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SULFUR DIOXIDE TRENDS IN MALTA:

A STATISTICAL COMPUTING APPROACH

NICHOLAS DESIRA

M.Sc. in Sustainable Environmental Resources Management

& Integrated Science and Technology

October 2012

Approved and recommended for acceptance as a dissertation in partial fulfillment of the requirements for the degree of Master of Science in Sustainable Environmental Resources Management & Integrated Science and Technology.

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SULFUR DIOXIDE TRENDS IN MALTA:

A STATISTICAL COMPUTING APPROACH

NICHOLAS DESIRA

A dissertation submitted to the Graduate Faculty of

JAMES MADISON UNIVERSITY - UNIVERSITY OF MALTA

In

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for the degree of

Master of Science in Sustainable Environmental Resources Management

& Integrated Science and Technology

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LIST OF ABBREVIATIONS

ANCOVA	-	Analysis of Covariance
csv	-	comma separated value
EEA-32	-	The 32 member states of the European Environment Agency
EIONET	-	European Environment Information and Observation Network
EU	-	European Union
EU-27	-	The 27 member states of the European Union
GIS	-	Geographical Information Systems
IntaMap	-	Inter Operability and Automated Mapping Project
MEPA	-	Malta Environment and Planning Authority
MPS	-	Marsa Power Station
PM	-	Particulate Matter
SO_2	-	Sulfur dioxide

ABSTRACT

A statistical investigation of data related to emissions and measurement of SO_2 in the Maltese islands encompassing the period 2004 to 2012 was conducted. The purpose was to investigate whether SO_2 levels were driven by the Marsa power station (MPS), which was considered to be the main source of SO_2 on the island. In addition, the study sought to establish spatial and temporal trends in the SO_2 concentrations measured throughout the islands.

Data was obtained from the Malta Environment and Planning Authority (4 fixed monitoring stations and a diffusion tube network) and also from the Enemalta Corporation (emissions of MPS). This was analysed using the Inter Operability and Automated Mapping Project (IntaMap) and GIS for mapping purposes, as well as R and SPSS packages for statistical processing.

The results have shown that average yearly emissions from the MPS decreased from approximately 858 g/hr to 780 g/hr between 2009 and 2012. Diffusion tube and monitoring station data have indicated overall decreases in SO_2 with certain localised areas showing increases. It was also determined that there were only two occasions when the 350 $\mu g/m^3$ hourly limit of Directive 2008/50/EC was exceeded. All the stations in the monitoring station network registered higher readings when the winds were Northerly or North-Westerly. The Kordin station was found to have the overall highest SO_2 readings while Għarb had the lowest.

Results suggested that emissions from the MPS had a more localised effect on SO_2 levels compared to previous research. However, a 3-predictor statistical ANCOVA analysis determined that while emissions from the MPS were statistically significant in determining the amount of SO_2 being measured in the monitoring stations, the results indicated that there were other contributors. These contributors could have included emissions from the Delimara power station emissions and marine vessels. On the other hand, a 2-predictor model using only readings registered with wind originating from the MPS direction showed that MPS emissions were only statistically relevant for Kordin. Hence, it can be concluded Kordin was the most likely area to be affected by MPS emissions while the effect on Msida, Żejtun and Għarb was negligible.

The overall findings of the study indicated that, although the MPS was still found to be a contributor of SO_2, other sources should now start to be monitored as well. It is recommended that the identification of new sources of SO_2 be a focus of future research, including examination of effects of the Delimara power station and marine vessels.

CHAPTER 1: INTRODUCTION

Air quality is a topic which has grown in importance in the last few decades, especially with initiatives such as the EU focus on clean air (EC, 2012). Sulfur dioxide (SO_2) is one of the air pollutants which is of relevance due to the fact that it is a product of combustion of sulfur-containing fossil fuels. In fact, in the 20^{th} century, SO_2 concentration in the atmosphere has significantly surpassed natural levels due to anthropogenic activities (Grübler, 2002).

Elevated SO_2 levels in the atmosphere raise both environmental as well as health concerns. Environmentally, SO_2 causes significant problems due to the fact that it is removed from the atmosphere via wet deposition. This results in precipitation having a lower pH, or acid rain. Acid rain causes considerable damage to the biotic environment and also causes corrosion of certain metals and stonework (Treissman *et al.*, 2003). With regards to health effects, SO_2 has been linked to respiratory disease, aggravation of cardiovascular illness (Brown *et al.*, 2003; Chen *et al.*, 2007) and also to increased mortality rates (Kan *et al.*, 2010).

On a positive note, SO_2 emissions in the European Economic Area have decreased by 76% between 1990 and 2009 (EEA, 2011). This shows significant advances with regards to mitigation efforts for this pollutant. In addition, it was determined that 70% of the SO_2 emissions in the region were attributable to fossil fuel use for energy production and

distribution (EEA, 2011). In 2010, the two power stations contributed *circa* 99% of the SO_2 emissions in Malta (EIONET, 2012). In addition, higher concentrations of SO_2 deposits were measured in the vicinity of the Marsa power station (MPS) (Vella *et al.*, 1996).

The purpose of this study is to quantitatively investigate whether the trends registered by the Maltese fixed sensor station network are still driven by the MPS, which was considered to be the main source of SO_2 on the island. In addition, the study seeks to establish spatial and temporal trends in the SO_2 concentrations measured throughout Malta by passive diffusion tubes and the continuous sensor station network.

Although SO_2 levels have decreased, monitoring is still very important due to strict regulatory procedures. The European Union has issued a number of Directives which regulate both immission (or ambient) levels, as well as emission levels of SO_2 (in terms of both loads and concentrations) from a number of sources. The key air quality legislative instrument is Directive 2008/50/EC on ambient air quality and cleaner air for Europe, which sets an hourly ambient limit value of 350 $\mu g/m^3$ and a daily average limit value of 125 $\mu g/m^3$. Meanwhile, Directive 2001/81/EC caps national emissions of SO_2 of all the 27 EU Member States, with Malta having an emission cap of 9000 Mg to be reached by 2010. Directive 2001/80/EC on large combustion plants sets limits on the maximum concentration of SO_2 in the waste gases emitted from large combustion plants, which include power plants.

In order to comply with Malta's requirements under the Ambient Air Quality Directive, the Malta Environment and Planning Authority manages 126 diffusion tube sites and also 4 automated real time monitoring stations (MEPA, 2012). In addition, the operator of the two power plants, Enemalta Corporation, continuously monitors emissions of SO_2 from both stations (Enemalta, 2012). However, in order to study the impact of the power plants on ambient levels of SO_2, an understanding of how concentrations of this pollutant change over space and time is required. This study will assist in the understanding of variations in SO_2 concentrations by identifying specific spatio-temporal trends. Although some studies have examined this subject, there have been no studies with a statistical computing focus. Hence, this study should help to enhance local air quality knowledge.

The hypothesis of this study is that the MPS was still a significant source of SO_2 during the study period, although to a lesser extent than suggested by previous research. It is expected that the results of this research will help address this issue and also highlight trends in SO_2 concentrations in Malta. These trends may take the form of chronological trends, trends related to power generation or even trends related to lifestyle and climatic factors. The limitations of this research included gaps in data due to technical issues and also the exclusion of data from the Delimara power station. These two limitations may have introduced distortion in the results, increasing the level of uncertainty in the statistical calculations. In addition, due to time and resources constraints, detailed examination of possible new sources of SO_2 that were suggested by the data were beyond the scope of this study.

This text shall commence with a detailed discussion of relevant literature to the subject matter (Chapter 2), including the role of SO_2 as a pollutant, legislation related to SO_2 mitigation, local research on SO_2 and also an account of the methods used in this study and their application in previous air quality studies. Hence, this section shall set the context of the study in relation to what is already known.

Chapter 3 shall then discuss the exact methodology applied in this study. The explanation shall discuss this in detail, both for repeatability purposes and also for future work aiming to further the findings of this study. In addition, this section shall serve to justify the methodology used by citing past research that used similar methodology. Chapter 4 will then present the findings obtained from the Chapter 3 methods and discuss their significance. This section will also seek to compare findings obtained using different methods, which will either confirm trends or else shed doubt on their existence.

The study shall then conclude in Chapter 5, in which the study's main findings shall be summarised. This section shall also include suggestions for future research, which shall again refer to the limitations of the study and build upon findings of the study.

CHAPTER 2: LITERATURE REVIEW

2.1 Introduction

This purpose of this chapter is to present the theoretical basis of this study. Relevant topics and past studies are included to highlight what is already known in the field and what exactly has been done with regards to empirical studies.

Since the focus of this study is SO_2, Section 2.2 shall first discuss this important pollutant. The discussion shall include a general overview of what SO_2 is, why it is important, the processes that lead to it being emitted and eventually deposited and finally, its effects on humans and the environment. This section serves the purpose of allowing a better understanding of why this study was attempted.

Section 2.3 shall then discuss what kind of legislation is in place to mitigate the emission and effects of SO_2. This shall focus on legislation which is applicable to Malta, since it is the area of study. The discussion of legislation helps to demonstrate what has already been done to reduce SO_2, the success of such measures and also gives context to the current situation.

Section 2.4 shall then place specific emphasis on the location of the study, Malta. The discussion shall include general characteristics of Malta, past local research on SO_2 and important entities in the local context. This will provide an overview of the scale of the

local problem, what is known about the problem, the important players and will also illustrate the gaps in knowledge that this study is aimed at bridging.

The review shall then conclude with Section 2.5, discussing methodologies applied in similar studies. This section shall start off with a short explanation of how statistical computing has been used in atmospheric chemistry in the past. Then, the specific software packages to be used in this study shall be examined in further detail, with specific examples of how they were used in the past being mentioned. This section serves to highlight why statistical computing is a very viable and important tool in the study of atmospheric chemistry, giving the reader an appreciation of the techniques available and their value.

2.2 Sulfur Dioxide

2.2.1 Structure and properties

SO_2 is a chemical compounds found naturally in the atmosphere as a colourless gas with a pungent odour when present at high concentrations (Hasenberg, 2008; ATSDR, 1998). The molecule itself consists of a central sulfur atom attached to two oxygen atoms. It is typically depicted with two double bonds, however, it also exists as two resonance forms, with the sulfur atom carrying a positive charge while a negative charge is delocalised over the oxygen atoms (i.e. carried from one to the other) as shown below. This allows it to act as a Lewis acid, i.e. accepting a pair of electrons in an acid-base reaction which also allows it to from ionic compounds (Housecroft & Sharpe, 2008).

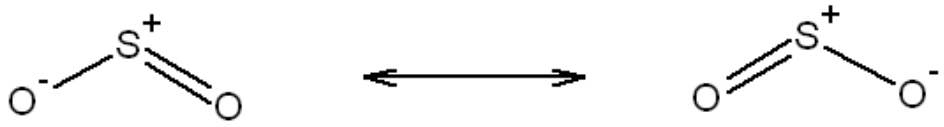

Figure 2.1: Structure of SO_2

SO_2 has a boiling point of 263 K (approximately -10 ºC) making it gaseous under standard atmospheric conditions. It is also non-combustible and fairly stable. In gaseous form it reacts slowly with oxygen, especially in the presence of UV radiation (Hasenberg, 2008; Housecroft & Sharpe, 2008). This is of relevance to this study due to the production of other compounds of sulfur such as sulfur trioxide (SO_3) and more importantly, sulfuric acid (H_2SO_4) (Housecroft & Sharpe, 2008).

2.2.2 Sources and presence in atmosphere

As a pollutant, SO_2 is of relevance due to the fact that it is a by-product of various anthropogenic activities. This is significant because emissions from these activities have surpassed natural SO_2 emissions in the 20th century (Smith *et al.*, 2001). Taking the early 1990s as an example, total anthropogenic SO_2 emissions accounted for approximately 65 Tg of sulfur per year (Benkovitz *et al.*, 1996) which clearly exceeded emissions from natural emissions of SO_2 which amounted to between 40 and 60 Tg of sulfur per year (Grübler, 2002).

