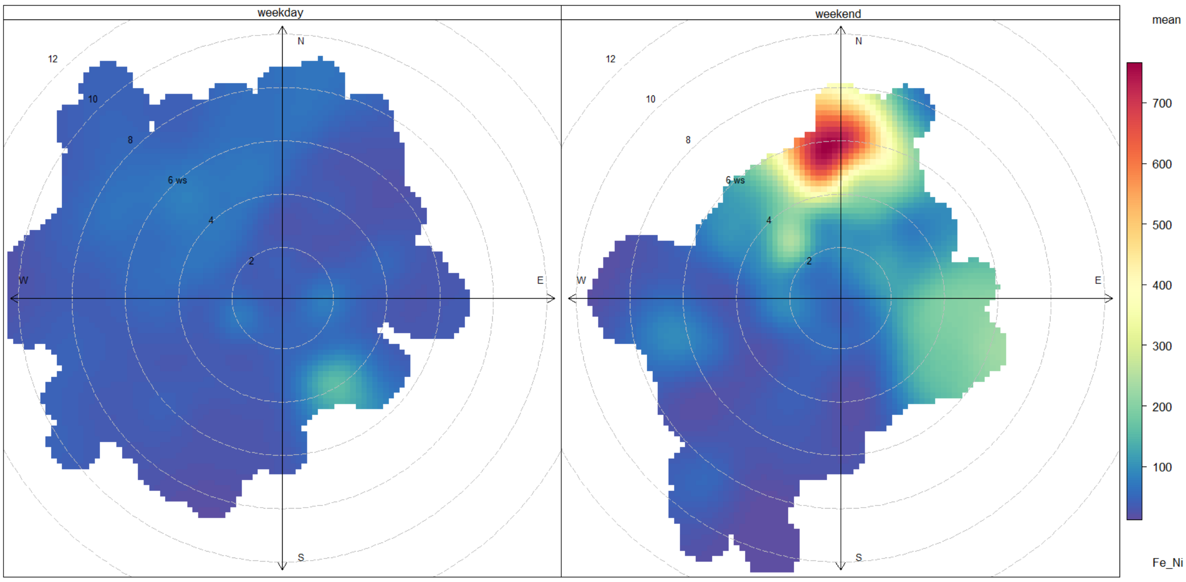
Weekday **Weekend**

Copper / Nickel



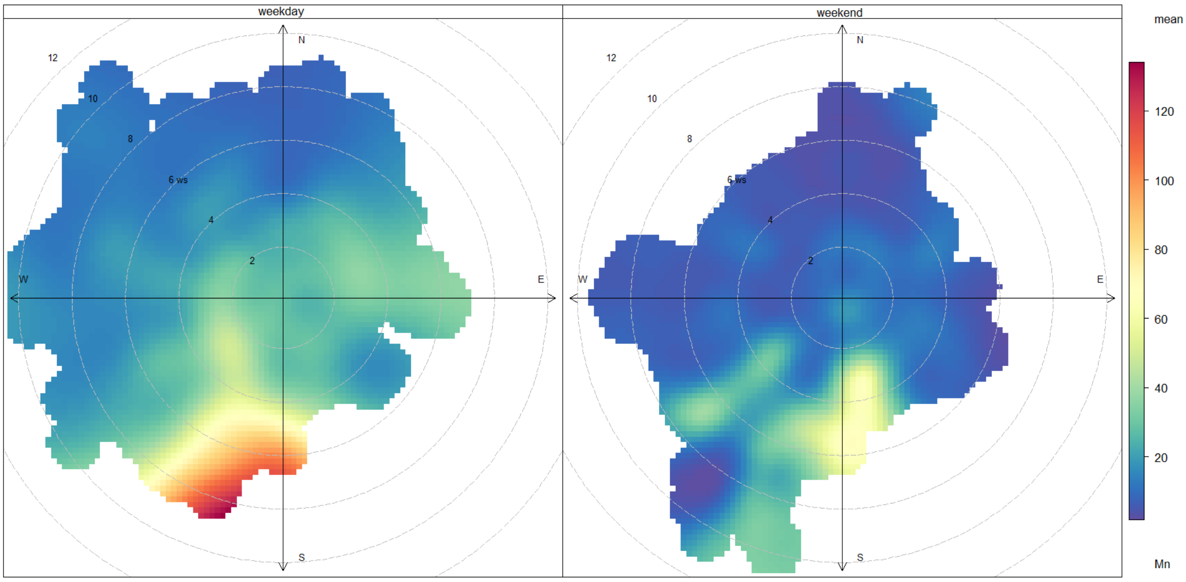
Weekday **Weekend**

Iron, $ng.m^{-3}$



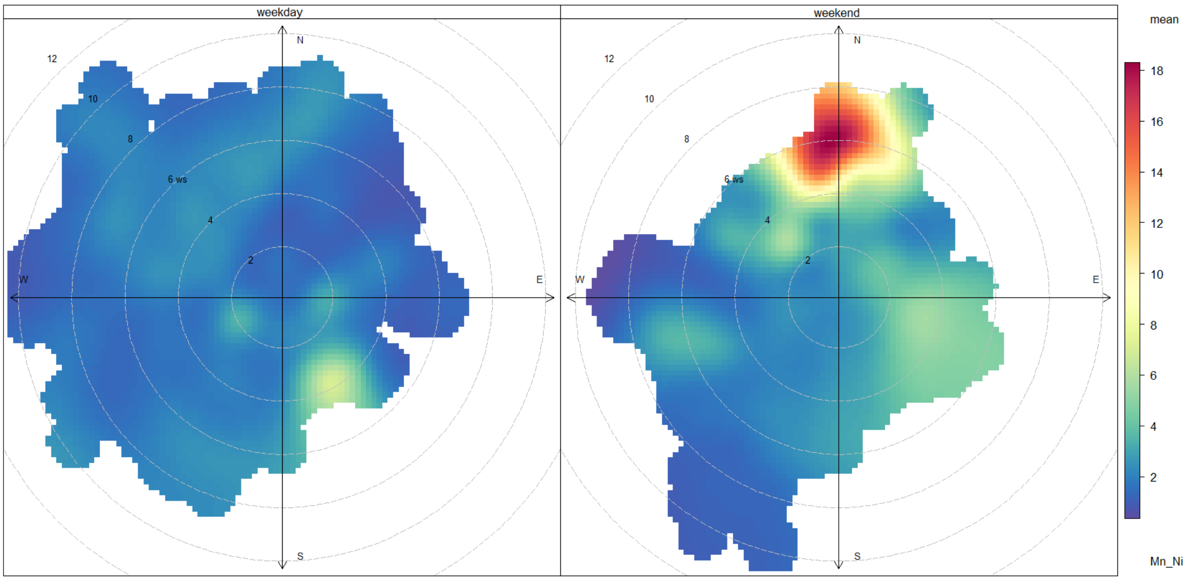
Weekday **Weekend**

Iron / Nickel



