Oxides of Nitrogen and Particulate Monitoring at Wagerup Refinery

An Analysis of Influences Detectable in Yarloop

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Glossary

NO Nitrogen Oxide Concentration (ppb)

$\mathrm{NO_2}$ Nitrogen Dioxide Concentration (ppb)

NO_x Total Nitrogen Oxides Concentration (ppb): equals NO + $\mathrm{NO_2}$

PM_{10} Airborne particulate matter less than 10 microns in diameter μgm^{-3}

$\mathrm{PM}_{2.5}$ Airborne particulate matter less than 2.5 microns in diameter μgm^{-3}

Blocked Bootstrap A version of the bootstrap re-sampling procedure which ameliorates the effects of serial correlation in the samples.

Bootstrap A non-parametric procedure for estimating confidence intervals or performing significance tests, used when the theoretical distribution of an estimator is uncertain or intractable. The bootstrap procedure is computationally intensive, and is based on re-sampling from the data.

Box and Whisker Plot A box and whisker plot provides summary information about the distribution of measurements. The central box represents the 25^{th} and 75^{th} quantiles. The middle line is the mean of the observations. The whiskers represent the largest and smallest observations within a cut off distance of the top and the bottom of the box. The cut off distance is set as 1.5 times the width of the box. Observations outside the range of the whiskers are considered outlying observations, and are displayed as points.

Generalised Linear Model A very versatile approach to statistical analysis, which allows data with non-normal error distributions to be analysed. The approach encompasses many of the common distributional forms of data, including Poisson models for count data, and Binomial models for success / failure data.

Kernel Density Estimate A non-parametric smooth estimate of the statistical distribution of some quantity. A kernel density estimate provides information about the shape of a distribution.

logit A transformation applied to a probability to map the (0,1) range onto the interval $(-\infty, \infty)$ The logit function is defined as $logit(p) = \log(\frac{p}{1-p})$.

lowess An algorithm for fitting a smooth curve to data. It uses a local regression, in which the line is fitted to points within a moving window about each data point. The local fit is based on a robust weighted regression.

RDA Residue Drying Area

TSP Total Suspended Particulates $\mu g m^{-3}$

Executive Summary

This report describes an analysis of Oxides of Nitrogen and airborne particulate data obtained from the Boundary Rd Yarloop monitoring station, and from air quality monitoring stations within the Wagerup refinery complex. It seeks to answer the following questions:

1. Is there any objective evidence of refinery operations influencing Oxides of Nitrogen and airborne particulates in Yarloop?
2. Are peak concentrations of particulate matter or Oxides of Nitrogen sufficient to cause irritant effects in Yarloop? Is it possible that taking hourly or daily average values masks transient peaks in these parameters, which are sufficient to cause irritation?
3. Is there any objective evidence of a relationship between refinery operations and the frequency of complaints?

An analysis of the effect of wind directions on peak concentrations of Oxides of Nitrogen and particulate matter was performed. The analysis revealed that:

1. Both Oxides of Nitrogen and airborne particulate concentrations tend to be higher when the wind is blowing from the direction of the refinery complex;
2. Oxides of Nitrogen appear to be elevated when the wind is from the direction of the refinery stacks;
3. Airborne particle concentrations appear to be elevated when the wind is blowing from the direction of the Residue Drying Area.
4. There is evidence that other sources, not located within the refinery, contribute to the concentrations of Oxides of Nitrogen and airborne particulates. In particular, winds from the direction of Yarloop result in increased $\mathrm{PM}_{2.5}$ concentrations and increased Nitrogen Oxides.

The distribution of PM_{10} during periods in which the wind blew from the Northern sector was used to estimate the total alkalinity of airborne particles. Even after making pessimistic (ie upwards) adjustments to the estimated NaOH concentrations there was no evidence of alkalinity sufficient to cause an irritant response.

The incidence of complaints is related to the proportion of each day with a northerly wind. Complaint incidence also increases with NO_x concentrations. Elevated NO_x concentrations probably serve as a marker for instances in which the refinery stack plumes reach ground level. This provides some objective evidence that complaints are related to refinery operations, and the most likely cause of complaints is odour associated with the plume.

Chapter 1

Background

Alcoa operate an Alumina refinery at Wagerup. The refinery is situated about 5 km north of the town of Yarloop. The local community has often complained of nuisance associated with the site. Reports include unpleasant smells, transitory irritant effects, and more controversially, the development of “multiple chemical sensitivity”. Complaints are more common during the winter months.

The Wagerup refinery has an extensive environmental monitoring programme which includes the following data sources:

- Particulate concentrations of air sampled at various locations within the refinery, and at Boundary Rd, Yarloop;
- Oxides of Nitrogen sampled within the refinery, and at Boundary Rd Yarloop;
- Measurements of total suspended particulate alkalinity at Boundary Rd Yarloop;
- Records of complaints by issue, date and by complainant.

Despite community concerns, there has been little objective evidence to date of any influence of refinery operations on Oxides of Nitrogen or airborne particulates in Yarloop. In particular the concentrations of particulates and Oxides of Nitrogen are well below relevant health standards for hourly averages, daily averages or annual averages [3, 2]

This report seeks to address several questions:

1. Is there any objective evidence of refinery operations influencing Oxides of Nitrogen or airborne particulates in Yarloop?

2. Are peak concentrations of particulate matter or Oxides of Nitrogen sufficient to cause irritant effects in Yarloop? Is it possible that taking hourly or daily average values masks transient peaks in these parameters, which are sufficient to cause irritation?

3. Is there any objective evidence of a relationship between refinery operations and the frequency of complaints?

The relationship between refinery operations and Oxides of Nitrogen and airborne particulates was investigated by an analysis of meteorological records from Bancell Rd and Oxides of Nitrogen and airborne particulates records from Boundary Rd Yarloop, and from sites within the refinery. This analysis is described in Chapter Two.

The potential irritant effect of peak concentrations was evaluated by considering the distribution of peak particulate concentrations, and the alkalinity of total suspended particulates. This analysis is described in Chapter Three.

The relationship between refinery operations and complaints data was investigated by a joint analysis of:

1. the history of complaints;

2. meteorological records from Bancell Rd and

3. Oxides of Nitrogen and airborne particulates records from Boundary Rd Yarloop.

This analysis is described in Chapter Four.

Chapters Two, Three and Four each provide a non–technical overview of the results and the conclusions of the analyses. Chapters Two and Four also have technical appendices, which detail the analyses performed.

Chapter Five provides a summary of the results, and conclusions of the analyses.

Throughout this report, reference to the ‘refinery’ should be understood to mean the refinery plant, the Residue Drying Areas and the stockpiles. It includes all the area within the refinery complex.

Chapter 2

Oxides of Nitrogen and Airborne Particulate Data

2.1 Background

There is an automated meteorological station at Bancell Rd, and automated atmospheric measurement stations are located at: Boundary Rd, Yarloop; The Upper Dam, The South Residue Drying Area (RDA) and the South West RDA. The following measurements are available at the measuring stations:

Bancell Rd Wind Direction (degrees), Wind Speed at 10m and at 3m (km/h), Temperature (°C), Solar Radiation, Barometric Pressure (mBar), Rainfall and Relative Humidity;

Boundary Rd Yarloop Nitric Oxide concentration (NO), Nitrogen Dioxide concentration ($\mathrm{NO_2}$), Total Oxides of Nitrogen (NO_x), PM_{10} and $\mathrm{PM}_{2.5}$;

Upper Dam Nitric Oxide concentration (NO), Nitrogen Dioxide concentration and Total Oxides of Nitrogen (NO_x);

South West RDA Total Suspended particulates (TSP);

South RDA Total Suspended particulates (TSP);

All of these variables are available as 6 minute averages. Unless otherwise qualified, any further reference to these variables should be understood to refer to 6 minute average values.

Any influence of plant operations on Oxides of Nitrogen or airborne particulates in Yarloop must involve wind transport. If the plant is a major source of Oxides of Nitrogen and particulate matter, we might expect to see higher values of NO, NO_2, NO_x, PM_{10} and $\mathrm{PM}_{2.5}$ during those months in which the wind is often from the North (since the monitoring station at Boundary Rd is South of the refinery).

2.2 Descriptive Statistics

Analysis of wind direction was restricted to those records containing a full set of monitoring data - ie the period March 2002 to January 2004 inclusive.

All of the Oxides of Nitrogen and airborne particulates parameters follow a long-tailed distribution. That is, most measurements are relatively low, but there are a few measurements which are many times the average value. These larger measurements are generated by transient peaks in the measured concentration. For illustrative purposes only, Figure 2.1 shows a histogram of the distribution of natural log NO_x concentrations at Boundary Rd. The very long tail of the distribution is apparent (even after taking logarithms).

Summary statistics (Median, 75^{th}, 95^{th} and 99^{th} percentiles and maximum) of the concentrations of NO, NO_2, NO_x, PM_{10} and $\mathrm{PM}_{2.5}$ at Boundary Rd are shown in Tables 2.1, 2.2, 2.3, 2.4 and 2.5 respectively. Each table displays the summary statistics by month.