Anthropogenic SO_2 is attributable to various processes; however, the main source is the burning of fossil fuels (Grübler, 2002). This occurs because coal and crude oil normally contain about 1-2% sulfur by weight on average, although sulfur can range from approximately 0.03% to 7.9% depending on the type of oil or coal used (Smith *et al.*, 2001; Soleimani *et al.*, 2007). Another important source is the smelting of sulphide ores during extraction of copper, lead and zinc. Other processes that contribute to sulfur emissions include the burning of biomass, marine bunker fuels and paper production (Grübler, 2002). These processes result in release of sulfur containing compounds, not necessarily SO_2. The ultimate oxidation product of such sulfur containing compounds in the atmosphere is the sulfate ion (SO_4^{2-}), as contained in sulfuric acid (H_2SO_4). Nevertheless, the convention is that emissions and atmospheric concentrations are reported as SO_2 equivalent or as sulfur equivalent (O'Neill, 1998). Sulfur emissions are being monitored extensively in the EU, the US and also in Asia. However, such monitoring efforts are not so established in other countries such as Australia, New Zealand and South Africa (Grübler, 2002; Benkovitz *et al.*, 1996).

Historically, sulfur emissions started to increase dramatically at a rate of about 4% *per annum* due to the extensive coal use instigated by the industrial revolution up to the 1920s. Following this period, sulfur emissions growth decreased to about 2% increase per year as sulfur-rich coal started to be replaced by oil (Grübler, 2002). These increases resulted in SO_2 emissions peaking globally around 1970. However, from 1975 onwards, global emissions have decreased slightly as shown in Figure 2.2 (Smith *et al.*, 2011).

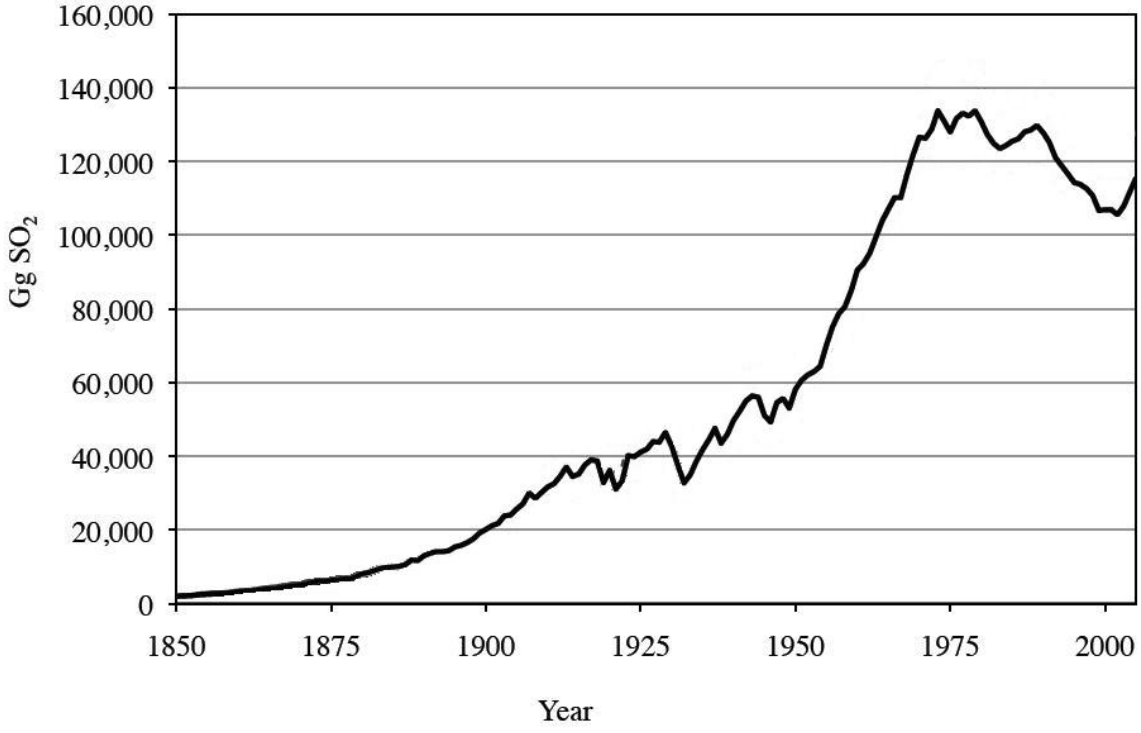

Figure 2.2: Global anthropogenic sulfur emissions (Smith *et al.*, 2011)

This decrease has been attributed to legislative mitigation efforts of SO_2 (Grübler, 2002). Of note is the fact that SO_2 emissions levels have again shown a recent increasing trend, due to the growing activity of emerging economies such as China (Smith *et al.*, 2011). This increase in emissions is marked in Figure 2.2 and is even more discernible in Figure 2.3, where China is included under the category "East Asia" (Smith *et al.*, 2011).

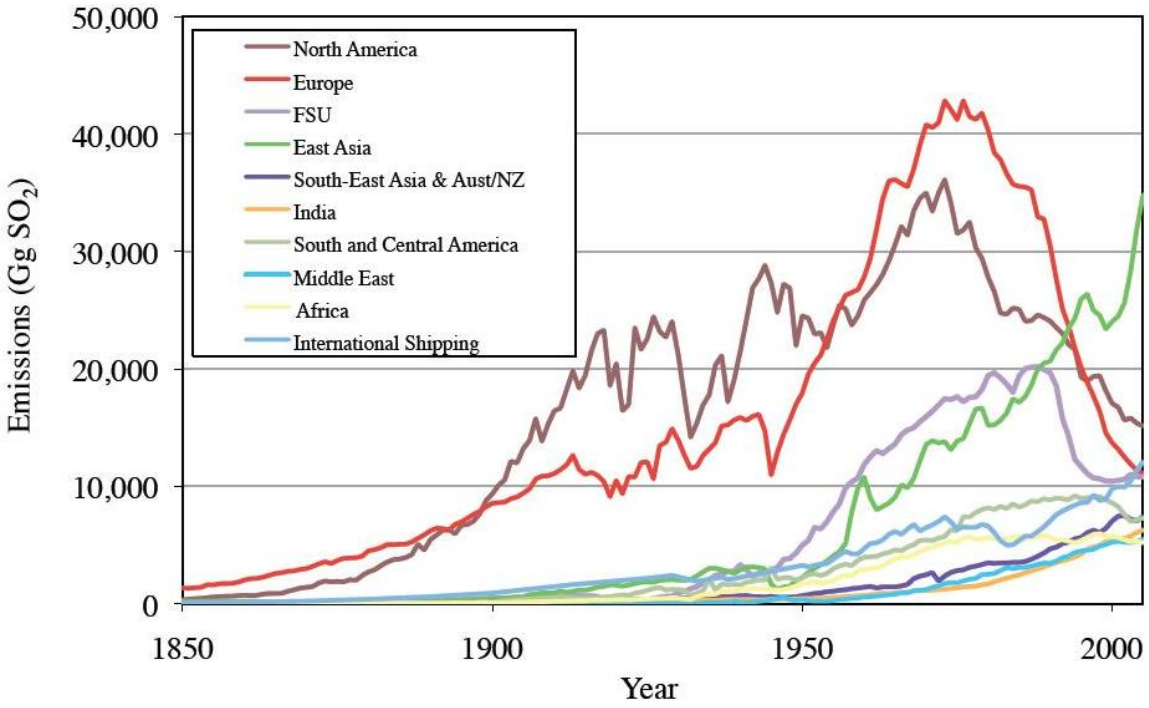

Figure 2.3: Global anthropogenic sulfur emissions by region (Smith *et al.*, 2011)

(North America includes both USA and Canada and East Asia includes Japan, China and South Korea)

Reviewing the European area (including Malta) in greater detail, Figure 2.4 shows that SO_2 emissions are on the decline, with an emissions decrease of 76% between 1990 and 2009 in the European Environment Agency (EEA-32) area (which includes the 27 EU member states plus Iceland, Liechtenstein, Norway, Switzerland and Turkey). This decrease has been attributed to legislative measures of the EU which shall be discussed in a later section (EEA, 2011).

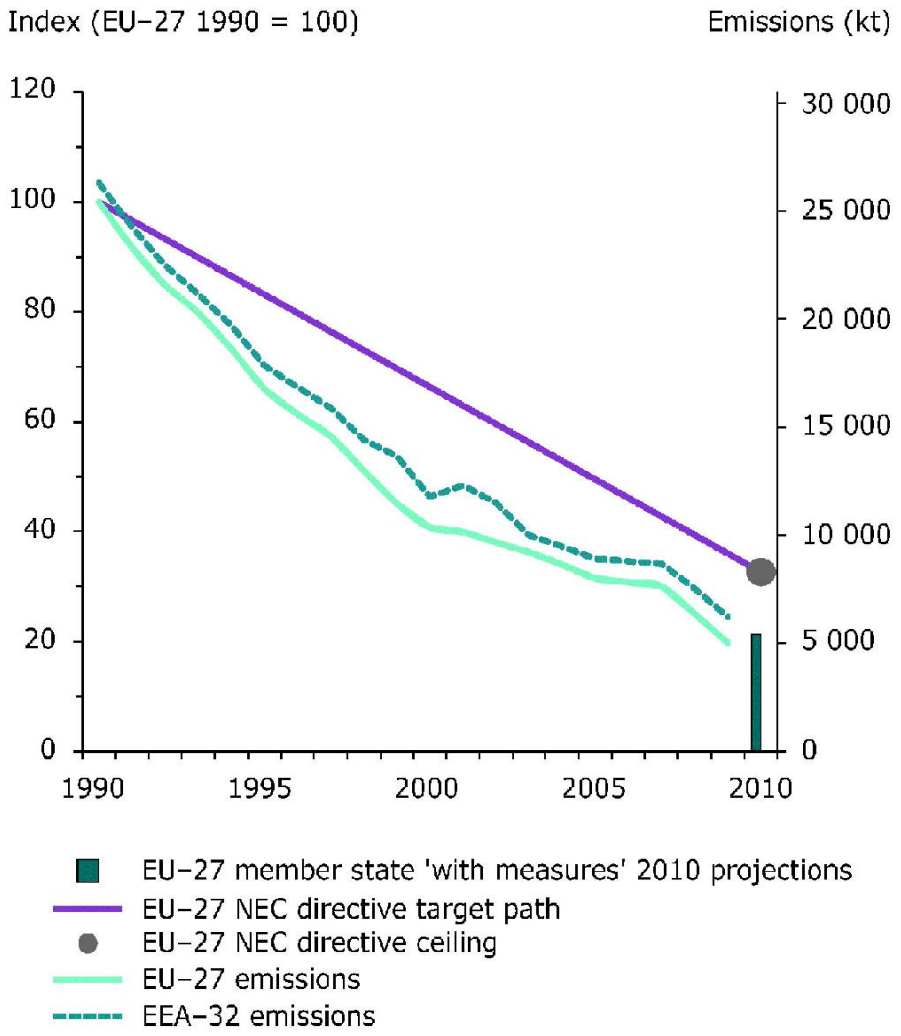

Figure 2.4: Anthropogenic sulfur emissions in the European area (EEA, 2011)

Additionally, research over the same region has shown that the greatest contributor of sulfur emissions is the energy sector, with energy production (electricity network) and energy use in industry accounting for a total of 83.6% of the sulfur emissions in the EEA-32 area (EEA, 2011). The distribution, as a relative percentage share, of emissions by source is shown in Figure 2.5.