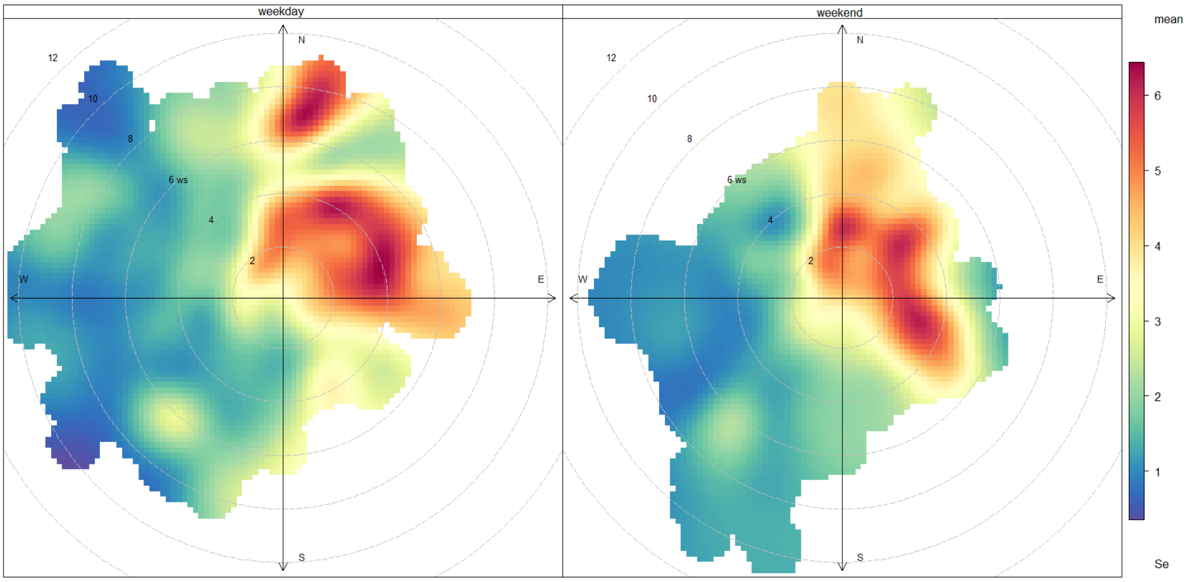
Weekday **Weekend**

Manganese, ng.m^{-3}



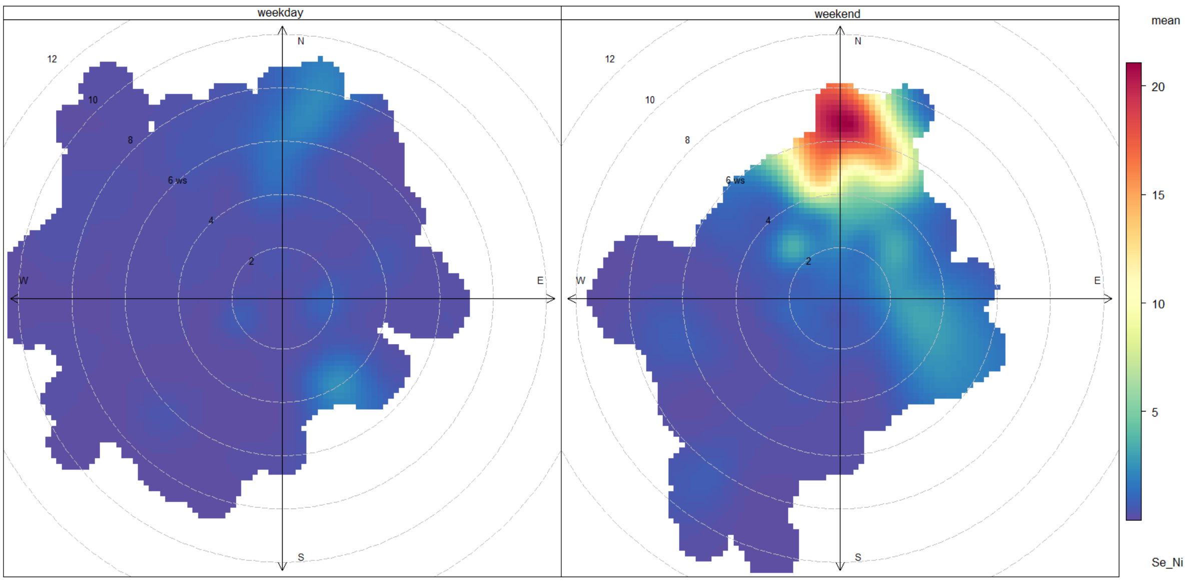
Weekday **Weekend**

Manganese / Nickel



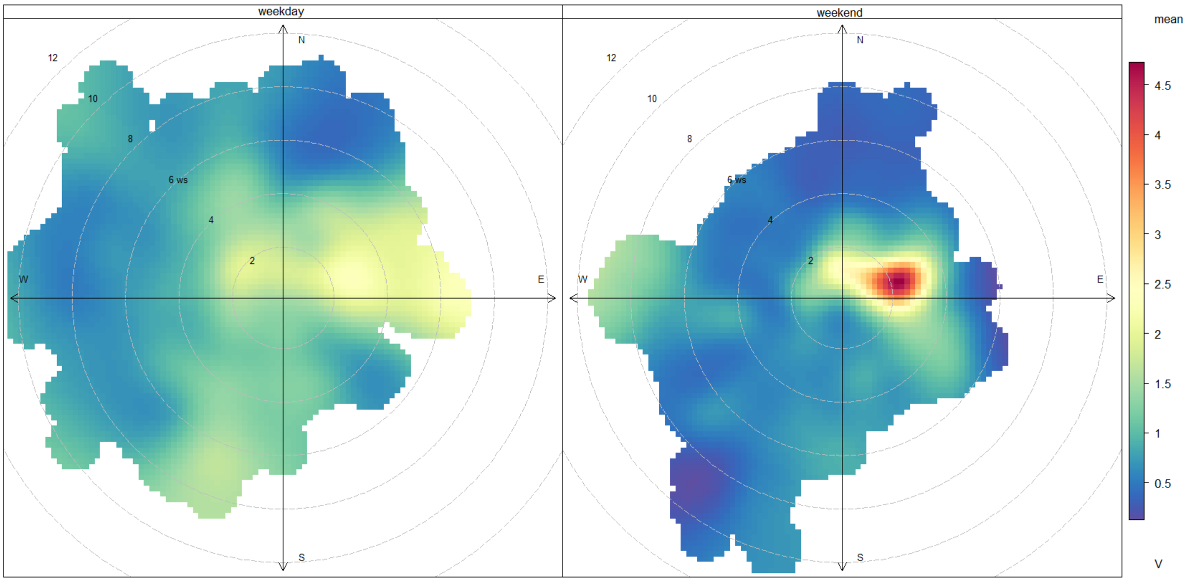
Weekday **Weekend**