Month	Median	75 Percentile	95 Percentile	99 Percentile	Max
January	1.2	3.1	3.7	5.5	21.9
February	1.1	2.3	5.8	16.2	48.2
March	0.0	0.2	0.9	3.6	36.1
April	0.2	0.5	2.0	14.5	46.3
May	0.1	0.3	1.7	4.8	29.7
June	0.0	0.2	1.4	17.9	71.7
July	0.0	0.1	0.8	2.9	20.8
August	0.0	0.1	1.0	5.2	47.0
September	−0.2	0.0	0.4	3.4	53.7
October	0.0	0.2	0.6	2.7	98.2
November	0.1	0.4	0.9	3.2	33.6
December	0.2	0.7	3.4	4.2	30.3

Table 2.1: Distribution of NO (ppb) Boundary Rd by Month. Note the negative median value for September - this is an artifact of the measurement process for NO. Very low concentrations of NO may give rise to negative measured values.

Month	Median	75 Percentile	95 Percentile	99 Percentile	Max
January	1.1	2.0	5.3	9.8	28.5
February	1.6	3.5	9.7	14.8	18.1
March	1.5	2.9	7.1	11.3	18.0
April	2.0	3.4	6.8	14.0	22.2
May	1.8	3.2	6.9	10.8	18.4
June	1.3	2.2	5.7	8.7	17.8
July	1.4	2.3	6.1	9.0	15.4
August	1.1	1.7	5.0	9.0	18.3
September	1.0	1.6	3.6	6.8	23.9
October	1.0	1.8	4.1	8.2	17.0
November	1.3	2.2	4.7	7.8	41.5
December	1.4	2.5	4.9	8.0	17.4

Table 2.2: Distribution of NO_2 (ppb) Boundary Rd by Month

Month	Median	75 Percentile	95 Percentile	99 Percentile	Max
January	3.0	4.3	7.5	14.5	34.4
February	3.0	4.6	16.3	26.4	53.1
March	1.5	3.1	8.1	14.6	46.2
April	2.2	3.9	8.8	23.6	51.6
May	1.9	3.6	8.4	14.5	39.8
June	1.4	2.4	7.1	27.3	83.7
July	1.4	2.4	6.7	10.8	33.7
August	1.1	1.9	6.1	14.5	53.4
September	0.7	1.3	3.7	10.2	66.3
October	1.0	1.9	4.5	11.4	108.8
November	1.5	2.5	5.4	10.2	44.9
December	2.0	3.8	6.2	10.9	36.1

Table 2.3: Distribution of NO_x (ppb) Boundary Rd by Month

Month	Median	75 Percentile	95 Percentile	99 Percentile	Max
January	17.7	25.8	51.2	120.7	676.7
February	17.0	25.0	43.3	94.9	593.6
March	18.2	28.3	55.8	117.6	1071.7
April	10.2	16.7	34.2	62.7	870.3
May	13.2	20.5	47.8	132.9	1342.4
June	9.5	14.3	24.9	50.6	297.6
July	9.7	14.2	22.4	30.7	93.3
August	9.5	14.4	24.8	39.5	404.8
September	10.4	15.6	27.1	47.3	187.5
October	11.2	17.4	40.0	115.6	447.9
November	15.7	24.8	58.4	120.7	1073.7
December	19.6	28.5	59.3	126.2	677.9

Table 2.4: Distribution of PM_{10} $(\mu g m^{-3})$ Boundary Rd by Month

Month	Median	75 Percentile	95 Percentile	99 Percentile	Max
January	6.9	9.7	17.4	29.6	94.2
February	7.3	10.0	16.1	29.4	129.8
March	7.1	10.3	22.8	37.0	149.8
April	5.8	8.9	15.2	25.1	93.5
May	7.1	12.0	22.1	40.6	132.3
June	5.1	7.2	12.0	17.5	50.7
July	5.1	7.1	11.2	17.2	56.7
August	5.5	7.6	12.0	18.1	68.4
September	5.3	7.5	11.8	16.6	65.9
October	5.4	8.0	15.0	26.6	126.0
November	6.8	10.7	24.0	52.7	551.9
December	7.2	10.3	19.2	37.2	137.8

Table 2.5: Distribution of $\mathrm{PM}_{2.5}$ $(\mu g m^{-3})$ Boundary Rd by Month

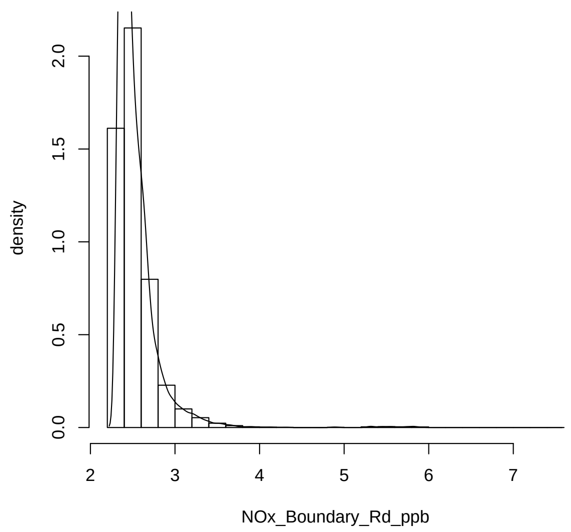

Figure 2.1: NO_x Distribution at Boundary Road, log ppb. The solid line is a kernel density estimate of the distribution.

2.3 Monthly Variation in Wind Direction, Oxides of Nitrogen and Airborne Particulates

Figure 2.2 shows box and whisker plots for the proportion of each day in which the wind is from the North ($350°$ to $25°$) by month. It is clear that there are substantial differences between months in wind direction. Throughout the winter months (May to August) the wind is often from the North; throughout the summer months the wind is rarely from the North.

Figures 2.3, 2.4 and 2.5 show the mean natural log concentration of NO, NO_2 and NO_x by month, respectively. All three measurements show a pronounced *reduction* during the winter months. That is, considered on a monthly basis, Oxides of Nitrogen (NO, NO_2 and NO_x) are lowest during those seasons when the wind is blowing from the direction of the plant.

Figures 2.6 and 2.7 show similar plots for the log mean values of PM_{10} and $\mathrm{PM}_{2.5}$ respectively. Again PM_{10} and $\mathrm{PM}_{2.5}$ values tend to be *lower* during the winter months, when the wind is blowing from the direction of the plant. It is, however, likely that drier conditions during the summer increase the lift off of dust.

If the effects of wind direction are considered in isolation from the effects of other meteorological conditions, it appears unlikely that the plant is a major source of the Oxides of Nitrogen or particulate matter detected at the Boundary Rd Yarloop monitoring station. These measurements are *lowest* when the wind is blowing from the refinery towards the monitoring station.

Wind transport, however, is a complex multi-factorial process; and most of the determining factors (eg temperature, wind direction, wind speed, humidity) show marked seasonal trends. It is possible that the effect of wind direction on Oxides of Nitrogen and airborne particulates is masked by relationships with other seasonally varying parameters. This issue can be resolved only by a joint analysis, which investigates the simultaneous effects of several meteorological variables.

2.4 Joint Analysis of Meteorological Conditions

Details of this analysis are provided in the technical appendix to this chapter. This section provides only an informal overview of the approach.

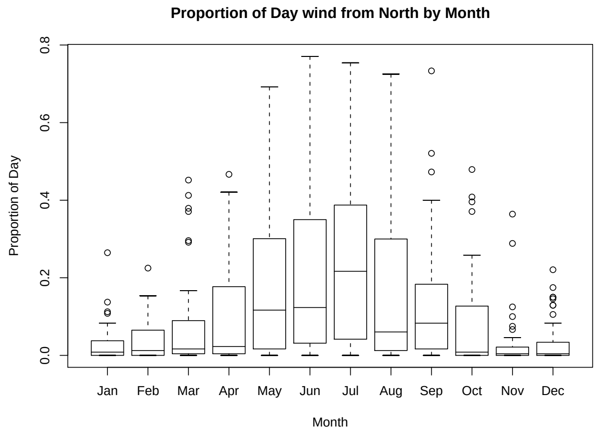

Figure 2.2: Proportion of Day with Wind from North by Month, at Boundary Road. The wind is often from the North during the winter months.

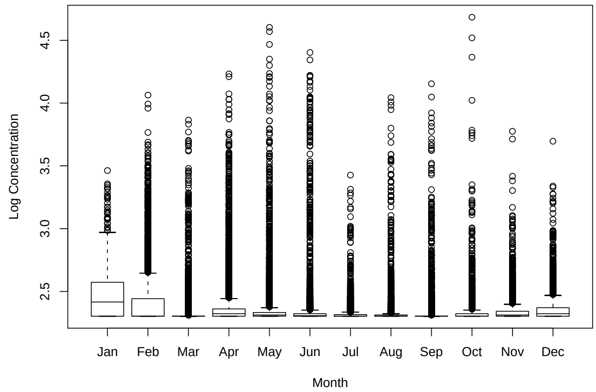

Figure 2.3: log Nitric Oxide Concentrations (ppb) by Month, at Boundary Road. Note the apparent decrease in Nitric Oxide concentration during the winter months.