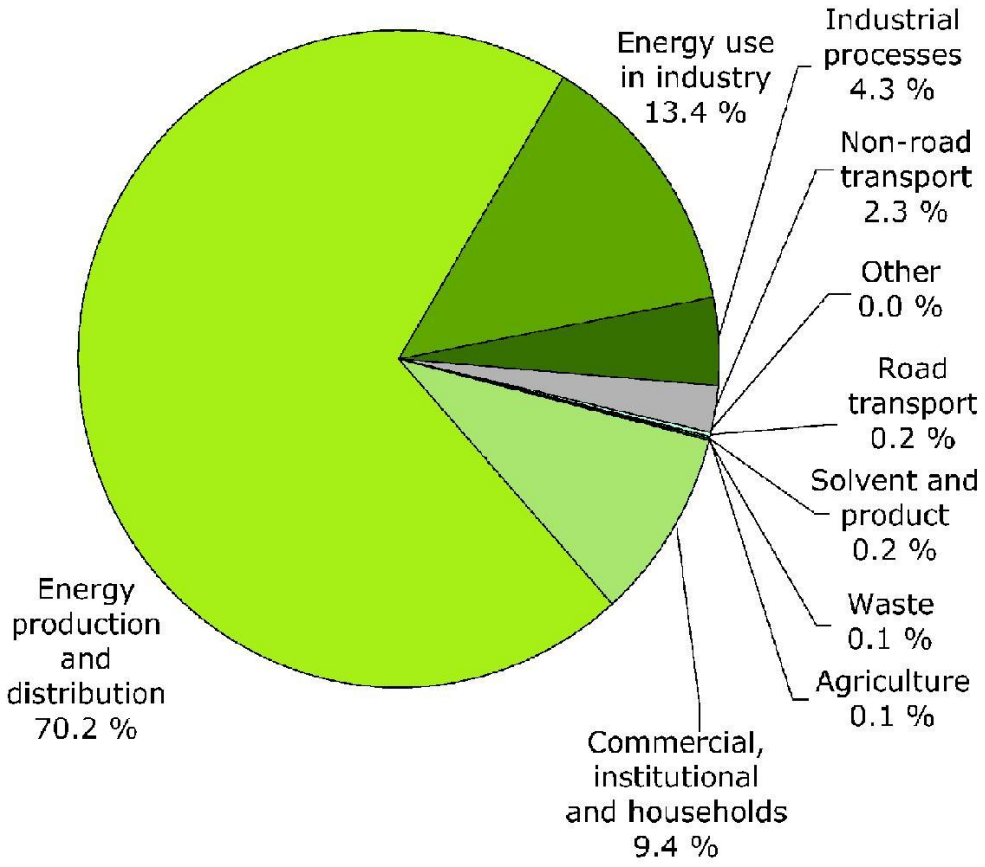

Figure 2.5: Sulfur emissions share in 2009 in the EEA-32 area (EEA, 2011)

The distribution of sources clearly shows that, as stated by Grübler (2002), the majority of sulfur emissions are attributable to fossil fuel combustion applications such as energy generation, transportation and commercial/industrial activity.

2.2.3 Health and environmental effects

The presence of high SO_2 concentrations in the atmosphere can be problematic for three main reasons. First of all it causes direct human health and environmental damage. Secondly, it results in acidification of rain and water bodies. In fact, this has been known to be very damaging to forest ecosystems that may be reliant on smaller water bodies. Thirdly, SO_2 that is converted to sulfates in the atmosphere causes a global cooling effect which may interfere with regional climates (Grübler, 2002). Hence SO_2 acts both as a primary pollutant, in the form of SO_2, and also as a secondary pollutant, mainly in the form of sulfates (Thurston, 2008).

SO_2 has been found to cause a number of direct harmful effects on humans. Short term exposure to high concentrations of SO_2 (more than 100 ppm) has been found to be an immediate danger to public health, causing breathing difficulties that may be fatal to vulnerable populations (ATSDR, 1998; Brown *et al.*, 2003; US NLM, 2012). Notably, a study by Kan *et al.* (2010) found that an average increase of as little as 10 $\mu g/m^3$ over a two day period may result in an associated 1% increase in total mortality. However, the study did not find a strong statistical relationship, with no relationship being found when adjustments for corresponding increases in nitrogen dioxide were factored into the calculations. In fact, similar correlation problems were encountered by Katsouyanni *et al.*, (1997) while investigating the relationship between mortality, SO_2 and particulate matter. In such cases, it would not be advisable to draw conclusions about individual components of the atmosphere, thus requiring further research (Moolgavkar *et al.*, 1995).

If further research corroborated the conclusions of Kan *et al.* (2010) there may be significant health effects even with relatively small SO_2 level fluctuations.

Other symptoms of high concentration short term exposure to SO_2 include stomach pains, inhibition of thyroid function, loss of smell, headache, nausea, vomiting, fever, convulsions and dizziness (US NLM, 2012).

Long term effects of SO_2 at lower concentrations have also been documented, but tend to exhibit different symptoms (Chen *et al.*, 2007). Persistent exposure to SO_2 may cause a number of respiratory conditions such as chronic bronchitis and emphysema. This has been linked to the gas being an irritant. Because of this, SO_2 may also affect the nose, throat and lungs, causing symptoms such as coughing and shortness of breath. It has also been noted that heart conditions such as cardiac dysrhythmia may be aggravated by long term exposure due to changes in heart rate caused by SO_2 (Chen *et al.*, 2007; US NLM, 2012). It should be noted that similar symptoms with both short term and long term exposure have been observed in livestock and wild animals (Treissman *et al.*, 2003).

The majority of the effects endured by humans occur directly from SO_2, however a lot of environmental damage occurs through secondary pollutants of sulfur. These sulfur species arise as sulfur compounds are oxidised from one species to another in the atmosphere according to the simplified scheme below:

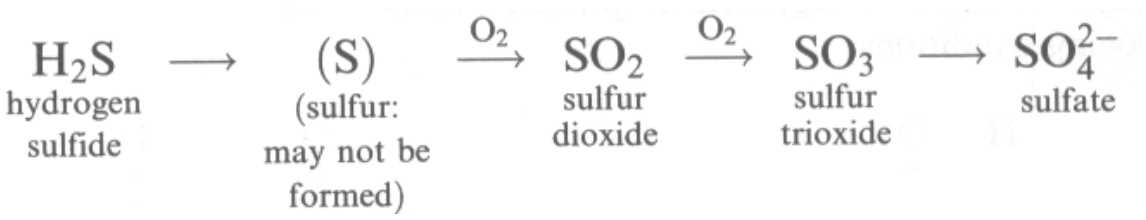

Figure 2.6: Sulfur reaction scheme in atmosphere (O'Neill, 1998)

Sulfates formed through this pathway can form particulate matter (possibly acidic) which is eventually deposited; this process is known as dry deposition. However, such particles are very small, with a typical diameter of 0.5 μm and may take 2-6 days to be deposited. Because of this, such particles may be found up to 4000 km from the point of origin depending on environmental conditions (O'Neill, 1998; Thurston, 2008). The physical particles themselves, due to their size, are classified as particulate matter (PM). Since they have a diameter smaller than 2.5 μm they are part of the group known as $PM_{2.5}$. These have been associated with health complications related to respiratory and cardiac conditions (Son *et al.*, 2012).

SO_2 and sulfates may also dissolve in water to form acidic aerosols and eventually precipitate, this is known as wet deposition. Wet deposition may occur through two processes: wash out and rain out. Rain out occurs when the sulfur species is incorporated into a cloud as an aerosol and is then precipitated out. Wash out occurs when sulfur species are dissolved by rain as it falls towards the ground. Both of these processes may result in precipitation having a pH lower than 5.6, known as acid rain (O'Neill, 1998).

Acid rain is a problem since it can cause considerable damage to the biotic environment and also corrosion of certain metals and stonework (Treissman *et al.*, 2003). Consequently, in the past few decades acid rain has been identified as a serious transboundary environmental problem that can have widespread effects on ecosystems (Likens & Bormann, 1974; Singh & Agrawal, 2008).

With regards to effects on biota, acid rain has been found to cause direct damage to plant tissue, such as roots and foliage, which reduces overall canopy cover in forests and may also lead to deaths of individual trees (Tomilnson, 1983). This is important both from an economic and environmental perspective, since such damage may cause significant crop losses (Singh & Agrawal, 2008).

Acid rain has also been found to increase the acidity of water bodies. In such cases, acidification of aquatic ecosystems harms the majority of species living in that environment (Singh & Agrawal, 2008). Invertebrates such as molluscs and crustaceans are particularly sensitive since acidic conditions inhibit their growth. In fact, some species can disappear completely at pHs lower than 6 (O'Neill, 1998; Schindler, 1988). Lower pHs may also cause leaching of ions such as aluminium, which may be toxic to some aquatic species (Schindler, 1988).

Soils close to water bodies have also been found to be vulnerable to acidification. At this stage, it should be noted that soils are more resistant to acidification than water bodies due to a greater buffering capacity. However, acidification can have very significant

effects on soil quality since acidic conditions in the soil or associated water body can leach away nutrients from the soil, reducing soil quality and possibly harming vegetation (Singh & Agrawal, 2008). Long term studies from the 1970s have shown that a slight drop in the pH of a stream in a forest ecosystem may cause significant losses of calcium and magnesium from soil (Frink *et al.*, 1996; Likens *et al.*, 1996). Despite recent mitigation efforts against acid rain, the decrease in soil buffering capacity has led to periodic acidification episodes that are only partially buffered by the top organic layer of the soil. In addition, accumulation of sulfur and nitrogen species in the soil system over the years still leads to calcium losses (Lawrence, 2002). One should note that nitrogen species may form nitric acid which also increases acidity. However, the sulfate anion has been found to be the major species associated with water acidity caused by atmospheric deposition (Kirchner & Lydersen, 1995). Because of these accumulations, soil acidification episodes are expected to continue until the sulfur and nitrogen deposits are depleted (Lawrence, 2002). Hence, some water bodies may require management strategies such as stocking of species to aid dwindling populations and satisfy water quality targets (Keller *et al.*, 1999). It has also been determined that poor land use patterns such as cutting down forested areas have been found to cause slight acidification of soil. Therefore, acid rain is not necessarily the only contributor to soil acidification but it has been determined to be the major one (Krug & Frink, 1983).

Acid rain has also been found to affect physiological behaviour in animals. For example, research by Kitamura & Ikuta (2001) has shown that spawning behaviour of brown trout and salmon is greatly inhibited even with slight acidification of water bodies.

Furthermore, carp were found to have higher levels of the hormone cortisol in acidic environments which resulted in immune system impairment (Nagae *et al.*, 2001). These effects can also be cumulative when felt at higher trophic levels. A typical example has been a noticeable decline in bird populations in areas affected by acidification. This has been attributed to the combined effect of a decline in fish populations in acidic rivers, forest canopy reductions resulting in bird migration and a lower reproductive success due to reduction in availability of calcium for bone growth and eggshell formation. In addition, exposure to leached metals and reduction in food availability may further aggravate bird population decline (Graveland, 1998).

One should also note that it is not just the biotic environment which is vulnerable to acid rain, but also the abiotic environment. It has been established that acid rain causes deterioration of limestone and marble structures (Okochi *et al*., 2000; Singh & Agrawal, 2008; Vella *et al.*, 1996). Moreover, it has also been determined that acid rain may also cause damage to manmade materials such as concrete over longer periods of time (Okochi *et al*., 2000). The effects of SO_2 on biotic and abiotic constituents can vary from a local to a regional scale depending on the source, the concentration of SO_2 and transportation of the gas in the atmosphere (Bhugwant *et al.*, 2009).

The final problem associated with SO_2 is alteration of climate. As discussed above, SO_2 may react to form sulfate particulate matter with a relatively small size. The typical diameter of 0.5 µm is within the range of the wavelength of visible light, which may cause scattering and reflection of sunlight (Thurston, 2008). Research by Menon *et al.*

(2002) has determined that clouds containing sulfate particles increase cloud albedo (reflection coefficient). This was found to occur due to physical changes in the cloud such as larger cloud condensation nuclei (size of particulate matter onto which water molecules coalesce) and larger cloud droplet effective radii (mean droplet size in a cloud) (Menon *et al.*, 2002). Additionally, there is evidence to suggest that sulfates increase both cloud cover and also cloud lifetime (Lohmann & Feichter, 1997).