Selenium, ng.m^{-3}



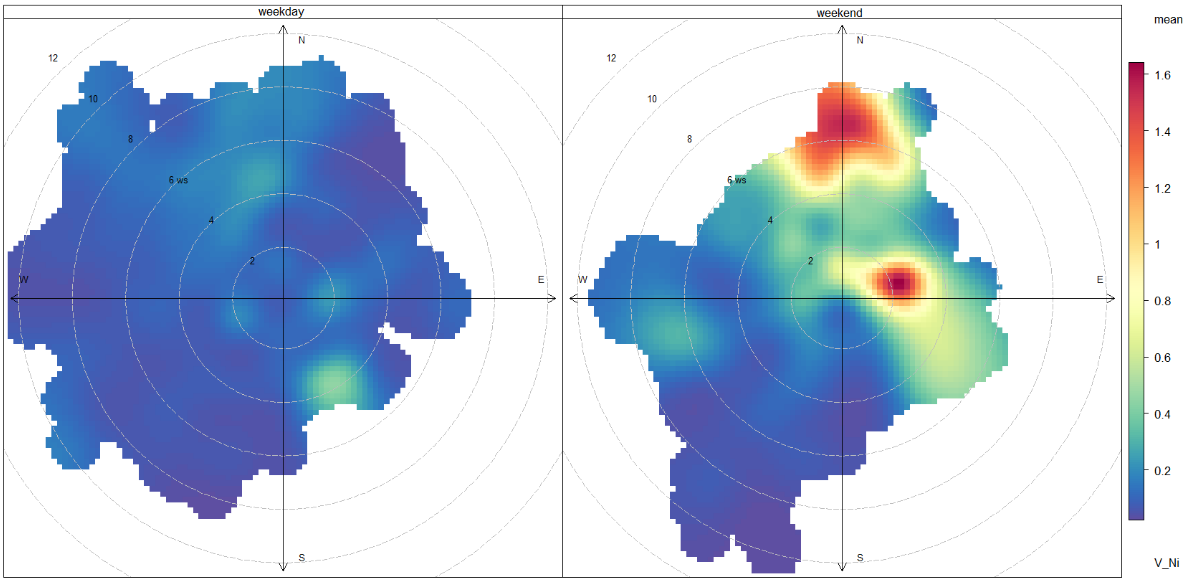
Weekday **Weekend**

Selenium / Nickel



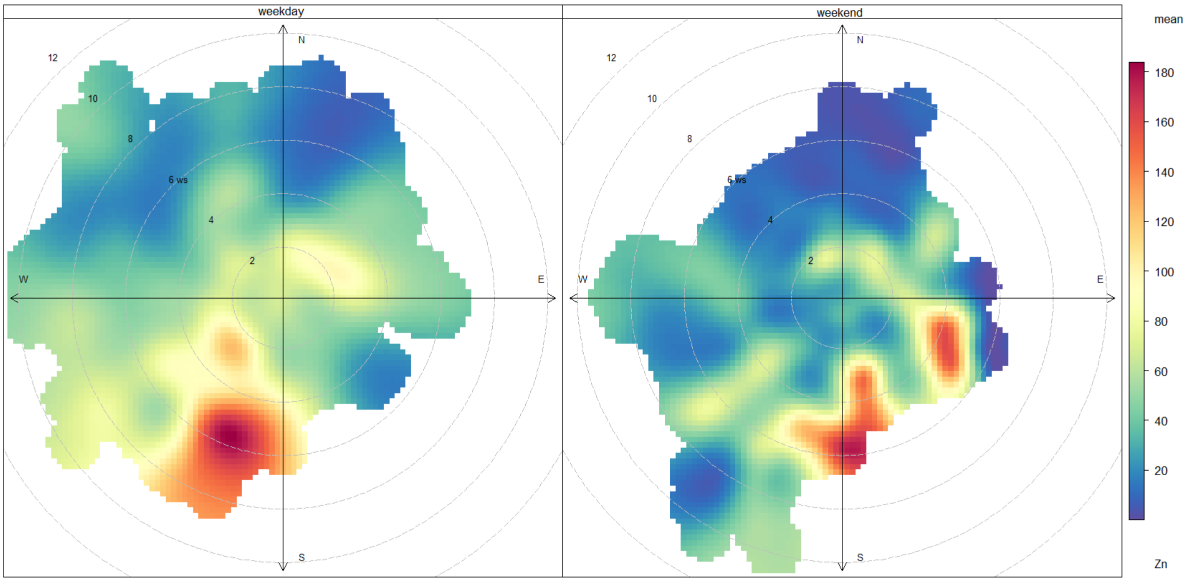
Weekday **Weekend**

Vanadium, ng.m^{-3}



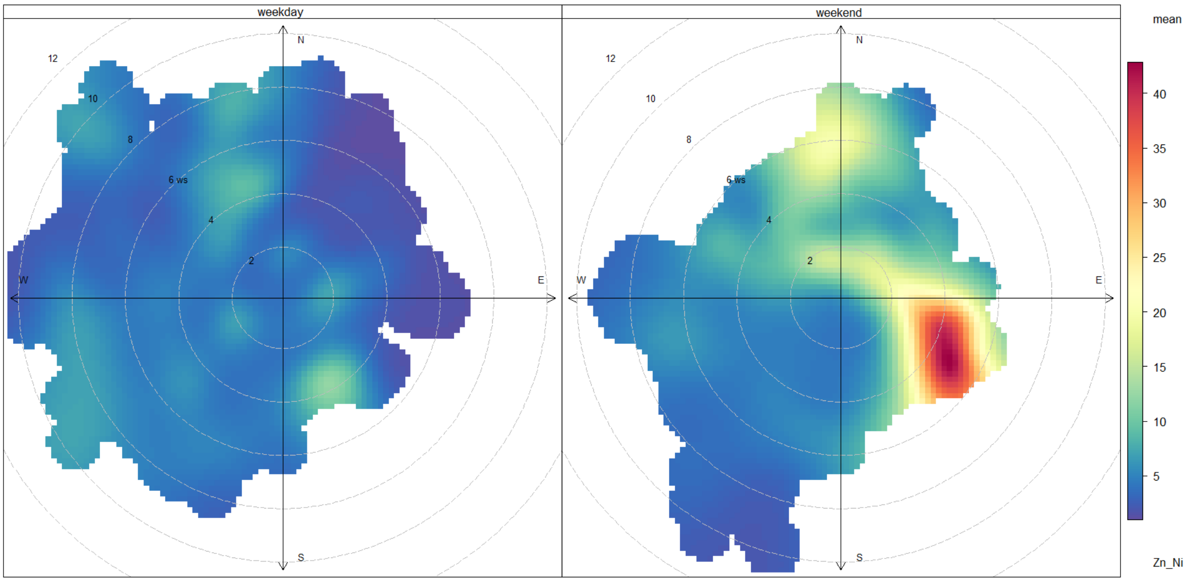
Weekday **Weekend**

Vanadium / Nickel



Weekday **Weekend**

Zinc, ng.m^{-3}



Weekday **Weekend**

Zinc / Nickel

Annex 3 - Daily Metals Concentrations

The following table gives the daily measured metals concentrations in ng.m^{-3}.