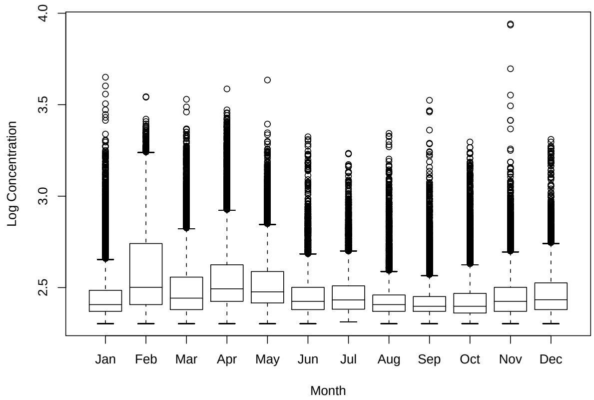

Figure 2.4: log Nitrogen Dioxide Concentrations (ppb) by Month, at Boundary Road. Note the slight decrease in concentration during the winter.

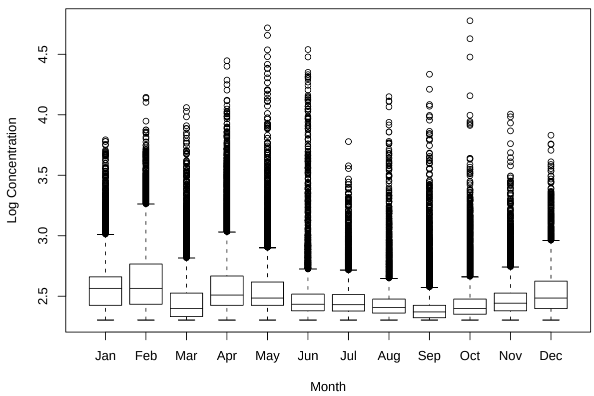

Figure 2.5: log Total Oxides of Nitrogen Concentrations (ppb) by Month, at Boundary Road. Note the decrease in concentration during the winter.

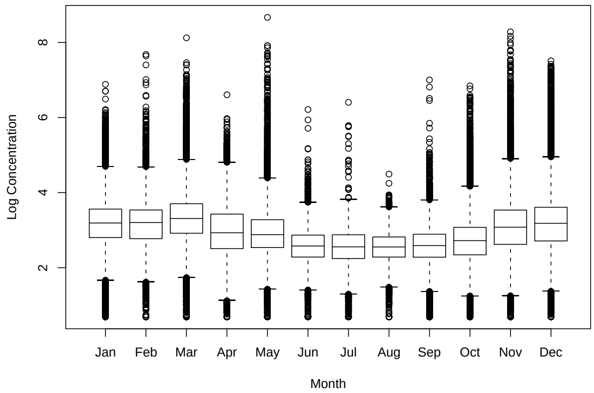

Figure 2.6: log PM_{10} $(\mu g m^{-3})$ by Month, at Boundary Road. Note the decrease in concentration during the winter.

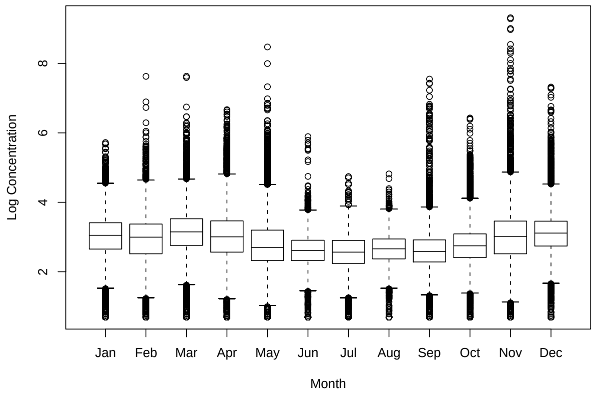

Figure 2.7: $\mathrm{PM}_{2.5}$ $(\mu g m^{-3})$ by Month, at Boundary Road. Note the decrease in concentration during the winter.

Since irritant effects (and therefore the most likely environmental nuisance associated with the refinery) are sensitive to short–term peak concentrations, we analyse the probability of a peak value of each Oxide of Nitrogen or airbone particulates parameter, rather than the mean value. A peak value is defined as being in the top 5% of all values. The rationale for this definition is given in the technical appendix to the Chapter.

The analysis was based on a generalised linear model for the probability that a 6 minute Oxides of Nitrogen or airborne particulates measurement will be a peak value. The model included terms for month, time of day, wind speed, temperature and terms for a smooth periodic function of wind direction (the periodic function was used to ensure that the estimated effect of a $360°$ wind direction was the same as the estimated effect of a $0°$ wind direction). The purpose of this model was to allow an analysis of the joint effect of these meteorological conditions. Specifically, we were looking to see whether or not there was any effect of wind direction, after having accounted for the effects of other meteorological variables.

The wind direction terms are then used to display the effect of wind direction on logit probability of a peak value (the logit transformation stretches out the $(0, 1)$ interval for a probability to $\pm$ infinity). A 95% confidence interval for the wind direction effect is calculated using a blocked bootstrap procedure. Details are given in the technical appendix.

2.4.1 Analysis of Oxides of Nitrogen

Figures 2.8, 2.9 and 2.10 show the change in logit probability of a peak value with wind direction for NO, NO_2 and NO_x respectively at Boundary Rd. In each plot the pink-shaded region corresponds to wind directions from $0°$ to $15°$. These wind directions encompass the calciners, liquor burner, and powerhouse stacks. The blue-shaded region (from $300°$ to $345°$) contains the RDAs, and the green-shaded region (from $160°$ to $220°$) contains most of the residential properties in Yarloop. The black lines represent the upper and lower 95% bootstrap confidence intervals for the wind direction effect. The red lines represent the best (see the technical appendix) estimate of the effect.

The wind direction effect is estimated much more poorly for NO than for NO_2 or NO_x; the confidence intervals are much wider, and give little or no information about the wind directions associated with the highest probability of peak NO values.

For $\mathrm{NO_2}$ and NO_x, however, there is a clearly defined wind direction effect, with relatively tight confidence intervals. Both of these parameters show a well defined peak direction associated with the direction of the refinery stacks (calciner, liquor burner and powerhouse). Both variables also show a peak which is associated with the direction of residential property in the town of Yarloop, and a peak in the direction of the RDAs ($300°$ to $345°$). In both of these figures, there seem to be several subsidiary peaks in the region $100°$ to $220°$. These subsidiary peaks are almost certainly an artifact of the modelling process, and represent harmonics in the fitted periodic function. These subsidiary peaks are poorly defined in comparison with their confidence intervals.

Nitrogen Oxides measurements are also available from the Upper Dam monitoring station, within the refinery. This is some five kilometres north of the Boundary Rd station, and a strong directional signal from this source provides a way of localising possible point sources of Nitrogen Oxides. Figures 2.11, 2.12 and 2.13 show plots of the wind direction effect on logit probability of a peak value at the Upper Dam, for Nitrogen Oxide, Nitrogen Dioxide and total Oxides of Nitrogen respectively.

In these plots, the pink region encompasses the direction of the calciner, liquor burning and powerhouse stacks ($200°$ to $210°$), and the green region represents the direction of most of the Yarloop properties ($185°$ to $200°$). Again, the black lines represent the upper and lower 95% confidence intervals, and the red line is the best estimate of the wind direction effect.

The most striking feature of these graphs is that all show a peak in the region $200°$ to $210°$. That is, the highest probability of a peak concentration of oxides of Nitrogen is found when the wind is blowing from the direction of the refinery stacks. At this location, however, the direction of the town of Yarloop and the refinery stacks are not well resolved. These plots also suggest elevated Oxides of Nitrogen concentrations associated with winds from $300°$ to $345°$.

Although the measurements at the Upper Dam cannot resolve the effect of refinery stacks and the Yarloop properties, when the Upper Dam results are considered in conjunction with the Boundary Rd results the implication is clear. The best defined peaks at the Upper Dam and at Boundary Rd both point in the direction of the refinery stacks. At each site, there also seems to be some elevation in Nitrogen oxide concentrations associated with winds from the residential properties at Yarloop. Both sites also provide some evidence of elevated concentrations associated with wind directions in the region of $300°$ to $360°$. This would be consistent with a distant, or more diffuse source of Oxides of Nitrogen.

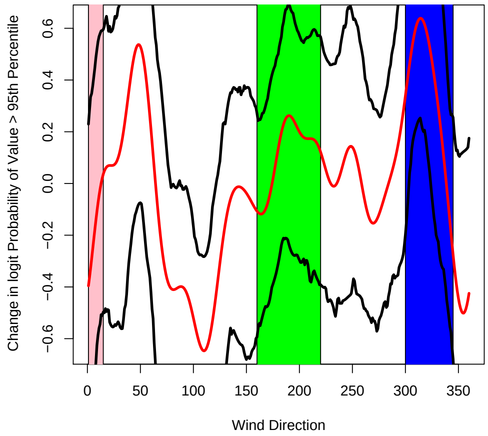

Figure 2.8: Effect of Wind Direction on Probability of Peak Nitric Oxide - Boundary Rd. Confidence intervals are wide relative to the size of the effect on logit probability, and any wind direction effect is poorly characterised.