The effect of sulfates on cloud albedo is not unbounded, it has been determined that sulfate concentrations beyond 0.5 g/m^3 cease to cause any significant effects in cloud reflectivity (Menon & Saxena, 1998). Nonetheless, acute peaks in sulfur concentrations have been found to cause changes in regional climates (Saxena *et al.*, 1997). A typical example would be regions near volcanoes, such as the Kilauea region in Hawaii, which experiences an average of 0.5 Tg SO_2 emissions per year (Elias & Sutton, 2007). Such volcanic activity, through increases in stratospheric and cloud sulfur aerosols, has been found to cause a decrease in mean maximum temperatures and an increase in mean minimum temperatures, essentially changing regional climates (Saxena *et al.*, 1997).

2.3 Legislation on SO_2 in the EU

The EU has issued a number of Directives which regulate ambient levels, emission levels and emission loads of SO_2 and other pollutants, however legislation related to these other pollutants is beyond the scope of this study and will not be discussed. The main legislative text defining standards across the region is Directive 2008/50/EC on ambient

air quality and cleaner air for Europe (known as the Ambient Air Quality Directive). This Directive obliges Member States to delineate zones and agglomerations for the purpose of air quality management (Stacey & Bush, 2002). Where a zone is defined as a delimited zone forming part of the territory of a Member State and an agglomeration is a zone with a population of 250,000 inhabitants or a particularly high population density (Directive 2008/50/EC, 2008). The specific zones and agglomerations for Malta shall be discussed later on in Section 2.4.3. The Ambient Air Quality Directive also defines ambient SO_2 limit values for safeguarding human health and also for the protection of vegetation as shown in the table below:

Limit target	Time Scale	SO_2 in $\mu g/m^3$
Human health	One hour	350[a]
	One day	125[b]
Vegetation protection	Yearly	20

Table 2.1: EU ambient level standards for SO_2 (Directive 2008/50/EC, 2008**)**
[a] Not to be exceeded more than 24 times a year
[b] Not to be exceeded more than 3 times a year

Another important directive is Directive 2001/81/EC on national emission ceilings for certain atmospheric pollutants. This directive caps the yearly national emissions of SO_2 of all the 27 EU Member States, with Malta having an emission cap of 9 Gg (i.e. Giga grammes, equivalent to a Kilo tonne) to be reached by 2010 (and maintained beyond that). The caps are shown in Table 2.2 below.

Member state	SO_2 emission cap (Gg)
Austria	39
Belgium	99
Bulgaria	836
Cyprus	39
Czech Republic	265
Denmark	55
Estonia	100
Finland	110
France	375
Germany	520
Greece	523
Hungary	500
Ireland	42
Italy	475
Latvia	101
Lithuania	145
Luxembourg	4
Malta	9
Netherlands	50
Poland	1397
Portugal	160
Romania	918
Slovakia	110
Slovenia	27
Spain	746
Sweden	67
United Kingdom	585
EU-27 Total	8848

Table 2.2: EU emissions caps for SO_2 (Directive 2001/81/EC, 2001**)**

Following Council Decision 81/462/EEC of 11th June 1981, the National Emission Ceilings Directive became the implementation of the 1979 Geneva Convention on Long-range Transboundary Air Pollution. The convention was amended in May 2012 and

Malta pledged to reduce SO_2 emissions to 77% of 2005 levels by 2020. This would cap Malta's emissions to around 3 Gg SO_2 per year (ECE/EB.AIR/2012/4, 2012). This convention is important because it provides a framework for cooperation with regards to air pollution and facilitated exchange of information, research and monitoring efforts (Council Decision 81/462/EEC, 1981).

Other policy measures in place are aimed at curbing emissions from specific sources. Three important directives in this area aim to mitigate SO_2 emissions from combustion plants and from fuel combustion in road vehicles and marine vessels. Directive 2001/80/EC on the limitation of emissions of certain pollutants into the air from large combustion plants aims to reduce SO_2 emissions from combustion plants with a thermal input greater than 50 MW. It should be noted that this directive applies to combustion plants in general, of which power plants (of importance to this study) are a subset. These standards apply for both existing plants and new plants, with specific deadlines allowing existing plants to comply with the emissions standards of this directive (Directive 2001/80/EC, 2001).

With regards to land based fuel combustion, the current legislation in place is Directive 2009/30/EC amending Directive 98/70/EC as regards the specification of petrol, diesel and gas-oil and introducing a mechanism to monitor and reduce greenhouse gas emissions. One of the main purposes of this directive is to reduce sulfur emissions from transportation vehicles. The directive defines sulfur content of fuels according to fuel type and/or fuel use as shown in the table below (Directive 2009/30/EC, 2009).

Fuel Type	EU standard (mg/kg)
Petrol	10
Diesel	10
Gas oil	10
Non-road Gas oil	20

Table 2.3: EU standards for fuel sulfur content (Directive 2009/30/EC, 2009**)**

Marine emissions on the other hand are regulated by Directive 2005/33/EC of the European Parliament and of the Council of 6 July 2005 amending Directive 1999/32/EC relating to a reduction in the sulphur content of certain liquid fuels. There are three main regulations included in this document. First of all, ships berthing or anchoring in EU ports are required to use fuel containing a maximum of 0.1% sulfur. Secondly, passenger ships on regular service in EU ports are required to use fuel containing a maximum of 1.5% sulfur. Thirdly, it includes measures to promote the use of emission abatement technologies (Directive 2005/33/EC, 2005).

From the legislation, it can be seen that the approach taken by the EU vis-à-vis SO_2 mitigation efforts is the use of control policies. For these to be effective, adequate monitoring and enforcement procedures need to be in place. Although the legislation discussed is applicable to the entire EU area, it is the responsibility of each member state to ensure that these policies are followed in their territory and that limit values are adhered to. Not only that, but member states are required to share information with other states and provide annual emissions reports to the EU commission to ensure compliance. Entities that are found to be exceeding standards may be penalised by the member state and member states exceeding national emissions caps may be fined by the European

Commission (EC, 2012). In the case of Malta, compliance with these regulations is enforced by the Malta Environment and Planning Authority (MEPA) and implemented by the individual industrial/economic operators such as the Enemalta Corporation (Enemalta, 2012; MEPA, 2012). The role of these two bodies shall be discussed in further detail in Section 2.4.

As mentioned in a previous section, EU SO_2 mitigation policies have been very successful with the majority of EU states reducing SO_2 emissions by more than 60% between 1990 and 2004 and a quarter of the countries surpassing 80% reductions (Vestreng *et al.*, 2007). This reduction can be seen in Figure 2.7 below. Note that the figure shows reductions in SO_2 emissions over time: red signifies the largest emissions reduction while dark and light blue signify an emissions increase. From the figure, it can be deduced that most of the reductions in SO_2 in Western Europe occurred between 1980 and 2000, following the legislative measures detailed above. On the other hand, Eastern Europe was increasing in emissions between 1980 and 1990, with significant decreases in emissions occurring between 1990 and 2000. As legislative efforts became more widespread between 2000 and 2004, the reduction in emissions became very uniform throughout Europe and is minimal (Vestreng *et al.*, 2007).

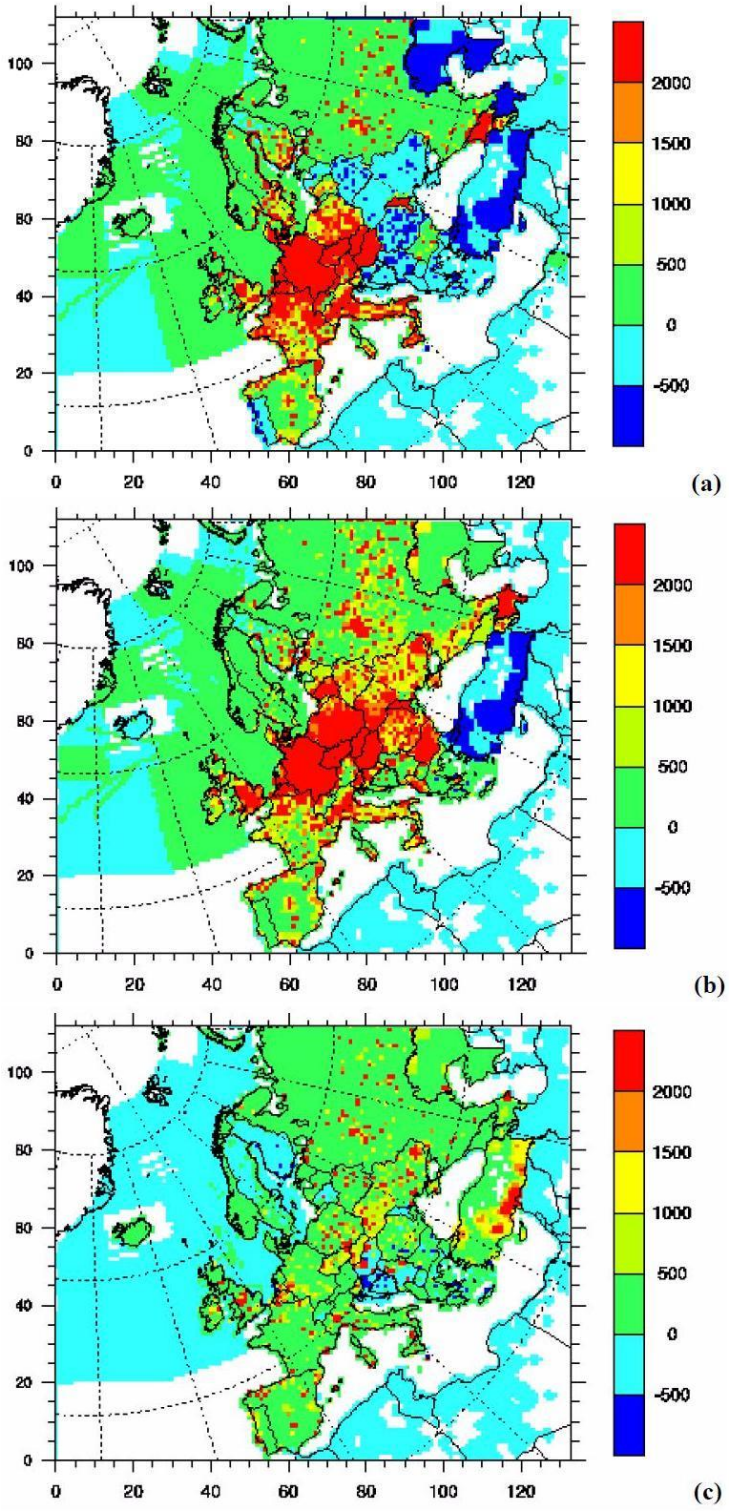

Figure 2.7: SO_2 emissions reductions in Mg SO_2/grid cell (Vestreng *et al.*, 2007)

(a) between 1980 and 1990; (b) between 1990 and 2000; (c) between 2000 and 2004

The success of the legislative efforts can also be demonstrated by looking at sectoral SO_2 emissions in the European area. As mentioned previously, the energy production and industrial sectors were established to be the largest contributors of sulfur emissions in the EEA-32 area (EEA, 2011). Hence, it is expected that significant reductions in emissions from these sectors would be seen over time. Figure 2.8 shows the contribution to total SO_2 emission reductions between 1990 and 2009 by sector, to highlight these reductions.