Date	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Se	V	Zn
25/02/2016	0.81	0.52	0.21	14.83	33.99	601.74	14.02	4.51	20.23	0.57	1.65	24.10
26/02/2016	1.39	0.67	0.11	5.40	10.00	397.45	16.38	0.99	31.65	7.17	1.09	32.30
27/02/2016	1.61	0.42	0.73	29.36	19.20	669.37	20.94	16.69	18.89	1.09	1.49	102.70
28/02/2016	1.29	0.26	0.13	0.01	20.64	515.05	10.72	5.22	11.73	6.89	1.09	77.57
29/02/2016	2.05	0.67	1.05	64.20	33.75	915.69	75.63	26.23	29.47	1.70	2.11	81.40
01/03/2016	0.36	0.15	0.39	23.98	11.39	470.84	32.03	17.52	6.69	0.76	0.71	125.36
02/03/2016	0.33	0.34	0.30	9.37	8.10	339.30	16.38	7.00	9.37	0.62	1.14	50.05
03/03/2016	0.49	1.21	0.66	15.11	17.31	653.96	27.01	11.16	9.74	0.75	2.26	44.78
04/03/2016	0.37	0.38	0.17	7.06	9.72	359.66	13.55	10.43	3.64	2.17	0.49	10.65
05/03/2016	0.18	0.07	0.01	0.01	4.00	98.42	2.89	0.21	2.10	4.33	0.31	3.11
06/03/2016	0.36	0.09	0.05	0.01	8.34	259.51	5.62	0.96	4.40	0.62	0.35	12.04
07/03/2016	0.40	1.14	0.24	4.58	13.73	540.46	19.50	6.79	7.30	1.16	1.91	80.39
08/03/2016	1.88	0.29	0.83	28.79	22.08	708.85	42.69	25.21	12.14	1.01	1.23	66.85
09/03/2016	29.44	6.69	8.68	478.86	271.00	10434.89	368.87	425.25	202.28	58.39	22.35	782.51
16/03/2016	0.47	0.30	0.27	115.87	18.20	909.53	41.75	7.18	8.33	7.36	2.07	34.16
17/03/2016	1.45	2.68	1.25	70.24	61.64	1462.70	48.38	36.91	64.10	7.65	3.75	116.27
18/03/2016	0.70	0.60	1.21	73.68	55.27	806.68	28.79	156.47	11.31	4.12	1.44	28.19
19/03/2016	0.10	0.10	0.11	11.61	3.69	185.32	4.98	2.05	4.49	3.36	0.60	9.14
20/03/2016	0.61	1.50	0.15	46.63	6.62	268.52	6.96	2.53	5.23	5.26	0.94	14.77
21/03/2016	0.59	0.20	0.21	16.02	14.82	585.41	16.49	5.26	7.06	3.05	1.24	46.99