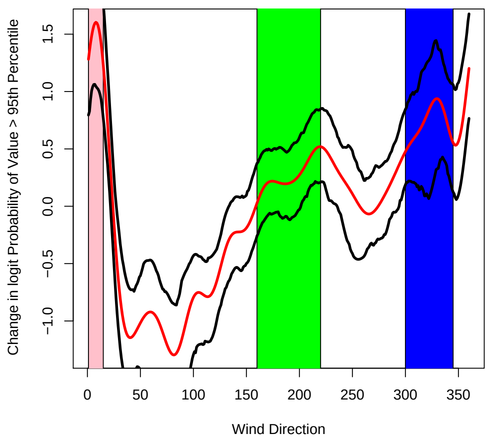

Figure 2.9: Effect of Wind Direction on Probability of Peak Nitrogen Dioxide - Boundary Rd. The pink region represents winds from the direction of the refinery stacks. The green region represents winds from the direction of Yarloop properties, and the blue region represents winds from the direction of the RDAs. The curves suggest a well defined source in the direction of the refinery stacks, and more diffuse sources in the direction of the RDAs and Yarloop.

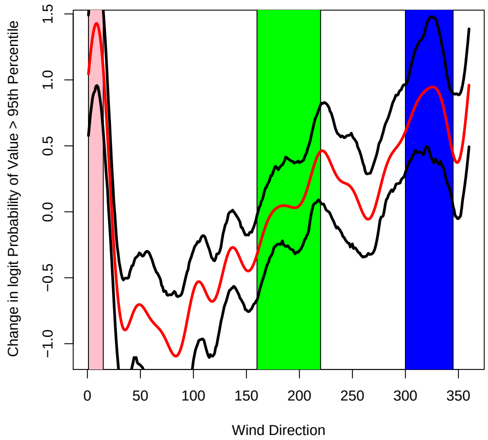

Figure 2.10: Effect of Wind Direction on Probability of Peak Nitrogen Oxides - Boundary Rd. The pink region represents winds from the direction of the refinery stacks. The green region represents winds from the direction of Yarloop properties, and the blue region represents winds from the direction of the RDAs. The curves suggest a well defined source in the direction of the refinery stacks, and more diffuse sources in the direction of the RDAs and Yarloop.

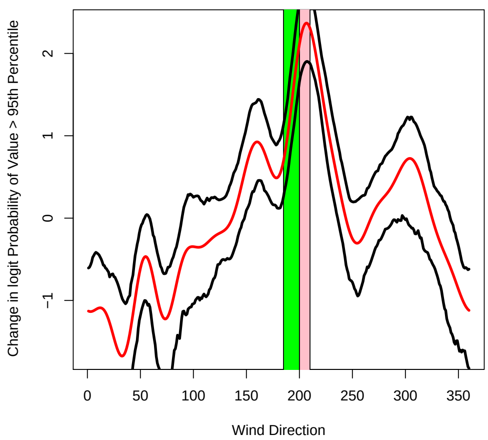

Figure 2.11: Effect of Wind Direction on Probability of Peak Nitric Oxide - Upper Dam. The pink region represents winds from the direction of the refinery stacks. The green region represents winds from the direction of Yarloop properties. The apparent peak at $300°$ cannot be linked to any potential source on the refinery complex.

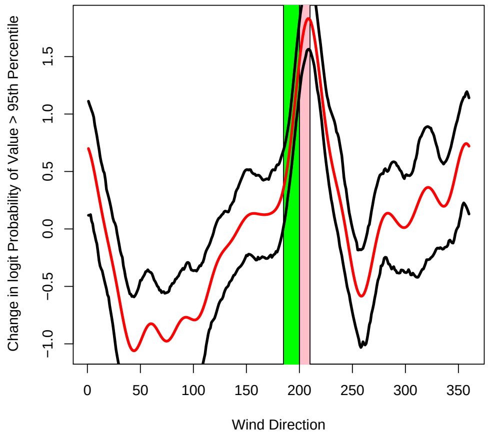

Figure 2.12: Effect of Wind Direction on Probability of Peak Nitrogen Dioxide - Upper Dam. The pink region represents winds from the direction of the refinery stacks. The green region represents winds from the direction of Yarloop properties. The apparent peak at $360°$ cannot be linked to any potential source on the refinery complex.

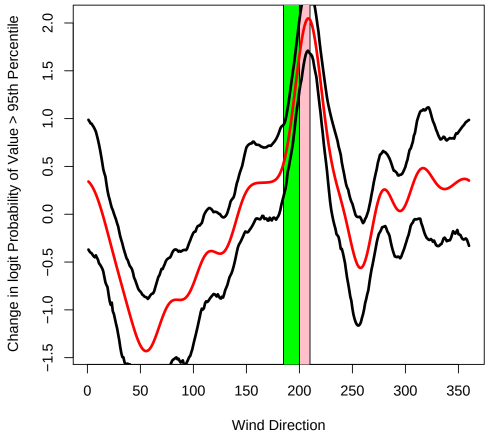

Figure 2.13: Effect of Wind Direction on Probability of Peak Nitrogen Oxides - Upper Dam. The pink region represents winds from the direction of the refinery stacks. The green region represents winds from the direction of Yarloop properties. The apparent peak at $360°$ cannot be linked to any potential source on the refinery complex.

2.4.2 Analysis of Particulate Concentrations

Figures 2.14, 2.15, 2.16 and 2.17 show wind direction profiles for PM_{10} and $\mathrm{PM}_{2.5}$ at Boundary Rd, and for Total Suspended Particulates at the South and South West RDAs, respectively.

At Boundary Rd PM_{10} and $\mathrm{PM}_{2.5}$ values show a very similar wind direction profile. Peak values of both parameters are associated with winds in the direction 275° to 360°. These directions include both the RDAs and the refinery stacks (calciner, liquor burning and powerhouse). In addition, the $\mathrm{PM}_{2.5}$ values show elevated probabilities of a peak value when the wind is in the direction of 200° to 275°. The Upper Dam site did not have records of PM_{10} or $\mathrm{PM}_{2.5}$, and it is therefore not possible to triangulate these directions to identify a geographical source.

The wind profile for TSP at the south RDA is very variable, but there does seem to be a peak at 350°; this is consistent with winds passing over the RDA to the monitoring station. At the South West RDA the wind profile is variable, but the lowest probability of a peak value occurs with the wind at 250° - when it is blowing from the monitoring station towards the RDA. The RDA monitoring sites are too close to the RDA to provide effective triangulation with the monitoring site at Boundary Rd.

It seems likely that the peak values of PM_{10} and $\mathrm{PM}_{2.5}$ at Boundary Rd are associated with wind from the direction of the refinery. It is not possible to localise this effect within the plant. The peak is consistent with a source from the RDAs, from the calciner stacks, from a combination of the two or indeed from any source in that direction.

2.5 Conclusions

Transport of Oxides of Nitrogen is a multifactorial process. When all available meteorological variables are taken into account there is evidence of an increased tendency towards peak concentrations in Yarloop when the wind is blowing from the refinery stacks (liquor burning, calciner and powerhouse). This provides objective evidence that refinery operations produce detectable increases in Oxides of Nitrogen concentration.

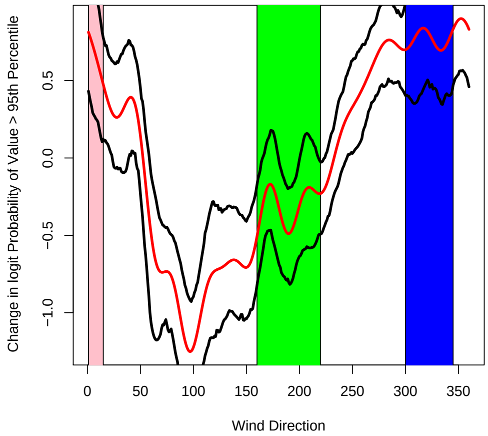

Figure 2.14: Effect of Wind Direction on Probability of Peak PM_{10} at Boundary Rd. The pink region represents winds from the direction of the refinery stacks. The green region represents winds from the direction of Yarloop properties, and the blue region represents winds from the direction of the RDAs. Winds from the direction of the refinery complex are associated with increased PM_{10} concentrations.

There is also an increased tendency towards peak concentrations of Oxides of Nitrogen when the wind is blowing from the direction of residential properties in Yarloop, and from the directions $345°$ to $360°$.

The observed peak concentrations of Oxides of Nitrogen are substantially below those that are likely to be irritant [3, 2].

The probability of peak values of PM_{10} occurring is greatest when wind is coming from the direction of the refinery - including the RDAs and stacks. The probability of peak values of $\mathrm{PM}_{2.5}$ occurring is greatest when wind is coming from the direction of the refinery – including the RDAs and stacks. The probability of peak values of $\mathrm{PM}_{2.5}$ occurring when wind is coming from the direction of Yarloop is not substantially less, however.

2.6 Technical Appendix

Analysis of wind direction was restricted to those records containing a full set of monitoring data - ie the period March 2002 to January 2004 inclusive.

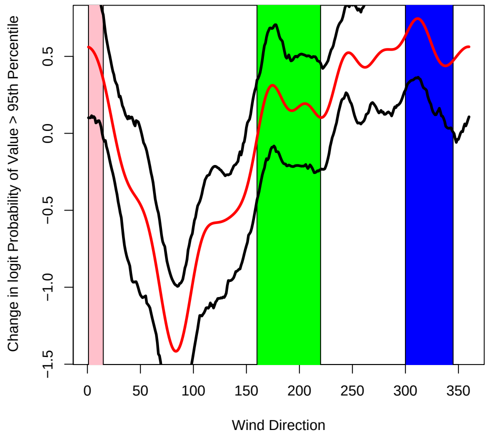

Figure 2.15: Effect of Wind Direction on Probability of Peak $\mathrm{PM}_{2.5}$ at Boundary Rd. The pink region represents winds from the direction of the refinery stacks. The green region represents winds from the direction of Yarloop properties, and the blue region represents winds from the direction of the RDAs. Winds from the direction of the refinery complex are associated with increased $\mathrm{PM}_{2.5}$ concentrations. There is some evidence of elevated $\mathrm{PM}_{2.5}$ associated with winds from the direction of Yarloop.