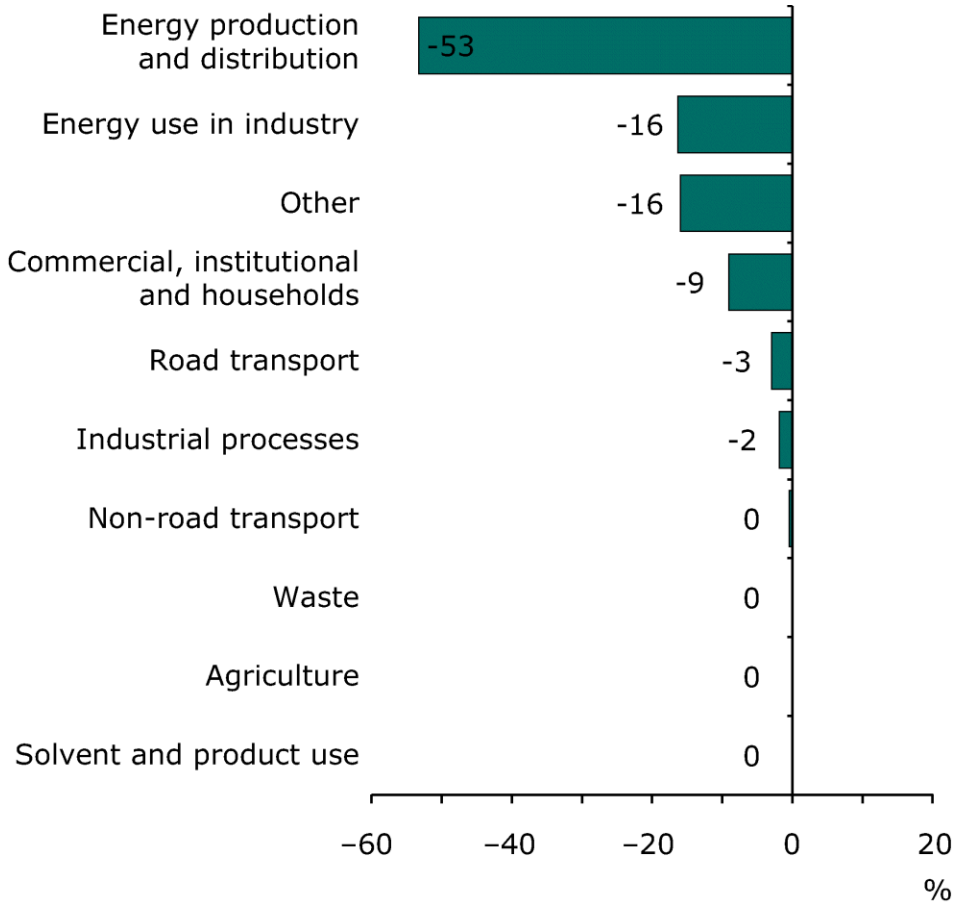

Figure 2.8: Contribution to total SO_2 reductions between 1990 and 2009 by sector (EEA, 2011)

According to the plot, 53% of reductions in total emissions are attributable to changes in the energy sector. Emissions from industrial processes and road transport were responsible for 16% and 3% respectively. This shows that EU efforts at reducing SO_2 emissions related to combustion processes, especially in the energy sector, were quite successful.

2.4 The case of Malta

2.4.1 Characteristics of Malta

The Maltese archipelago consists of three main islands, Malta, Gozo and Comino, with a total population of 417,617 as of 2010. The total land area of the islands is 316 km^2, with Malta being the biggest of the three islands. The islands are located about 93 km South of Sicily and are located at around 36°00'00" North, 14°36'00" East (DOI, 2012; NSO, 2012). A map of the islands is shown in Figure 2.9 below.

The landmass of the islands is characterized by hilly terrain and a coastline which has several indentations forming natural harbours, bays and beaches (DOI, 2012). Geologically, the islands are composed of a series of sedimentary rock strata of marine origin. The rock strata series is composed of five layers (from bottom to top layer): Lower Coralline Limestone, Globigerina Limestone, Blue Clay, Greensand and Upper Coralline Limestone (Pedley *et al.*, 1976).

Figure 2.9: Map of Malta (DOI, 2012)

For the purposes of this text, the Globigerina limestone layer is the most significant since it is used locally as a construction material (Pedley *et al.*, 1976; Vella *et al.*, 1996). This is important since limestone is mainly composed of calcite, which is a carbonate of calcium (formula: $CaCO_3$). Calcium carbonate has been found to corrode in the presence of acidic substances as shown in the reactions below (Tecer, 1999):

$$CaCO_{3(S)} + H_2SO_{4(aq)} \rightarrow CaSO_{4(s)} + H_2CO_{3(aq)}$$

$$CaCO_{3(S)} + H_2CO_{3(aq)} \rightarrow Ca^{2+}_{(aq)} + 2\ HCO_3^-{}_{(aq)}$$

$$CaCO_{3(S)} + H_2O_{(l)} \rightarrow Ca^{2+}_{(aq)} + OH^-_{(aq)} + HCO_3^-{}_{(aq)}$$

Climate-wise, the island has a typical semi-arid Mediterranean climate with mild, wet winters and hot, dry summers (Chetcuti *et al.*, 1992). The fact that Malta is surrounded by the sea is of great influence to the climate, making it cooler and more humid than larger inland areas while also reducing temperature fluctuations (Galdies, 2011). However, the fact that the islands are exposed makes conditions quite windy, with only around 8% of the days in a year being windless (Schembri, 1997). This is important when looking at atmospheric pollutants since such conditions affect the transportation of the gas in the atmosphere (Bhugwant *et al.*, 2009). A study of the average monthly wind speed between the years 1961-1990 has shown a yearly average wind speed of 8.8 knots or 16.3 km/hr (Galdies, 2011). The monthly average wind speed trends are shown in the figure below:

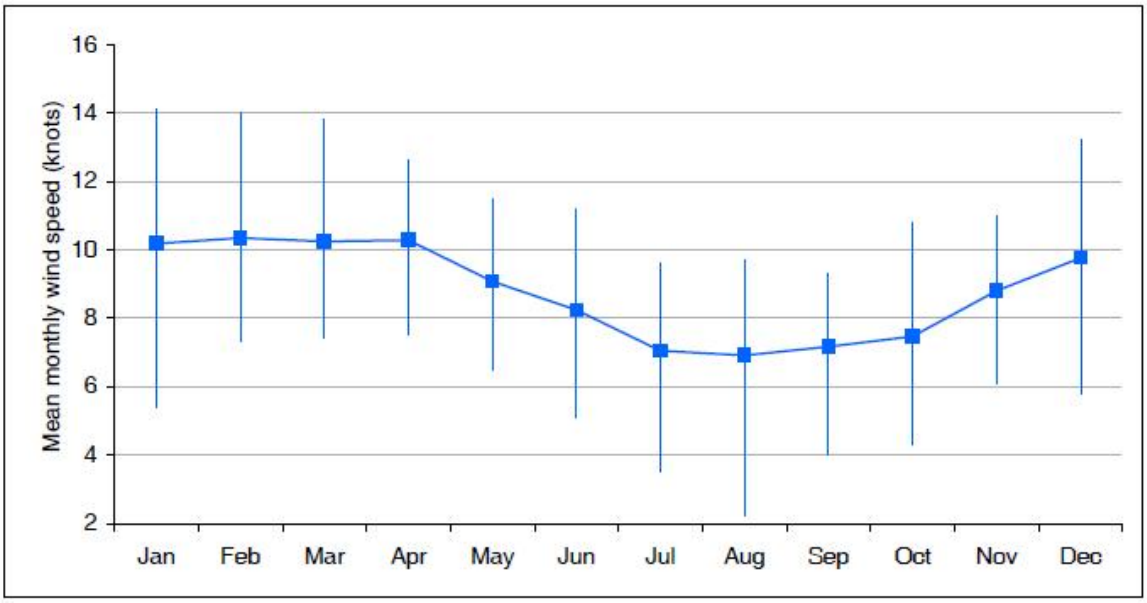

Figure 2.10: Average monthly wind speed in Malta between 1961-1990 (Galdies, 2011)

The study also showed that January demonstrated the largest variability and tended to have stronger wind gusts. It should be noted that statistical tests have shown no significant difference at 95% confidence level in the wind speed means between 1961-1994 and 1995-2010 (Galdies, 2011). Hence, for the purposes of this study, it can be assumed that the average wind speed patterns follow the above trends. With regards to direction, the predominant wind direction is North West (NW) as shown by the wind rose below:

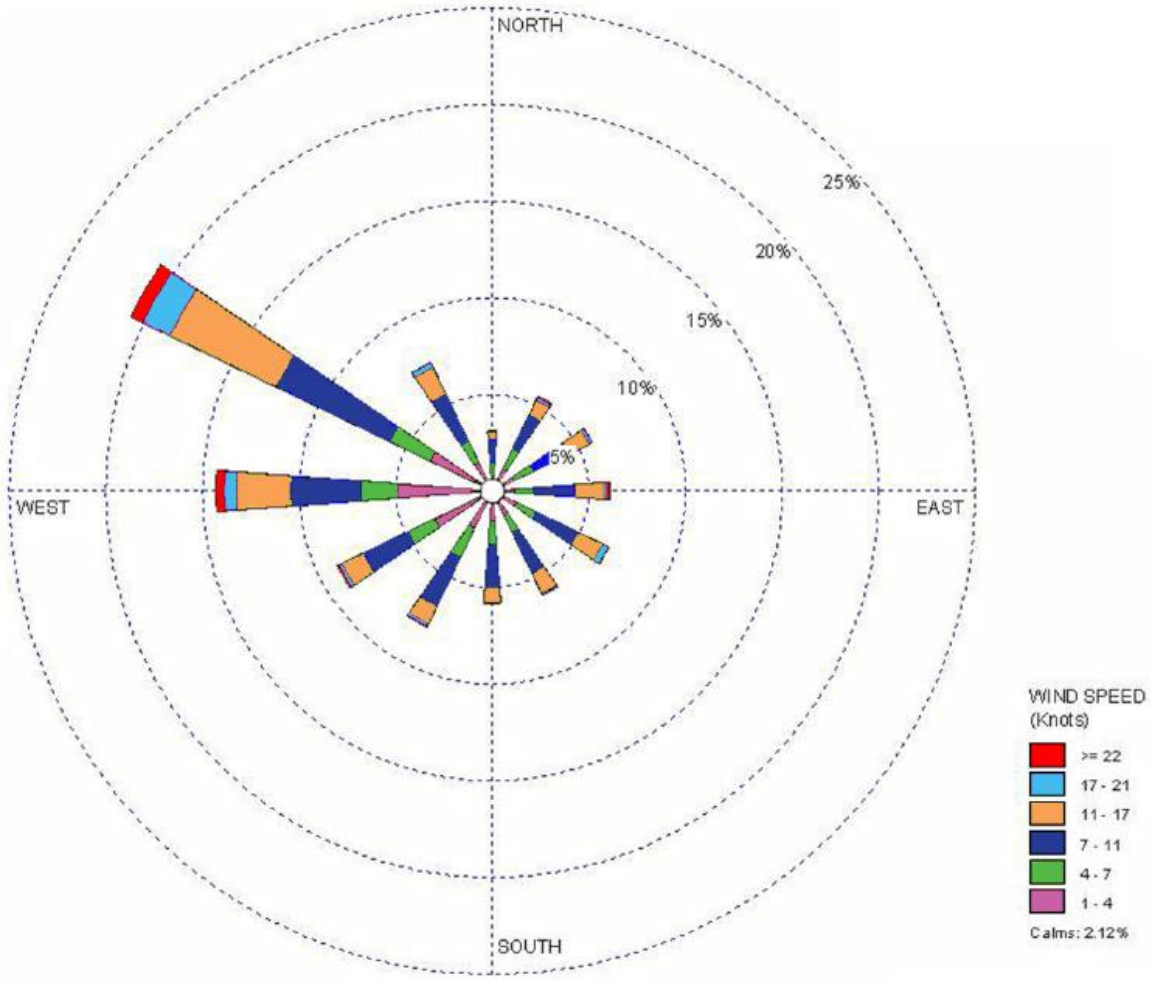

Figure 2.11: Wind rose for the period 1997-2006 (Galdies, 2011)

As can be seen, more than 25% (adding both NW components) of annual winds originate from the NW direction. This is very significant for modelling purposes and also for planning of sites that may emit atmospheric pollutants.

2.4.2 Previous research on SO_2

Locally, very little academic research has been done on the subject of SO_2. The oldest academic research project found was by Caruana and Demanuele (1991) who examined local trends in SO_2. It should be noted that at the time of the study, only the MPS was operational, since the Delimara main power plant was erected in 1990 and the first two 60 MW steam units were commissioned in 1992 (Enemalta, 2012). This is relevant because the study established that the MPS was the major contributor of SO_2 on the island, with relatively minor contributions from motor vehicles and the manufacturing and construction industries (Caruana & Demanuele, 1991).