Date	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Se	V	Zn
22/03/2016	0.84	0.48	0.37	32.67	21.22	782.66	28.64	12.71	33.42	3.04	2.03	147.62
23/03/2016	0.53	0.19	0.44	10.70	22.05	874.75	34.16	17.01	11.18	1.92	1.76	73.43
24/03/2016	0.01	0.17	0.29	13.40	16.96	649.19	20.94	26.12	10.48	1.52	1.10	66.91
25/03/2016	0.06	0.11	0.08	0.01	7.75	270.91	7.83	2.99	4.99	1.73	0.40	12.45
26/03/2016	0.01	0.26	0.64	47.98	13.19	339.55	30.45	26.02	7.16	1.37	0.65	53.26
27/03/2016	0.01	0.04	0.01	0.01	2.63	96.73	2.03	1.78	2.11	1.29	0.13	6.33
28/03/2016	0.01	0.04	0.12	0.01	4.64	176.61	3.75	4.50	2.23	1.77	0.23	5.18
29/03/2016	0.01	0.06	0.30	8.02	10.78	372.42	12.65	8.78	9.94	1.26	0.53	32.02
30/03/2016	0.01	0.09	0.31	3.19	17.09	689.56	20.07	11.83	5.82	1.22	1.42	62.08
31/03/2016	0.90	0.47	1.12	27.40	28.65	1005.72	30.66	27.72	16.03	2.73	1.71	62.61
01/04/2016	0.49	0.63	1.20	75.43	22.84	725.84	86.54	32.20	36.83	2.05	1.90	173.59
02/04/2016	0.04	0.49	0.70	62.27	16.52	382.17	85.10	28.79	34.11	2.21	1.12	230.33
03/04/2016	0.01	0.24	0.38	27.60	9.61	269.69	39.26	13.68	12.28	1.89	0.57	51.29
04/04/2016	0.62	0.20	0.39	13.97	18.82	682.32	37.07	14.38	8.40	1.80	0.90	43.38
05/04/2016	0.01	0.12	0.25	10.98	16.52	624.25	32.49	11.91	7.30	1.59	0.93	63.89
06/04/2016	0.01	0.09	0.63	9.05	12.32	590.77	20.33	27.04	5.46	1.05	0.79	46.07
07/04/2016	0.01	0.09	0.23	0.01	13.09	498.33	21.90	5.86	9.78	1.04	0.77	28.97
08/04/2016	0.36	0.34	0.79	41.70	20.90	730.87	25.01	40.56	7.74	3.40	1.56	46.40
09/04/2016	0.01	0.12	0.05	0.01	6.22	181.99	5.54	2.23	3.84	1.13	0.23	8.35
10/04/2016	0.20	0.14	0.17	0.01	5.91	206.93	4.68	0.95	5.96	1.81	0.42	8.55
11/04/2016	0.27	0.32	0.72	28.02	13.70	848.16	42.29	50.42	15.82	3.65	2.10	59.65
12/04/2016	0.84	0.14	0.46	18.20	23.27	731.62	22.44	25.12	14.35	2.87	1.91	44.60
13/04/2016	1.62	0.69	1.01	57.43	30.84	956.51	64.92	58.15	18.26	3.07	3.10	119.64
14/04/2016	0.70	0.27	0.46	25.14	14.41	591.04	24.24	25.62	23.01	5.00	1.58	92.78
15/04/2016	0.30	0.19	0.26	3.59	13.03	460.58	21.02	9.74	22.74	5.05	0.81	120.23
16/04/2016	0.01	0.05	0.06	0.01	4.21	173.30	3.95	0.13	4.52	3.16	0.26	4.08
17/04/2016	0.01	0.19	0.06	0.01	64.11	207.61	4.39	1.93	3.87	1.15	0.50	21.20
18/04/2016	0.09	0.12	0.34	0.01	13.72	625.66	22.69	8.77	5.31	1.44	0.85	20.94

Date	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Se	V	Zn
19/04/2016	0.16	0.30	0.65	22.79	20.36	695.12	26.55	18.09	11.64	2.94	1.52	44.42
20/04/2016	0.15	0.17	0.49	27.22	12.99	488.23	19.95	10.94	6.80	3.15	1.26	40.36
21/04/2016	0.61	0.42	5.32	72.68	29.08	1262.10	60.29	33.20	27.83	6.59	2.38	139.74
22/04/2016	0.24	0.18	0.39	25.49	10.15	489.00	25.43	14.44	7.47	6.44	0.88	83.13
23/04/2016	0.06	0.11	0.13	7.18	5.55	184.60	5.06	1.97	6.14	5.89	0.37	12.68
24/04/2016	0.09	0.09	0.08	8.44	4.41	175.47	3.70	2.19	3.77	4.33	0.34	10.32
25/04/2016	0.01	0.14	0.34	10.78	9.53	320.45	15.73	6.22	3.64	3.16	0.73	17.57
26/04/2016	0.01	0.37	0.19	8.83	7.39	232.83	6.54	3.55	2.98	3.38	1.04	52.29
27/04/2016	0.05	0.34	0.39	24.52	12.38	411.24	19.89	16.17	3.93	5.56	1.81	25.68
28/04/2016	0.01	0.15	0.64	50.50	16.72	642.92	50.57	22.69	13.10	5.47	1.14	116.71
29/04/2016	0.01	0.09	0.23	18.88	11.34	350.61	10.90	7.91	6.85	4.09	0.60	33.09
30/04/2016	0.18	0.17	0.16	9.66	11.00	449.27	7.65	4.21	5.34	4.02	0.50	17.72
01/05/2016	0.06	0.20	0.43	36.58	10.03	305.98	21.19	14.96	10.07	4.30	0.77	62.17
02/05/2016	0.01	0.09	0.12	11.73	5.75	254.67	12.26	5.19	2.72	4.01	0.53	20.70
03/05/2016	0.01	0.11	0.34	0.01	15.35	607.61	22.06	11.02	5.06	1.59	0.89	22.56
04/05/2016	1.35	0.44	1.41	161.51	24.49	991.15	76.60	68.49	31.57	1.47	2.02	320.75
05/05/2016	0.13	0.41	1.14	98.99	24.70	831.48	85.06	29.55	28.99	2.98	1.40	161.24
06/05/2016	2.09	0.76	2.48	55.55	37.14	1555.73	58.59	56.26	29.69	5.93	3.24	159.02
07/05/2016	1.05	0.29	0.17	0.01	15.90	461.48	16.49	2.28	11.77	6.75	1.92	24.82
08/05/2016	0.92	0.29	0.13	0.01	8.19	409.93	12.50	2.87	11.39	8.21	2.04	350.59
09/05/2016	1.00	0.44	2.04	11.99	14.16	759.60	27.99	15.63	14.36	6.04	2.43	37.25
10/05/2016	1.44	0.44	0.80	24.15	18.73	799.64	24.69	36.58	17.08	9.83	2.16	66.78
11/05/2016	0.76	0.26	0.57	22.06	19.38	680.72	22.93	27.09	9.77	4.58	2.19	39.92
12/05/2016	0.52	0.28	0.96	41.38	17.82	686.82	26.46	48.73	14.90	5.25	2.43	44.02
13/05/2016	0.01	0.15	0.51	25.57	10.09	526.18	59.89	16.72	5.58	1.66	0.88	15.71
14/05/2016	0.10	0.18	0.80	0.01	6.74	250.89	5.74	2.31	8.01	3.88	0.52	14.19
15/05/2016	0.35	0.65	0.21	0.01	9.72	282.84	10.75	6.76	12.64	2.36	0.73	63.26
16/05/2016	0.15	0.15	0.24	1.78	15.05	544.06	28.19	11.50	13.90	0.87	0.96	59.87