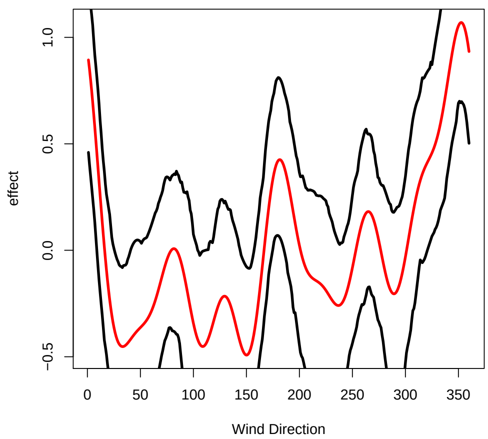

Figure 2.16: Effect of Wind Direction on Probability of Peak TSP at the South RDA. The confidence intervals are wide, and any wind direction effect is poorly defined. There does seem to be a peak in the direction of $360°$.

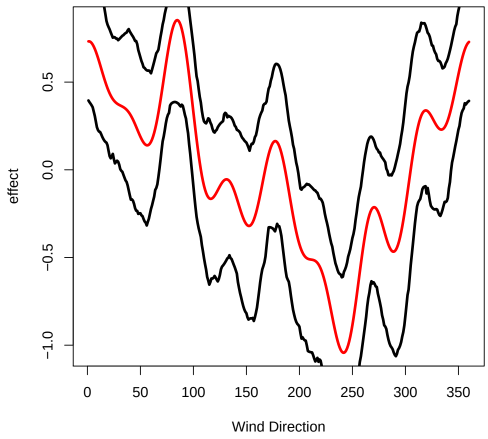

Figure 2.17: Effect of Wind Direction on Probability of Peak TSP at the South West RDA.The confidence intervals are wide, and any wind direction effect is poorly defined. There does seem to be a peak in the direction of $360°$.

Daily and hourly averages of Oxides of Nitrogen and particle concentrations in Yarloop are well below the established health limits for these variables [2]. Therefore, if there are any irritant effects of Oxides of Nitrogen or airborne particulates they are likely to be caused by transient peak values in these variables. We therefore analyse the concentrations in terms of the probability of obtaining a peak value. In these analyses a “peak” value of any concentration is defined as being any value within the top 5% of all values. This definition represents a balance between the need to identify effects on rare peak observations, and the decrease in power (increase in variability) of the analysis as more extreme definitions of “peak” values are adopted.

The analysis was based on a generalised linear model for the probability that each six minute period represented a “peak” value of each Oxides of Nitrogen or airborne particulates parameter. This analysis looked at the effect of wind direction simultaneously with the effect of other environmental conditions (*vide infra*). A binary variable was constructed for each Oxides of Nitrogen or airborne particulates parameter - set “TRUE” if the parameter was in the top 5% of values. The binary variable was analysed using a Generalised Linear Model [8], The analysis was undertaken with a logit link, and a Binomial error model.

Wind direction data are circular. A wind direction of 360° is very similar to a wind direction of 1°. The model therefore incorporates wind direction effects using a Fourier series model of the form:

$$W = \sum_{i=1}^{k} \alpha_i \sin(\frac{2\pi ix}{360}) + \beta_i \cos(\frac{2\pi ix}{360})$$

Where W is the effect of wind direction $x°$, k is the number of Fourier terms in the model, and $\alpha_{1...k}$ and $\beta_{1...k}$ are parameters to be estimated from the data. The Fourier model is a periodic function of wind direction, ie, it is constrained to predict the same wind effect for 360° as for 0°. The number of Fourier terms k was set as 12. A twelfth order series provides a flexible model for the wind direction effect, and is readily estimated given the number of observations. The value was limited to twelve because of the computational cost of the bootstrap analysis (*vide infra*).

Other terms in the model for mean pollutant concentration included month of the year (a factor with 12 levels), hour of the day (a factor with 24 levels), temperature at 2 metres and at 10 metres, relative humidity, solar radiation, wind velocity, barometric pressure and rainfall.

The coefficients $\alpha_{1...k}$ and $\beta_{1...k}$ of the fitted model were extracted, and used to identify the contribution of each angle of wind direction to the mean concentration of the substance concerned.

Given the serial correlation between successive observations, confidence intervals were calculated using a bootstrap procedure [6]. Serial correlation between observations was accommodated using a blocked bootstrap [5], with blocks set to 240 six minute observations (ie one day). Choice of block size is problematic; the analyses were repeated with varying block sizes, and the results were very similar for blocksizes of 480. For each analysis, 1,000 bootstrap simulations were performed, and used to generate point-wise 95% confidence intervals for the impact of each degree of wind direction on the probability of pollutant levels.

Chapter 3

Alkalinity of Airborne Particles

3.1 Background

In a study conducted between 26^{th} August and 2^{nd} September 2002, Morawska *et al* [9] measured the particle concentration at Boundary Rd, when the wind was blowing from the Northern quadrant ($315°$ to $45°$). The accumulated PM_{10} particle samples were titrated for alkalinity, and used to estimate an equivalent concentration of Sodium Hydroxide - which was found to be $0.255 \pm 0.007 \mu g m^{-3}$, for the PM_{10} fraction. This concentration represents a weekly average - and peak concentrations could be substantially greater.

3.2 Estimation of Peak Concentrations

During the period concerned, the mean PM_{10} concentration for wind directions from the Northern Quadrant was $11.67 \mu g m^{-3}$. If we assume that transient equivalent concentrations of NaOH are directly proportional to the PM_{10} concentration *whilst the wind is blowing from the Northern quadrant*, then we may estimate the NaOH equivalent concentration at any value of PM_{10} as follows:

$$N = \frac{N_{mean} P}{P_{mean}}$$

Where N is the estimated alkalinity (equivalent mols of NaOH), P is the value of PM_{10} for which alkalinity is to be estimated, P_{mean} is the average PM_{10} whilst the wind is from the Northern quadrant during the period 26^{th} August 2002, to 2^{nd} September 2002 (ie 0.255) and N_{mean} is the average alkalinity during the period 26^{th} August 2002, to 2^{nd} September 2002. This expression, of course, is relevant only for those values of PM_{10} measured whilst the wind is blowing from the Northern quadrant.

Using this expression, we may estimate the peak NaOH equivalents each day, from the peak Northern quadrant PM_{10} values each day. The peak estimate, however, is likely to be too low. This is because:

- The Morawska experiment captured particlate matter when the wind was from the Northern quadrant - but the likely source of alkaline particles should be over a angle of less than $45°$. This will dilute the alkalinity estimate.

- The finest time resolution available is 6 minutes. It is possible that peak values within this sampling interval are substantially greater than average values.

If we double the estimated peak values for each of these factors, we have a four fold increase in estimated NaOH equivalents.

Using this procedure, we calculate the estimated peak NaOH concentration each day from the peak PM_{10} when the wind is in the Northern quadrant. The overall maximum estimated NaOH concentration is $93\mu gm^{-3}$. Figure 3.1 shows the daily maximum estimated NaOH equivalent concentration plotted by month.

3.3 Conclusions

This concentration peak estimated NaOH equivalent concentration of $93\mu gm^{-3}$ is substantially below the Threshold Limit Value (TLV) for NaOH of $2000\mu gm^{-3}$ [1]. It is therefore unlikely to produce irritant responses. Furthermore, the daily estimated peak concentration is *lowest* during the winter months when there are most complaints (see below). Daily peak concentrations during the winter months are generally below $20\mu gm^{-3}$, - around 1% of the TLV.

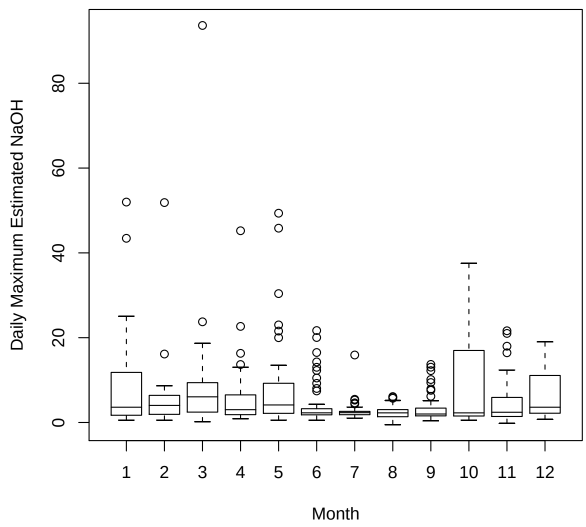

Figure 3.1: Peak Daily Estimated NaOH Equivalents by Month Boundary Rd

On the basis of conservative estimates of peak alkalinity, (ie estimates which are likely to *over estimate* alkalinity), there is no evidence of particles with alkalinity sufficient to cause an irritant response. It is considered unlikely that complaints are generated by a irritant response to airborne alkaline particles.