The study included both experimental and Gaussian Plume modelling to generate local SO_2 trends. The sampling sites chosen were: Ċirkewwa, Blata l-Bajda, MPS, Marsa, Paola and Marsaxlokk. The results indicated that unacceptable levels of SO_2 could be found in the towns surrounding the MPS, mainly Ħamrun, Marsa and Paola, under low wind conditions and depending on wind direction (Caruana & Demanuele, 1991).

The study encountered some problems due to the fact that the SO_2 concentrations calculated using the Gaussian Plume modelling were significantly higher than those of

the experimental results. For example, the model estimated that in the Marsa area the SO_2 concentration would be 1200 µg/m^3 at a wind speed of 2 knots (3.7 km/hr) and 880 µg/m^3 at 8 knots (14.8 km/hr). However, the highest experimental reading for Marsa was 322 µg/m^3 which occurred with a NNE wind at a speed of 10 knots (18.5 km/hr). This created an inconsistency since it was assumed that higher wind speeds would result in a lower SO_2 concentration. However, it was concluded that the inconsistencies were a result of the assumptions of the Gaussian Plume model. Particularly, the model assumed uniform terrain, a power station that operated under full capacity all the time and constant wind speed. The fact that Malta is rather hilly, with frequent changes in wind speed and direction introduced significant inaccuracy in the model results. Additionally, the MPS very rarely operated at full capacity (Caruana & Demanuele, 1991).

The study determined experimentally that the average SO_2 concentration in the Marsa area ranged between 290 to 320 µg/m^3. This was an issue since this concentration range was higher than the European primary standard of 250 µg/m^3 present at the time. The authors blamed the high concentration on low chimney height (83 metres) and lack of SO_2 abatement technology. Some of the suggestions made by the study included increasing power station stack height, use of desulfurisation technologies and 24 hour monitoring of SO_2 concentrations in various locations (Caruana & Demanuele, 1991).

In the following year, a study was conducted by Azzopardi (1992) to determine the effect of atmospheric sulfur compounds on local Globigerina limestone. Although the author stated that no significant generalisations could be made due to the small sample used,

some conclusions could be made. The study found that acid effects on Globigerina limestone were slower than expected under the lab conditions used. However, changes in weight, total porosity and microporosity indicated that deterioration of the limestone was indeed occurring after acid exposure (Azzopardi, 1992).

Another study was later undertaken by Vella *et al.* (1996) with the aim of using limestone surface analysis as a indicator of long-term SO_2 concentration trends. The study included 25 different sampling locations around the island, with the majority located around the MPS. Concurring with the results of Caruana and Demanuele (1991), the study concluded that the main source of sulfur emissions was the MPS (Vella *et al.*, 1996). These results were plotted as a contour map as shown below:

Figure 2.12: Sulfur content contour map (Vella *et al.*, 1996)

Note that in the above diagram, the dots indicate the sampling points and PS indicates the location of the MPS. The results generated three trends: that sulfur emissions are higher closer to the MPS; that sulfur concentration is not symmetrical about the MPS; and that the highest concentrations are found to the South East of the MPS. In fact, the distribution was found to be in accordance with the direction of the NW prevailing wind (Vella *et al.*, 1996).

Following this study, no further academic research could be found. Although certain trends have been established by these studies, changing policies, advancements in technology and the lack of consideration for the Delimara power station highlight the need for further research with regards to SO_2.

2.4.3 Power generation, SO_2 standards and monitoring

Since previous research has established the strong link between power generation and SO_2 emissions in Malta, it is important to examine this sector thoroughly (Caruana & Demanuele, 1991; Vella *et al.*, 1996).

The Enemalta Corporation is the main electricity producer and distributer in Malta, with two power plants in operation: Marsa and Delimara. The MPS has a total operating capacity of 267 MW, consisting of a combination of eight steam turbines and an open cycle gas turbine. The Delimara power station currently has a total capacity of 304 MW, consisting of two 60 MW steam turbines, two 37 MW open cycle gas turbines and a 110 MW combined-cycle turbine. As of May 2010, the steam boilers operate on 0.7% sulfur fuel oil while the gas and combined cycle turbines operate on distillate fuel oil. Additionally, the Marsa power plant is scheduled for decomissioning with the power being compensated by a 200 MW interconnector with Sicily and a 144 MW extension in the Delimara power station consisting of combined cycle diesel engines running on heavy fuel oil (Enemalta, 2012). However, both projects are scheduled for the near future and shall be considered to be beyond the scope of this study.

As stated in a previous section, Malta is subject to EU polices regarding ambient levels and emissions standards for SO_2. Enemalta is responsible for ensuring that SO_2 emissions from power plants are in compliance with Directive 2001/80/EC on the limitation of emissions of certain pollutants into the air from large combustion plants. This is achieved through the use of low sulfur fuels and continuous monitoring of flue gas emissions. However, it should be noted that currently, only Delimara power station is subject to emission limit values under the large combustion plants directive. The MPS was exempted from complying with emission limit values, on condition that the power plant does not operate for more than 20,000 hours starting from 1st January 2008 and ending no later than 31st December 2015 (Enemalta, 2012).

On the other hand, compliance with SO_2 ambient levels for the purposes of Directive 2008/50/EC on ambient air quality and cleaner air for Europe is the responsibility of MEPA. For the purpose of zoning and agglomerations, Stacey and Bush (2002) suggested the delineation of only one agglomeration in Malta with a population greater than 250,000, as shown in Figure 4.13 below. The authors of the study referred to this agglomeration as the "Valletta-Sliema agglomeration". This agglomeration represents the part of the island around which most anthropogenic activity is focused. Areas not included in this agglomeration were grouped in a single zone referred to as the "Maltese zone".

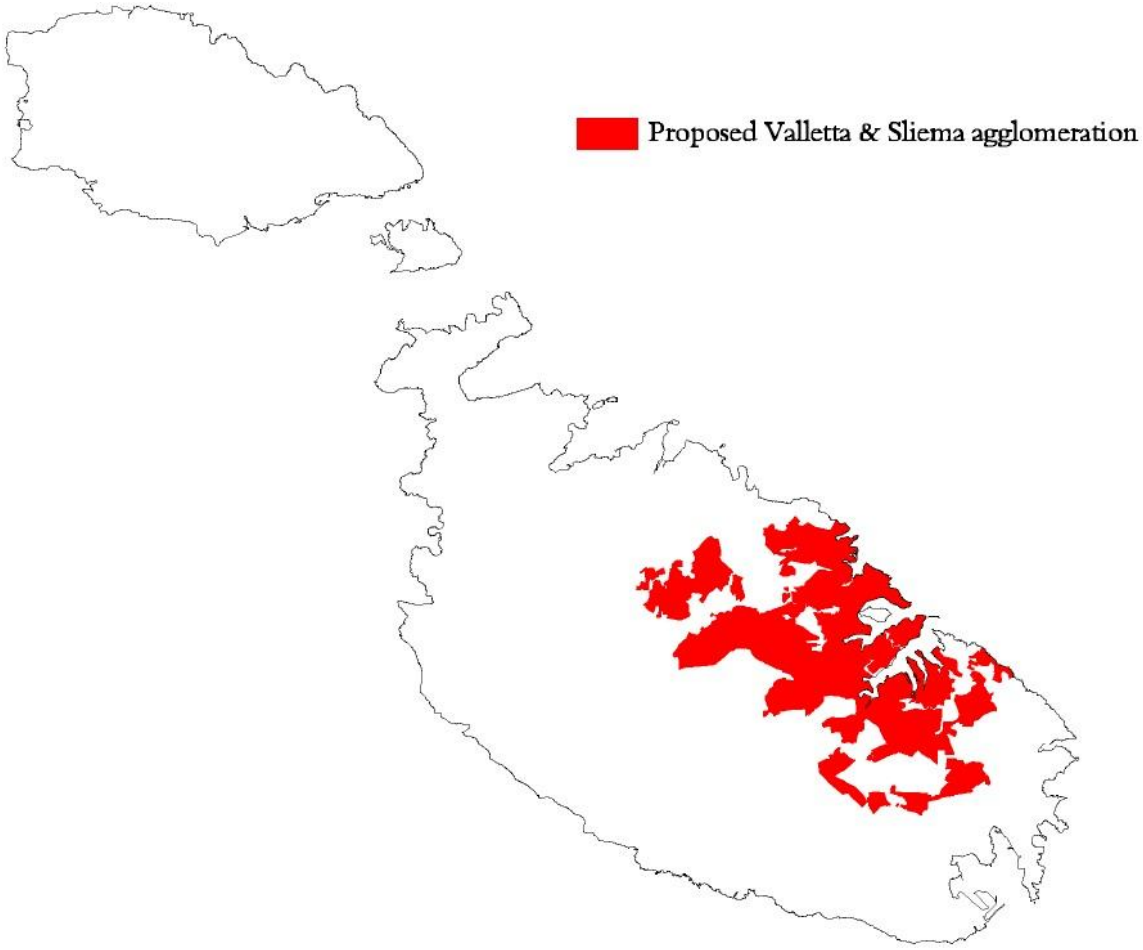

Figure 2.13: Proposed agglomeration for Malta (Stacey & Bush, 2002)

Monitoring is achieved through regular measurements of air quality throughout the island. The monitoring network includes 126 diffusion tube sites and also 4 automated real time monitoring stations collecting continuous data at Għarb, Kordin, Msida and Żejtun. The location of the real time monitoring stations is shown in Figure 2.14 below. MEPA is also responsible for compiling annual emissions for Malta for the purposes of Directive 2001/81/EC on national emission ceilings for certain atmospheric pollutants (MEPA, 2012).

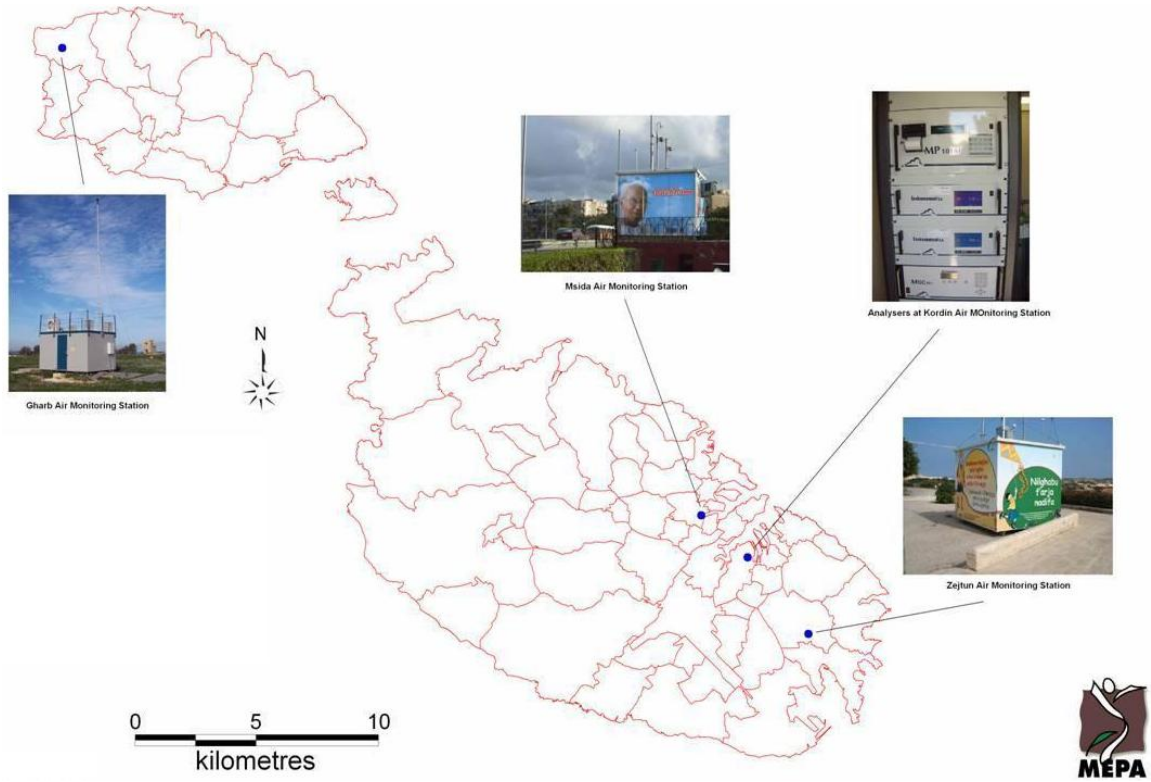

Figure 2.14: Location of continuous monitoring stations (MEPA, 2012)

It should be noted that on entering the EU in 2004 Malta, together with all the other EU Member States, had to achieve compliance with SO_2 ceilings by 2010. A 2006 MEPA report showed that till 2005, Malta had not yet achieved this ceiling and that following the introduction of several policy measures, it was expected that compliance be reached by 2010 (MEPA, 2006). In this regard, official reported data from the European Environment Information and Observation Network (EIONET) database shows the following:

Year	Reported emission (Gg SO_2)
2000	24.3
2001	25.9
2002	25.2
2003	27.4
2004	11.1
2005	11.4
2006	11.5
2007	11.8
2008	10.8
2009	8.0
2010	8.1

Table 2.4: Malta emission inventory, 2000-2010 (EIONET, 2012)

Hence, it should be noted that the EIONET data shows that Malta actually achieved compliance in the year 2009, ahead of projections and following an SO_2 emissions reduction of around 66.7% from 2000 levels.