Date	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Se	V	Zn
17/05/2016	0.54	0.21	0.54	43.30	23.50	715.51	29.44	23.57	8.56	1.22	2.76	54.54
18/05/2016	0.51	0.24	0.60	37.24	20.21	532.97	27.30	25.95	18.04	1.36	2.27	51.51
19/05/2016	0.01	0.25	0.23	2.12	12.30	393.14	18.33	7.50	15.73	0.88	0.76	94.69
20/05/2016	0.00	0.07	0.24	4.35	13.46	412.42	13.01	7.59	6.18	0.87	1.08	44.52
21/05/2016	0.01	0.31	0.09	0.01	5.92	144.50	7.45	3.23	3.35	0.80	0.45	10.61
22/05/2016	0.01	0.61	0.02	0.01	4.70	126.85	3.47	2.04	4.80	0.73	0.33	5.05
23/05/2016	8.97	0.28	0.26	0.01	15.88	288.18	10.37	6.30	14.98	3.37	0.62	58.16
24/05/2016	0.57	0.39	0.47	11.24	22.33	469.63	17.75	22.36	15.03	5.32	0.80	73.42
25/05/2016	0.01	0.23	0.48	20.78	10.41	361.09	23.67	20.59	3.69	4.61	0.94	7.78
26/05/2016	0.29	0.18	0.41	2.11	21.11	716.68	32.98	10.18	10.40	0.91	1.86	36.75
27/05/2016	1.00	0.48	0.44	33.49	36.85	584.77	25.01	9.59	18.62	5.89	3.71	103.96
28/05/2016	0.22	0.42	0.32	4.53	33.83	300.87	9.96	3.16	10.70	3.32	10.29	60.19
29/05/2016	0.65	0.14	0.07	0.01	4.24	127.58	3.16	1.66	5.67	3.25	0.63	8.53
30/05/2016	3.72	0.08	0.04	0.01	3.37	86.49	3.04	1.19	4.58	2.90	0.39	7.37
31/05/2016	0.25	0.07	0.13	0.01	4.43	196.72	7.90	2.88	3.67	7.46	0.46	6.09
01/06/2016	0.01	1.07	0.20	0.01	6.35	159.70	10.28	4.67	2.93	3.55	0.27	9.22
02/06/2016	0.06	0.20	0.44	0.01	9.50	243.17	13.26	10.20	4.70	1.46	0.46	7.61
03/06/2016	0.29	0.22	0.26	0.01	10.96	286.24	11.42	12.55	7.52	8.48	1.14	18.59
04/06/2016	0.69	0.14	0.08	0.01	4.55	190.24	4.99	1.57	6.72	14.16	1.07	12.73
05/06/2016	0.01	0.14	0.06	0.01	3.34	232.11	8.35	1.43	5.26	6.57	0.82	5.55
06/06/2016	0.58	0.45	0.35	5.40	15.79	577.26	20.36	9.13	25.00	5.34	1.42	43.25
07/06/2016	0.79	0.32	0.57	5.68	15.71	553.07	26.21	14.81	7.97	2.01	1.47	59.43
08/06/2016	0.75	0.40	1.66	30.17	18.73	888.83	30.60	49.79	11.83	4.86	4.00	69.30
09/06/2016	0.05	0.30	0.47	1.17	10.19	655.74	21.94	12.41	24.52	2.65	1.19	47.37
10/06/2016	0.78	0.33	0.48	28.19	24.29	610.15	24.54	25.51	9.44	3.23	1.00	47.80
11/06/2016	0.39	0.28	0.12	0.01	5.17	231.16	9.60	3.46	9.96	5.03	1.56	14.83
12/06/2016	0.56	0.19	0.20	1.91	5.93	188.55	12.79	9.17	12.92	7.58	1.32	46.34
13/06/2016	0.25	0.17	0.20	0.01	10.69	293.14	8.86	10.67	4.00	6.67	0.51	13.93