Chapter 4

Environmental Measurements and Community Complaints

4.1 Objectives and Background

This chapter describes a study undertaken to investigate the relationship between meteorological factors, Oxides of Nitrogen, airborne particulates and the incidence of complaints. In particular, the study seeks to establish whether or not there is any relationship between wind direction, particle concentration, Oxides of Nitrogen and incidence of complaints. Such a relationship would provide objective evidence of an association between refinery outputs and community complaints. The nature of the relationship might also suggest possible mitigation strategies.

Wind direction is of interest because of the observed high frequency of winds from the North during the winter months. Winds from this direction cross the refinery before reaching the town of Yarloop - and complaints are more frequent in the winter months (*see below*).

Particle concentrations are potentially interesting because particles originating from the calciner stacks or the RDAs may be alkaline [9], and particles may make a direct contribution to dust.

Nitrogen Oxide (NO_x) concentration is present at concentrations far too low to generate irritant responses [2]; but it may act as a marker for the refinery plumes. That is, peak measurements of NO_x may indicate that a plume has reached ground level near to the measuring station.

4.2 Descriptive Statistics for Complaints Data

Complaints records are available from 24th April 2000 to 18th September 2004. Comprehensive Oxides of Nitrogen and airborne particulates data are only available for the period March 2002 to January 2004. Analysis of complaints which do not refer to the relationship with air quality are for the entire period of complaints data; but analyses relating complaints to air quality are restricted to the period for which Oxides of Nitrogen and airborne particulates data exist.

Complaints are classified by the issue type. Only two issue types are sufficiently common to warrant separate analysis: Health issues and Odour issues. Individual complainants have been assigned unique identifiers; this allows an analysis of the distribution of the number of complaints made by each complainant. No individual complainants are named in this report.

From the period 24th April 2000 to 18th September 2004 there were 3124 complaints, lodged by 250 complainants. The distribution of the number of complaints made by each complainant is shown in Figure 4.1. The mean number of complaints per complainer was 12.5, and the variance 895.1. If each complainant were equally likely to complain, and each complaint was independent, one would expect the distribution of the number of complaints per complainant to follow a truncated Poisson distribution. From elementary probability theory, the variance to mean ratio for a truncated Poisson distribution is less than 1 for all values of the mean. The observed data are therefore strongly inconsistent with a truncated Poisson distribution. We may conclude that either:

1. All complainants are not equally likely to complain; or
2. Complaints are not independent (ie once a complaint has been made, a complainant is more likely to complain again); or
3. both 1. and 2. above.

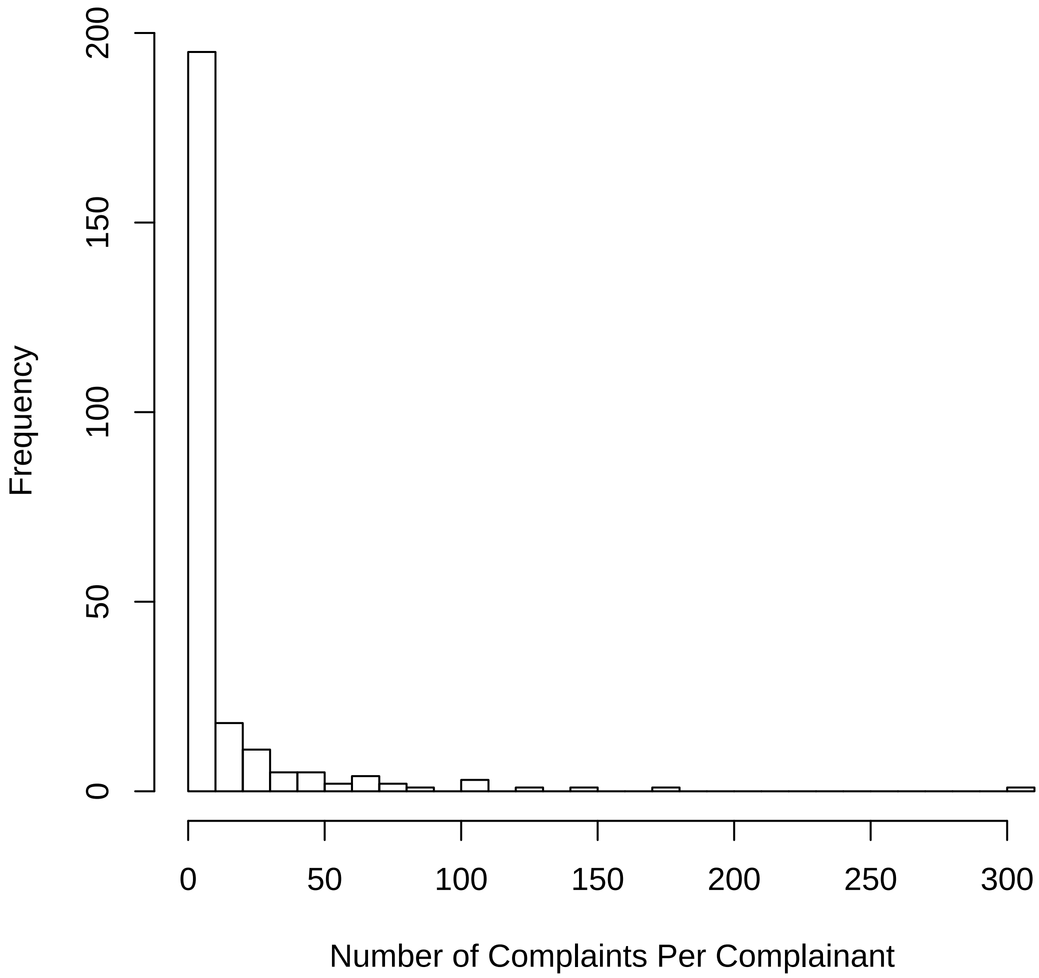

Figure 4.1: Distribution of Number of Complaints made by Each Complainant

More than half of the complaints were made by the 16 individuals who complained on 50 or more occasions. For the purposes of discussion, we categorise individuals who have made more than 50 complaints as *high frequency complainants*, and other individuals as *low frequency complainants*. The threshold of 50 complaints was chosen so as to split the total complaints evenly between "high" and "low" frequency complainants. Table 4.1 summarises the number of complaints by issue type (all issues, odour and health) and complainant type (all complainants, high and low frequency complainants). All issue types show a similar pattern - a relatively few individuals generate a large proportion of the total number of complaints.

It is possible that high frequency and low frequency complainants are responding to different environmental, social or personal circumstances. To investigate this potential difference, analyses were repeated for complaints made by low frequency complainants (those 234 complainants who complained on 50 or less occasions) and for complaints made by high frequency complainants (those 16 complainants who lodged more than 50 complaints).

	Complainant Type		
Issue	All (250 Complainants)	High Frequency (16 Complainants)	Low Frequency (234 Complainants)
Total	3124	1665	1459
Odour	2687	1482	1205
Health	376	169	207

Table 4.1: Number of Complaints by Issue and by Complainant Frequency.

4.3 Overview of Analysis

Box and whisker plots for the number of complaints each day were plotted against month.

For each complaint type, the natural log of the number of complaints each day (plus 1 to avoid the problem with the log of zero) was plotted against each of the meteorological, Oxides of Nitrogen and airborne particulates summary variables. Given the low number of complaints per day, the relationships are noisy. The underlying trend was illustrated by fitting a robust trend line using the lowess [4] line (with span of 0.5).

A generalised linear model was used to investigate the relationship between daily incidence of each complaint type, and meteorological, Oxides of Nitrogen and airborne particulates conditions. Details of the generalised linear model are given in the technical appendix to this chapter. Confidence intervals for each parameter were constructed using a blocked bootstrap procedure [6, 5].

For each day, the following meteorological, Oxides of Nitrogen and airborne particulates summaries were constructed:

Wind.N The proportion of the day with the wind from the North (ie wind direction $\geq 350°$ and wind direction $\leq 25°$).

Wind.NW The proportion of the day with the wind from the North West (ie wind direction $\geq 300°$ and wind direction $\leq 350°$).

PM_{10}**.p** The proportion of the day with an elevated PM_{10} measurement (where elevated is defined as being above the 95^{th} percentile).

$\mathrm{PM}_{2.5}$**.p** The proportion of the day with an elevated $\mathrm{PM}_{2.5}$ measurement (where elevated is defined as being above the 95^{th} percentile).

NOx.p The proportion of the day with an elevated NO_x measurement (where elevated is defined as being above the 95^{th} percentile).

Temp The daily mean temperature at a height of 2m.

Most of the quantities used in this analysis show pronounced differences between months. The environmental variables are therefore quite strongly correlated with each other. It is not possible to produce an un-ambiguous analysis of the effects of each environmental variable - since the strength of relationship calculated for any one environmental variable depends on which other variables are included in the model. The results produced in this analysis allow an assessment of the effects of each environmental variable *when all of the other variables have been included in the model*.

Analyses were repeated using a factor to represent month (ie using 11 degrees of freedom to fit the yearly pattern of response). Results were broadly similar to those obtained without using month - but the confidence intervals were wider. These results are not presented, since they provide little further information. It seems unlikely that unknown seasonally variable environmental factors are masking the effect of the environmental variables which *have* been included in the model.