2.5 Statistical computing techniques

2.5.1 Introduction to statistical computing in atmospheric chemistry

Computer mathematical models and statistical techniques have been shown to be an essential tool in atmospheric chemistry (Benkovitz *et al.*, 1996). Various techniques are used to determine the extent of the effects of pollutants on variables such as human health and the environment. Such statistical techniques have been used to make a range of diverse associations such as short/long term exposure and mortality, age group and amount of emissions and ratios of different pollutants from emissions sources such as

biomass burning and marine vessels (Brunekreef, 2010; McLaren *et al.*, 2012; Menz & Kühling, 2011; Sinha *et al*., 2003; Wang *et al.*, 2002).

Various tools and techniques are available depending on the purpose of analysis. Monte Carlo simulations are used to quantify emissions in situations where there are significant uncertainties in the amounts (Lu *et al.*, 2011). Dispersion models such as the Industrial Source Complex – AMS/EPA Regulatory Model (ISC-AERMOD) and the Hybrid Single Particle Lagrangian Integrated Trajectory Model (HYSPLIT) may be used to predict pollutant trajectories, origin and/or pollutant concentrations over an area (HYSPLIT, 2012; Yassin & Al-Awadhi, 2012). Data mining packages such as R may be used to process large amounts of data to generate predictive relationships, associations and other statistical functions (Han & Kamber, 2006; R-project, 2012). Mapping packages such as the Inter Operability and Automated Mapping Project (IntaMap) and Geographical Information Systems (GIS) may be used to map data and/or statistical functions for visualisation (ESRI, 2007; IntaMap, 2012).

Emphasis shall only be placed on the packages to be used in this study and there will be no significant discussion regarding the other techniques. Specifically, this study shall make use of R and SPSS for statistical processing and GIS and IntaMap for mapping of data.

2.5.2 R environment

R is a free programming language and software environment package which is specifically tailored for statistical computing and graphical output. R provides statistical tools such as linear and nonlinear modelling, classical statistics, time-series analysis and clustering. R is capable of processing significant amounts of data and producing "publication-quality" output. The software is meant to be used as a complete stand-alone system (R-project, 2012). Such data mining packages have been found useful in processing of pollution data from sensors and also the generation of statistical associations for atmospheric pollutants (Ma *et al.*, 2008; Martinez-Ballesteros *et al.*, 2010).

Additionally, since R is built as a computer language, new functions can be defined by users. This allows the creation of what are known as "packages" which are created by users and shared across the R community. Such packages can be downloaded for specific uses and include alternative clustering techniques, classification techniques, fonts and Monte Carlo models (R-project, 2012). Particularly interesting to this study is the "openair" package. This package includes a set of tools for the analysis of air pollution data and includes specific functions for time series analysis and dispersion analysis (Carslaw & Ropkins, 2012).

In fact, Alija *et al.* (2011) used R and the openair package to analyse a long air pollution time series in an undisclosed location in Spain. The study included the analysis of ozone,

nitrogen dioxide and particulate matter. The authors used the package to generate summary plots that condensed the data, to determine seasonal trends in pollutants and also combined the air pollution data with meteorological data to produce polar emission plots showing concentration of pollutants in each direction (Alija *et al.*, 2011).

2.5.3 SPSS

SPSS is an acronym for Statistical Package for the Social Sciences which is a software package produced by IBM. The base package is more user friendly than R and allows quick analysis of data by offering functions that allow determining of relationships, clusters, trends and predictions. Some of the specific functions available include descriptive statistics such as comparison of means and ANCOVA and predictive functions such as linear regression and factor analysis (IBM, 2012).

SPSS is widely used in a variety of sectors, including air quality. Slini *et al.* (2002) used SPSS linear regression analysis for the prediction of ozone levels in Athens. The resulting model was considered to be "acceptable" by the researchers given the high variability in atmospheric predictions. However, the model produced was not considered to be sufficient by itself for accurate predictions (Slini *et al.*, 2002). Locally, Saliba *et al.* (2008) used SPSS to conduct a 10 year study of surface ozone concentrations in Gozo. The authors of this study used Analysis of Covariance (ANCOVA) regression to produce a model describing ozone levels. ANCOVA was found to be suitable since it allows predictions using variables that may be both categorical (referred to as factors) and also

metric (referred to as covariates) in scale. By fitting this model to the 10 years of data, the study produced a usable model to predict ozone levels in Gozo (Saliba *et al.*, 2008). It should be noted that ANCOVA will also be used in this study.

2.5.4 Mapping Packages

GIS is a tool that facilitates representation of geographical information. It does so by superimposing georeferenced data onto maps through the use of layering. Different layers represent different information which can be manipulated and analysed by the user. The use of layers allows users to integrate various data groups into a single project (ESRI, 2007). In the case of this study, the GIS package ArcGIS 10 by the company Esri shall be used (ESRI, 2012).

GIS has been found to be a very useful tool in air quality monitoring. To name a few examples, GIS has been used to assemble gridded emissions inventories, map spatial and temporal variations in urban air quality and to model dust transportation (Chattopadhyay *et al.*, 2010; Indracanti *et al.*, 2007; Matejicek, 2005; Matejicek *et al.*, 2008).

On the other hand, IntaMap is a non-commercial software project funded by the European Commision and started in 2006 to facilitate the exchange of information in air quality monitoring. IntaMap is slightly similar to GIS in that it allows mapping of data. However, IntaMap is intended as a web based real-time mapping tool for environmental variables. The main function of IntaMap is to use geostatistics to interpolate (i.e. generate

data values in between discrete data sets to generate a continuum) data such as emissions values from point sources and generate a complete map of the study area (IntaMap, 2012). IntaMap has been successfully used by the European Environment Agency and also in applications such as rainfall and radioactivity monitoring (Stoehlker *et al.*, 2009; IntaMap, 2012).

2.6 Summary

A few general remarks may be made following this review. Anthropogenic activities, mainly combustion for energy related processes, have in the past century led to a high presence of SO_2 in the atmosphere. This has resulted in significant impacts of both the environment and human health. Notable effects include aggravation of respiratory conditions in humans, acidification of soil and water bodies and effects on local climates.

However, international legislative efforts over the last 30 years have resulted in a decrease in SO_2 emissions. This has been seen both globally, regionally (in the EU) and also in Malta. In Malta's case, past research has found that the MPS was the major emitter of SO_2 on the island. However, research on this subject was concluded before Delimara power station was operational and before the existence of MEPA's monitoring network. This research can be facilitated through software techniques such as data mining, mapping packages and statistical packages, where a large amount of data, such as that compiled by an air quality network, can be reliably examined for statistical trends and to generate predictive models.

CHAPTER 3: METHODOLOGY

3.1 Introduction

This chapter shall discuss the exact methodology applied in this study. The analysis involved five main stages: data compilation, cleaning and integration, mapping of points and interpolation, general numerical analysis, R analysis and SPSS analysis. Each of the following sections shall discuss each stage in more detail and the exact methodology applied. These descriptions shall also justify the methodology used by citing past research that used similar methodology.

3.2 Data compilation, cleaning and integration

This section shall describe the methodology used in this study in an approximately chronological order. The first stage was the collection of data for the statistical analysis from MEPA and Enemalta. It should be stated that most of the data sets used in this research, such as emission levels from the MPS and ambient levels from Malta's fixed station network for the measurement of air quality, are also freely available from the MEPA and Enemalta websites (Enemalta, 2012; MEPA 2012). Specifically, the table below details the different data sets collected and their source:

Data set number	Data set contents	Source
1	Averaged yearly diffusion tube SO_2 readings	MEPA
2	MPS emission rates for M1 chimney	Enemalta
3	MPS emission rates for M2 chimney	Enemalta
4	MPS emission rates for M3 chimney	Enemalta
5	MPS emission rates for M4 chimney	Enemalta
6	MPS wind data	Enemalta
7	MPS stack properties	Enemalta
8	SO_2 readings from Għarb station	MEPA
9	SO_2 readings from Kordin station	MEPA
10	SO_2 readings from Msida station	MEPA
11	SO_2 readings from Żejtun station	MEPA
12	Wind data from Għarb station	MEPA
13	Wind data from Kordin station	MEPA
14	Wind data from Msida station	MEPA
15	Wind data from Żejtun station	MEPA

Table 3.1: Data sets obtained for study

The data sets included different fields, covered different time averaging periods and some were also collected over different time scales. The table below lists the data sets (as numbered in Table 3.1), the period covered, the frequency of data collection and also the relevant fields included:

Data set no.	Period	Freq.	Fields
1	2004 - 2010	Yearly	Tube location (WGS 84 coordinates), Average yearly SO_2 reading ($\mu g/m^3$)
2	01/08/2009 - 01/03/2012	Hourly	Time, Emissions concentration ($\mu g/m^3$)
3	01/08/2009 - 01/03/2012	Hourly	As above
4	01/08/2009 - 01/03/2012	Hourly	As above
5	01/08/2009 - 01/03/2012	Hourly	As above
6	15/05/2010 - 31/12/2010	Hourly	Time, Wind speed (m/s) & Direction (º)
7	N/A*	N/A*	Flue gas flow rate per chimney (Nm^3/hr)
8	01/06/2007 - 31/12/2010	Hourly	Time, SO_2 reading ($\mu g/m^3$)
9	01/01/2007 - 31/12/2010	Hourly	As above
10	01/01/2007 - 31/12/2010	Hourly	As above
11	01/01/2007 - 17/12/2010	Hourly	As above
12	01/01/2008 - 31/12/2010	Hourly	Time, Wind speed (m/s) & Direction (º)
13	01/01/2007 - 31/12/2011	Hourly	As above
14	01/01/2008 - 31/12/2010	Hourly	As above
15	01/01/2007 - 31/12/2011	Hourly	As above

Table 3.2: Data sets contents

* Data obtained as a calculated normalised average, applicable over whole time period

As expected, such large data sets may include missing or invalid data or else data in a different format than that required. Missing or invalid data in this case would be expected to have been caused by either equipment failure or scheduled shutdown. Errors during data transmission or recording may also have occurred, resulting in invalid readings. Different formats would also be expected due to different software being used or different standards (e.g. different date formats or coordinate systems). Hence, data needed to be "cleaned" of these inconsistencies to produce a usable data set (Han & Kamber, 2006).

There are various methods of handling these inconsistencies such as: deletion of the entry, manual filling of data, global constants, use of a mean, regression and interpolation

(Eischeid *et al.*, 1995; Han & Kamber, 2006; Li & Shue, 2004). In this case, deletion of invalid records was chosen as the best option for two main reasons. First of all, algorithms to predict missing values typically depend on valid values obtained at the same time from a number of geographically proximate locations (Eischeid *et al.*, 1995). In the case of emission levels from the MPS, there was only one source, hence this was not possible. Secondly, the use of other locations to produce predicted values assumes similarity between nearby stations, which may eclipse anomalous trends that may have been present (Li & Shue, 2004). This is especially true with regards to the readings from the four continuous monitoring stations. Since they may differ significantly in location, use of other stations to predict missing readings might result in significant deviations from what would actually be present.