Date	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Se	V	Zn
14/06/2016	0.81	0.38	0.89	58.31	25.47	905.27	28.01	80.07	23.55	5.08	2.13	178.00
15/06/2016	0.51	0.20	0.75	29.02	14.93	501.32	22.53	36.78	20.72	7.64	0.82	44.63
16/06/2016	0.62	0.26	0.39	16.73	13.18	415.65	15.82	13.37	7.92	1.66	0.69	51.85
21/06/2016	0.19	0.63	0.72	55.88	18.52	529.38	54.16	26.01	26.44	0.68	0.97	214.86
22/06/2016	0.01	0.59	0.88	60.42	29.12	712.80	95.96	46.69	44.29	1.05	1.04	290.85
23/06/2016	1.03	0.36	0.65	4.01	23.51	668.25	26.30	11.55	15.50	4.40	3.69	67.38
24/06/2016	0.14	0.13	0.32	0.01	15.75	654.59	16.85	21.83	5.41	0.68	1.35	34.29
25/06/2016	0.55	0.15	0.33	0.01	20.70	320.41	8.00	5.18	7.01	0.67	1.20	18.92
26/06/2016	0.05	0.11	0.07	0.01	6.69	136.74	29.24	3.97	5.46	0.99	0.38	20.69
27/06/2016	0.01	0.03	0.30	0.01	8.79	349.67	13.25	6.03	1.39	0.80	0.30	9.11
28/06/2016	0.43	0.46	0.89	62.95	22.33	642.48	71.79	35.29	29.54	1.13	0.97	151.93
29/06/2016	0.30	0.57	1.98	185.98	33.37	1153.98	177.04	93.56	29.72	2.14	1.06	123.70
30/06/2016	0.01	0.08	0.48	6.32	13.23	382.92	13.47	10.68	5.10	1.49	0.81	55.35
01/07/2016	0.01	0.08	0.28	0.01	11.39	366.09	11.90	13.42	10.27	0.63	1.00	53.18
02/07/2016	0.01	0.14	0.13	0.01	6.75	237.65	6.24	10.11	5.26	0.97	1.37	35.46
03/07/2016	0.01	0.07	0.10	0.01	6.43	222.68	4.50	8.59	9.04	0.97	0.39	50.32
04/07/2016	0.01	0.14	0.61	16.81	14.76	443.01	22.46	14.98	7.76	0.69	0.87	64.83
05/07/2016	0.01	0.07	0.22	0.01	8.32	291.11	6.78	8.56	2.48	0.71	0.59	5.34
06/07/2016	0.01	0.11	0.42	14.85	15.46	532.95	35.42	13.80	9.70	0.85	0.99	40.20
07/07/2016	0.01	0.28	0.84	67.60	18.02	495.34	60.10	30.05	24.40	0.55	0.97	195.45
08/07/2016	0.01	0.16	0.64	0.80	10.85	330.07	17.00	9.07	7.89	0.99	0.64	70.13
09/07/2016	0.01	0.32	0.83	67.41	11.22	342.82	60.09	27.44	16.98	0.97	0.79	115.45
10/07/2016	0.01	0.05	0.06	0.01	4.33	92.84	8.41	11.94	8.33	0.26	0.22	40.76
11/07/2016	0.53	0.06	0.19	0.01	8.58	419.89	17.17	8.37	2.46	0.21	0.34	100.25
12/07/2016	0.28	0.14	0.20	0.01	10.76	303.79	7.88	6.41	7.18	0.17	1.15	103.38
27/07/2016	0.12	0.48	0.40	5.49	27.35	872.33	46.06	13.57	17.67	1.44	1.26	79.18

Appendix A2: Monitoring Studies

Date	As	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Se	V	Zn
28/07/2016	0.08	0.12	0.45	5.07	16.71	557.32	17.74	11.94	5.68	1.30	0.89	63.92
29/07/2016	0.07	0.10	0.17	0.01	15.87	438.21	10.83	5.27	3.37	2.04	0.86	29.52
30/07/2016	0.15	0.11	0.59	0.01	8.40	262.35	5.72	1.28	6.18	1.00	0.63	27.46
31/07/2016	0.01	0.07	0.04	0.01	4.56	120.42	1.95	0.79	3.46	0.99	0.27	3.48
01/08/2016	0.01	0.07	0.18	0.01	10.01	332.88	7.99	3.74	3.33	1.17	0.74	20.67
02/08/2016	0.01	0.26	0.48	33.30	10.98	275.22	43.50	15.59	12.43	1.22	0.29	48.18
03/08/2016	0.01	0.10	0.28	0.01	9.78	359.92	9.98	8.96	4.91	0.98	0.59	60.99
04/08/2016	0.01	0.05	0.47	0.01	8.94	372.97	12.69	8.92	8.48	1.04	0.52	26.07
05/08/2016	0.01	0.06	0.12	0.01	11.14	343.94	10.48	2.47	3.37	1.11	0.72	8.26
06/08/2016	0.01	0.04	0.07	0.01	5.95	176.45	6.83	1.88	3.40	1.36	0.62	17.34
07/08/2016	0.01	0.07	0.28	0.01	3.87	177.33	6.81	1.55	3.02	1.38	0.54	11.67
08/08/2016	0.01	0.08	0.19	0.01	8.40	429.61	14.41	4.79	3.70	0.96	0.81	11.67
09/08/2016	0.01	0.12	0.22	0.01	10.67	532.90	13.03	4.52	6.24	1.19	1.09	16.47