4.4 Results

Figure 4.2 shows box and whisker plots for the daily incidence of each complaint type. There are clear increases in total complaints and odour-related complaints during the winter months, and there is some suggestion that health-related complaints increase during the winter. There is a fairly close agreement between the monthly incidence of complaints, and the monthly proportion of each day with a northerly wind (see Figure 2.2).

Figures 4.3, 4.4 and 4.5 show plots of log complaints incidence vs ambient measurements for total complaints, odour-related complaints and health-related complaints respectively. The red line on each plot is the estimated lowess fit to the data [4].

There does seem to be evidence of a relationship between the incidence of complaints and the proportion of each day with a northerly or north westerly wind. The relationship is apparent for total complaints and for odour-related complaints, but the incidence of health-related complaints is too low to draw conclusions.

The bootstrap confidence intervals from the generalised linear model are presented in Table 4.2. These results are obtained with a bootstrap block size of 7 days, but the results were essentially unchanged as the block size varied from 4 to 14. For total complaints, low frequency complainants show a statistically significant increase with $\mathrm{PM}_{2.5}$, NO_x and wind direction, and a just statistically significant decrease with temperature; High frequency complainants however have a statistically significant relationship only for wind.

For odour complaints, low frequency complainants are statistically significantly related to wind direction and NO_x, but high frequency complainants are statistically significantly related only to wind direction.

Health-related complaints are statistically significantly related to wind direction, but not to the other parameters, except for NO_x for low frequency complainants.

4.5 Conclusions

Overall there is some evidence that the incidence of complaints is related to objective, measurable features of ambient conditions. It is not possible, however, to rule out complaints being driven by other variables which are not available in this study, but which show strong seasonal trends.

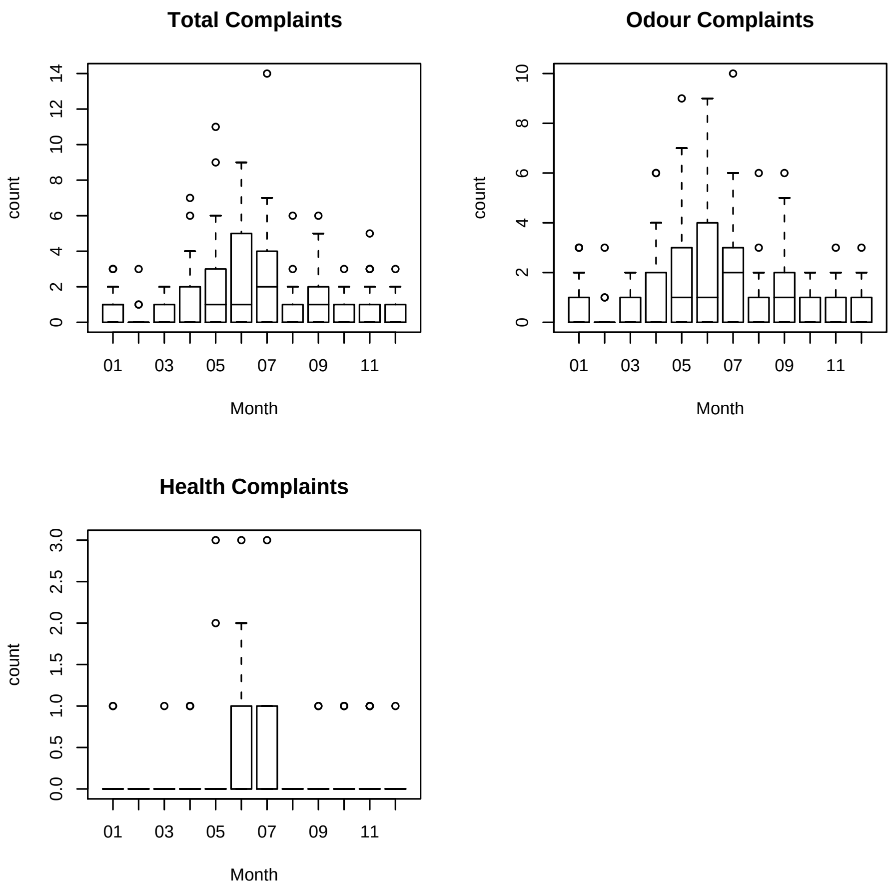

Figure 4.2: Incidence of Complaints by Issue Type and Month. Total complaints are dominated by odour issues, and both total complaints and odour issue complaints peak during the winter months. There is some suggestion that health-related complaints also increase during the winter months.

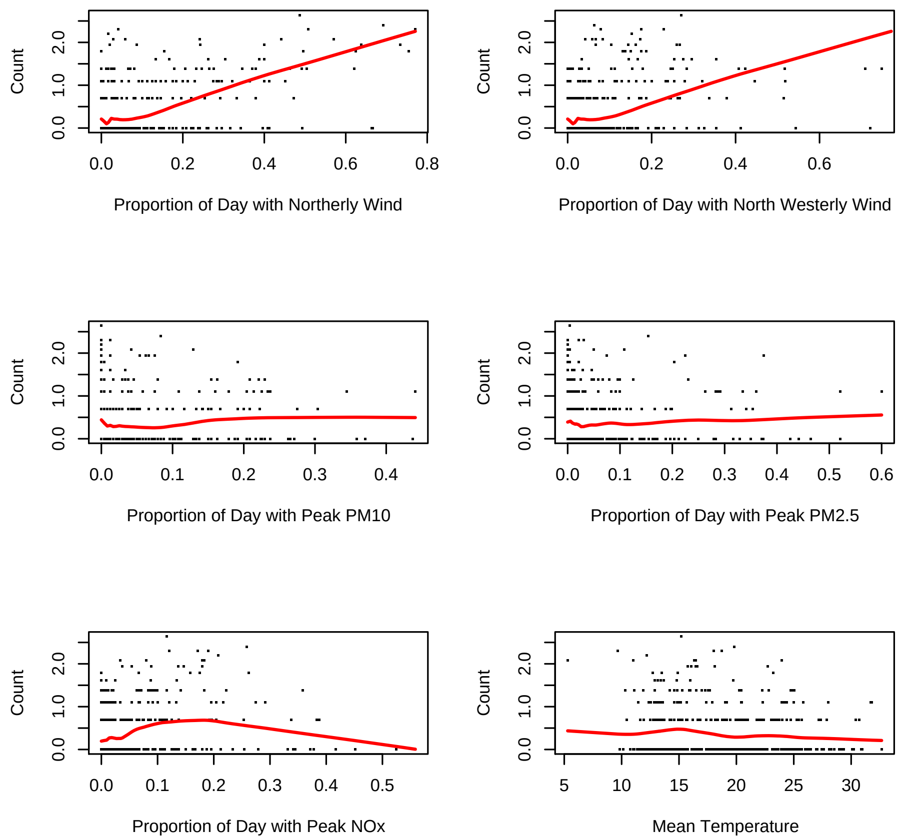

Figure 4.3: Incidence of All Complaints by Oxides of Nitrogen, Airborne Particulates and Meteorological Variables. The red line is a lowess fit. There is evidence of an increase in complaint frequency with the proportion of the day having a northerly wind and a north westerly wind.

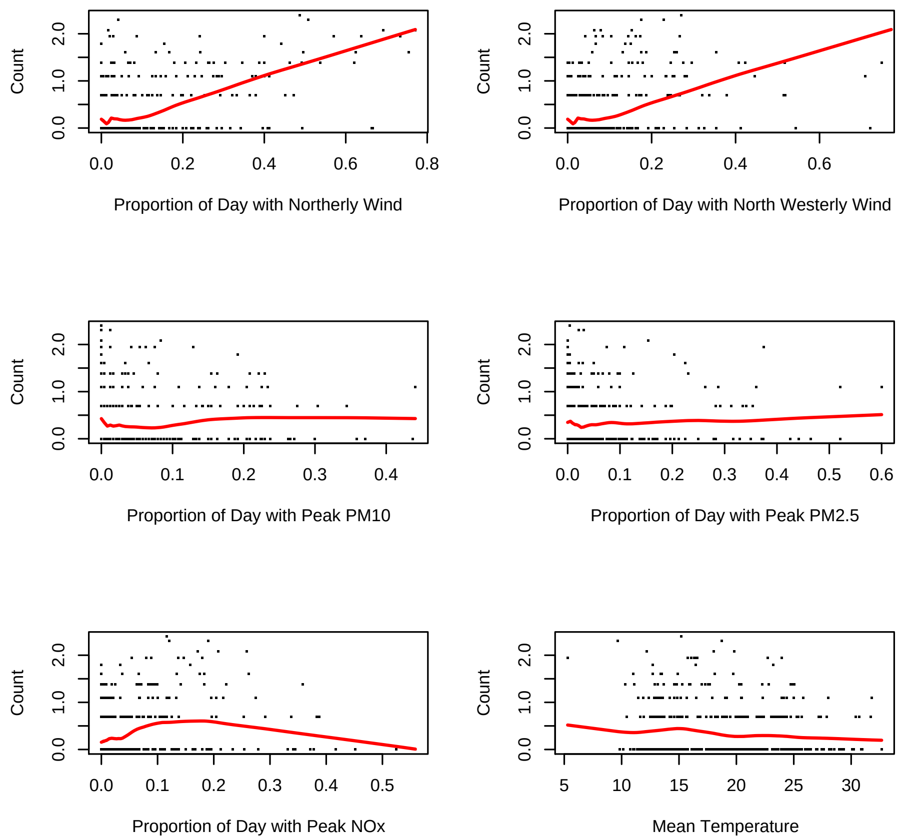

Figure 4.4: Incidence of Odour Complaints by Oxides of Nitrogen, Airborne Particulates and Meteorological Variables. The red line is a lowess fit. There is evidence of an increase in complaint frequency with the proportion of the day having a northerly wind and a north westerly wind.

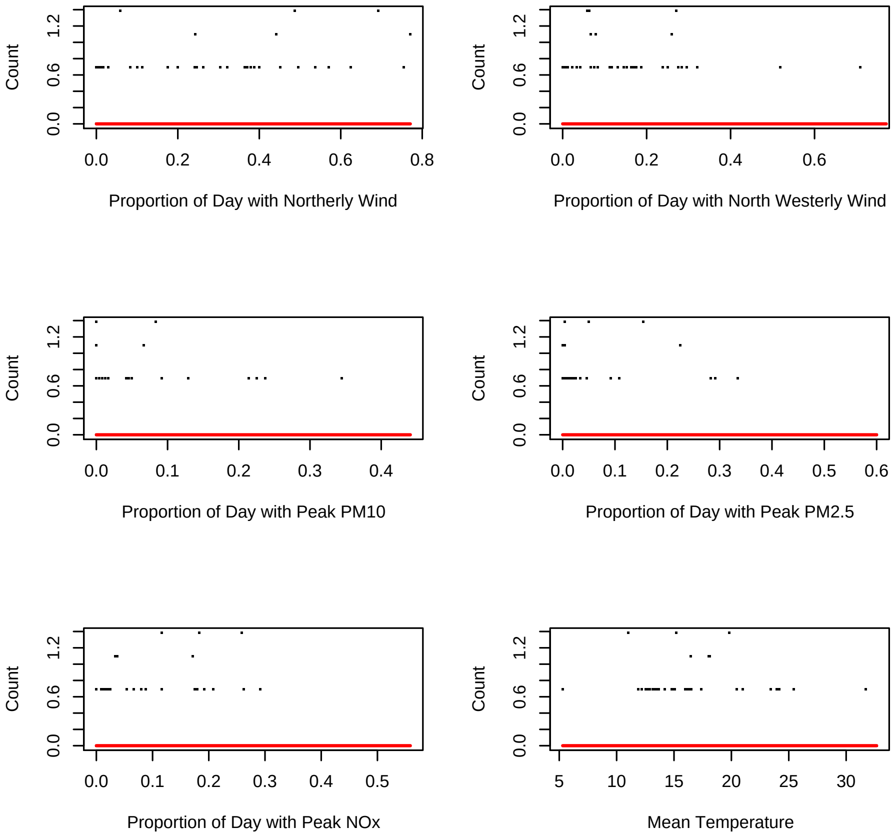

Figure 4.5: Incidence of Health Related Complaints by Oxides of Nitrogen, Airborne Particulates and Meteorological Variables. The red line is a lowess fit. The incidence is too low to provide much evidence for any relationship with environmental measurements.

Total complaints and odour-related complaints show a near identical pattern of response - since odour complaints make up the majority of complaints. There is evidence that complaints are increased when the wind is often from the direction of the refinery (the North and North West). There is also evidence that the complaints are increased when much of the day shows elevated NO_x measurements and elevated $\mathrm{PM}_{2.5}$ measurements. NO_x is unlikely to be the causative agent for odour-related complaints; but periods with increased incidence of elevated NO_x concentrations are likely to be periods with increased impact from the stack plumes. Peak $\mathrm{PM}_{2.5}$ levels may be associated with airborne material from the stacks, from the RDA and possibly from Yarloop.

These results are not definitive, but provide some support for the hypothesis that for low frequency complainants, odour-related complaints (and therefore the total number of complaints) are influenced by airborne material from the refinery complex – either from the stacks or from the RDAs. For high frequency complainants, the lack of a statistically significant relationship with complaint incidence and Oxides of Nitrogen and airborne particulates may suggest that other factors are involved.

4.6 Technical Appendix

The incidence of each complaint type was analysed using a generalised linear model [7] with a Poisson error distribution and a logistic link. The model included all the environmental variables described above. Maximum likelihood estimates of all the linear model coefficients were obtained. There is one important caveat with this analysis. The generalised linear model statistics are based on the assumption that counts on successive days are independent - conditional on the values of the predictor (meteorological and ambient) variables. This assumption may be incorrect for two reasons:-

- The complaints data follow a contagious distribution - once a complaint has been made, there is a transitory lower threshold for further complaints. In this way, a single event may trigger not one, but a series of complaints over several days.
- There are underlying environmental or social processes not included in the analysis, but which show strong autocorrelation over time.

For this reason, standard errors for linear model parameters were obtained using a blocked bootstrap procedure [5], to ameliorate the effects of serial correlation. The analysis was repeated with the block size varying from 4 to 14 days. Results were stable across the range of block sizes, and results for a block size of 7 are presented.

Interpretation is complicated by the strong correlations between the various seasonally variable quantities. The approach used provides a test of the hypothesis that each variable has no relationship with complaint incidence *after having allowed for the effect of all other variables*.

Complainant Type	Environmental Variable	Confidence Interval by Issue Type: Total			Odour			Health		
		Low	Est	High	Low	Est	High	Low	Est	High
high	Temp	−0.10	−0.04	0.01	−0.09	−0.04	0.02	−0.23	−0.08	0.05
	Wind.N	1.74	3.00	3.94	1.51	2.74	3.73	2.94	5.02	6.91
	Wind.NW	0.37	1.65	3.05	0.57	1.77	2.97	−4.66	0.86	3.90
	PM10	−5.65	−1.27	1.65	−4.83	−1.03	1.71	−23.18	−4.70	6.51
	PM25	−0.31	1.58	5.73	−0.21	1.43	5.61	−6.56	3.60	14.49
	NOx	−1.13	0.50	2.56	−1.11	0.55	2.33	−5.79	−0.02	3.79
low	Temp	−0.11	−0.06	−0.01	−0.12	−0.06	0.00	−0.13	−0.06	−0.01
	Wind.N	1.66	2.51	3.36	1.50	2.51	3.48	0.90	2.56	3.70
	Wind.NW	−1.17	0.22	1.55	−1.07	0.48	1.95	−3.30	−0.48	1.79
	PM10	−2.53	−0.02	2.45	−4.31	−0.88	2.32	−2.17	1.06	4.26
	PM25	0.43	1.97	3.49	−0.53	1.73	4.01	−0.57	2.40	4.36
	NOx	0.71	1.82	3.73	0.01	1.49	3.46	0.51	2.42	5.27

Table 4.2: Bootstrap confidence intervals for generalised linear model coefficients for environmental variables. The analysis is from a blocked bootstrap with a block size of 7 days. The table shows confidence intervals for each environmental variable, complaint issue and complainant type. Parameters in which the upper (High) and lower (Low) confidence intervals have the same sign are statistically significant. The point estimates (best supported values) for the parameters are given in the column headed “Est”

Chapter 5

Conclusions

It is clear that ambient Oxides of Nitrogen and airborne particulates parameters are strongly influenced by wind direction, and that a wind direction from the refinery increases both particulate and Oxides of Nitrogen concentrations at Boundary Rd Yarloop. Although this is an observational study, not a designed experiment, it does provide some support for the hypothesis that refinery operations generate elevations in oxides of nitrogen and particulate matter. That conclusion cannot be definitive without further experimental work.

Any elevations in concentrations of Oxides of Nitrogen seem to be of little health or amenity significance. The main interest in these data is that they support the approach used to localise (approximately) the source of emissions. Peak Oxides of Nitrogen concentration are well below the levels associated with irritant effects [2].

The particulate concentrations might be of greater potential significance. We have established that wind directions from the refinery are associated with higher particulate concentrations (allowing for other variables such as temperature). This lends some support to the hypothesis that the refinery contributes to ambient particulate matter at Boundary Rd. Furthermore, these wind directions occur much more frequently during the winter months, when complaints are more frequent.

When the PM_{10} data and wind direction are used to estimate likely NaOH concentrations, however, we see no overall increase in likely NaOH concentrations during the winter months. Furthermore, even using pessimistic assumptions about peak NaOH equivalent concentrations, particle alkalinity is unlikely to be sufficient to cause an irritant response.

In summary, it is possible that complaints are increased by airborne material from the refinery. The source within the refinery cannot be localised. There is no evidence that complaints are due to an irritant response to alkaline particles.

The analyses do not establish the relative importance of the RDAs or the stacks (liquor burning, calciner and powerhouse) as sources of particulate material.

Complaints do seem to be more common when the wind is blowing from the North, and they may be increased when there are elevated Oxides of Nitrogen concentrations. These elevated Oxides of Nitrogen concentrations are far too small to be of physiological significance, but they may serve as a marker for the stack plumes. In other words, days experiencing a higher proportion of time with peak NO_x levels are likely to be days in which the stack plumes ground in Yarloop. Plume odour is the most probable cause of complaints (and indeed odour is the most common issue for complaints).

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