Following the removal of inconsistent records, the variables were edited to usable formats. The most important change, which was necessary for the hourly data readings, was the change of the time stamp to a “dd/mm/yyyy hh:mm” format. This was necessary since this is the format required by the openair package in R. Additionally, this would facilitate integration of data by providing a unique and identifiable time code (i.e. a "key field" in database terms) for each reading across different data sets.

There were also three other required changes for the data to be usable. First, all geographical coordinates were converted to the Universal Transverse Mercator (UTM) coordinate system (Note: Malta is found in the UTM zone 33N or EPSG 23033). This was required since the IntaMap system uses the UTM coordinate system (IntaMap,

2012). Secondly, the emission levels or flue gas concentrations obtained from Enemalta did not include the waste gas flow rates for each chimney. In addition, as is required by law (Directive 2001/81/EC, 2001), emission levels are reported on a chimney by chimney basis. Hence, the waste gas flow rates for each chimney were used to calculate the mass emission rate of SO_2 (in g/hr) from each chimney per hour. The mass emission rate for the whole plant was subsequently calculated by adding up the mass emission rates for the four chimneys at the MPS. This change was needed to obtain a number representing a specific amount of SO_2 being emitted, thus allowing for statistical analysis, with total emissions being a predictor. Thirdly, the wind data from the MPS was rotated by 180º to obtain a new field representing the direction where the wind is blowing relative to the MPS. This field was found to be useful to express the direction, towards which, SO_2 would be transported after emission from the MPS.

The separated and cleaned data sets were then integrated into useful data sets. Most of the data sets were in separate files, organised by date or by location. These separate files had to be integrated into single data sets for the whole time period. This also required that different data sets, such as the SO_2 readings and wind readings from the monitoring stations, be joined. Since some data sets covered different time periods, only data sets required for a specific analysis were joined together, e.g. for the analysis of pollution readings from monitoring stations, only the SO_2 readings and wind readings from the monitoring stations were joined. This served two functions: reducing the number of fields in the data set to minimise processing time and maximising the number of records by maximising the time overlap between the data sets. The disadvantage of the method used

was that several data files needed to be produced to account for the different data set permutations required for the different analyses. Thus, the maximisation of overlap improved the statistical significance of results, so the advantages of this methodology were deemed to outweigh the disadvantages.

Following the data integration, the data sets were converted into comma separated value (csv) format or else into spreadsheets (Microsoft Excel was used). The csv format was required for the R and IntaMap stages while spreadsheets were used for GIS and SPSS.

3.3 Mapping of points and interpolation

The next stage of the study involved the mapping of spatial data and interpolations. ArcGIS 10 was used to produce maps of the location of the diffusion tube network, the monitoring stations and the power stations. This was done through the conversion of spreadsheets containing coordinates of the locations into a GIS format. The resulting layers were then formatted and the maps exported.

IntaMap was then used in conjunction with the diffusion tube network data to produce yearly average maps of SO_2 across the islands. Through the use of this package, the spatial points lacking data were calculated from nearby known points through interpolation. IntaMap provides three interpolation methods: Ordinary Kriging, Projected Sequential Gaussian Processes and Copula Kriging. Ordinary Kriging is normally used with data sets with less than 1000 points, as was the case with this study (IntaMap, 2012).

Although there are other forms of Kriging, the advantage of Ordinary Kriging is that there are no specific trends in the data set, thus allowing any present trends in the data to develop naturally (Childs, 2004). In fact, Wong *et al.* (2004) successfully used Ordinary Kriging with regards to ozone and PM emissions in California. The interpolation diagram produced was automatically overlaid on a map of Malta by IntaMap and this was then exported into a more convenient format.

3.4 General numerical analysis

The different data sets were individually imported into R. The data was then analysed to give general numerical values such as time periods of the data set, minima, maxima and means.

Although simple in nature, this analysis was used as a general overview of the data sets, allowing comparison of similar data sets, such as the mean readings of the different monitoring stations. It should be noted that a similar analysis could have been completed using other software such as Excel or SPSS, however, R made it easier to handle the multiple large data sets.

3.5 Analysis using R

The next stage of the project involved a more rigorous statistical analysis. Several analyses of the data were made using R and the openair package (Carslaw & Ropkins,

2012), requiring the following five data sets to be compiled (as part of the data integration phase):

- Wind data, divided by location
- MPS emissions data
- MPS emissions and wind data
- Monitoring stations SO_2 readings
- Monitoring stations SO_2 and wind readings

These data sets were imported into R using openair's "import" function, which recognises time stamps of the appropriate format, automatically creating a chronological order. Openair functions also recognise correctly labelled fields such as wind speed, "ws", wind direction, "wd" and different locations, "site". Additionally, certain preset pollutants, such as PM and SO_2 are recognised by the package (Carslaw, 2012). The imported data was then analysed separately using openair functions.

The first data set to be analysed was the wind data, using the function "windRose". This function summarises the wind data as a wind rose, requiring an input of time stamp, wind speed and wind direction (Carslaw, 2012). This was done separately for the different wind monitoring locations.

This was followed by the analysis of the MPS emissions data. This was done through a combination of three functions: "timePlot", "trendLevel" and "timeVariation". Each

function only required time stamp and emissions as inputs. The timePlot function was used to give a graphical representation of the emissions versus time, with a choice of different time scales for averaging the plot. The trendLevel function was used to condense the data and categorise it by year, month and hour, showing different levels of emissions according to a colour scale. The timeVariation function was used to generate plots of emissions categorised by time of day, weekday and month (Carslaw, 2012). The latter function was found to be particularly useful to visualise everyday trends in emissions.

The MPS emissions and wind data set was used to produce what the author has called "inverse pollution roses". Differing from wind roses, pollution roses show amount of pollutant and direction where the pollutant is being transported to or originating from. In particular, inverse pollution roses are plotted with the wind direction rotated by 180º and therefore show where the pollutant is being transported to. These can be produced by using the "pollutionRose" function in R. Similar to the windRose function, pollutionRose required three inputs, however in this case the inputs were time stamp, power station emission and rotated wind direction.

The monitoring station SO_2 readings data set was analysed in a similar fashion to the power station emissions i.e. using timePlot, trendLevel and timeVariation. However, in this case, the inputs were time stamp and SO_2 concentration reading. Additionally, another variable "site" was used to classify the readings according to the monitoring station.

The monitoring stations SO_2 and wind direction data set contained five variables: time stamp, emissions reading, wind direction, wind speed and site. As above, a pollution rose was produced; in this case the plots generated were used to show the direction from which the SO_2 readings was being transported. Two other functions: "polarPlot" and "percentileRose" were used with this data set. A polar plot can be used to show the concentration of pollutant (colour coded) as a bivariate plot of wind speed and direction. This was used to show at what wind speeds and direction the higher concentrations of pollutant were being detected. On the other hand a percentile rose was used to generate a bivariate plot of wind direction and SO_2 reading, with the percentile levels shown as a colour coding. This plot was used to demonstrate the distribution of readings (especially the outliers) with respect to wind direction.

All of the plots produced were exported to a usable format. Additionally, the monitoring station polar plots were imported into GIS and overlaid over the appropriate monitoring stations. Lines were then drawn onto the map and extrapolated to show where the highest concentrations of readings were originating. This extrapolation was used to determine likely sources of SO_2 according to the data available.

3.6 SPSS analysis

Emissions readings, the wind speed, direction and SO_2 concentration readings from the different monitoring stations were separately loaded into SPSS. As was done by Saliba *et*

al. (2008), wind direction was divided into different sectors, to increase the likelihood of generating statistically significant relationships. The division of the categories is shown in Figure 3.1 below:

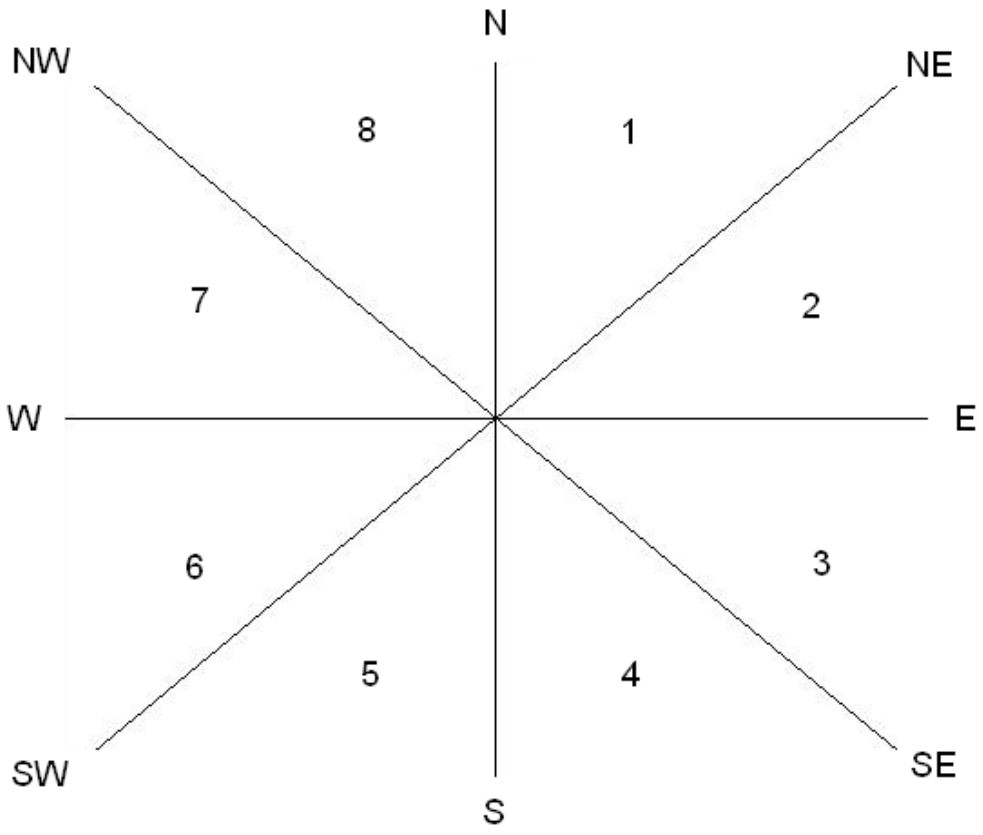

Figure 3.1: Illustration of wind categories

Following a similar methodology to that of Saliba *et al.* (2008), an ANCOVA regression model was fitted to the data using SPSS, with the dependent variable being emissions. The model was fitted using wind direction as a factor (since it was categorical) and wind speed and emissions as covariates (since they were metric). The resulting model and outputs were then recorded and interpreted. A second analysis, omitting wind direction

and using only readings originating from the quadrant (i.e. two wind categories) representing the MPS was then attempted. This second analysis was used to establish whether emissions from MPS were statistically significant. All the results were then collected and interpreted as discussed in Chapter 4.

3.7 Summary

This chapter described the methodology of how the analysis was performed. The data used and its initial processing has been described in Section 3.2. The products of this process were a number of data sets that could be used in later analyses. Section 3.3 described how the data was mapped spatially onto GIS and also the procedure used in IntaMap. Section 3.4 detailed how basic statistics were produced for each of the data sets available. The use of R, including each of the specific functions used was described in Section 3.5. The input requirements and the significance of the output obtained for each function was also discussed in this section. Section 3.6 discussed the SPSS analysis, including the type of statistical analysis used and also the categorisation of the variables. With the methodology defined, the analysis was completed, with the following chapter discussing the results obtained.

CHAPTER 4: RESULTS & DISCUSSION

4.1 Introduction

This chapter shall discuss the results obtained from the methodology described in Chapter 3. First, the location of the fixed monitoring stations, the diffusion tubes and the power stations shall be discussed. This is followed by the general numerical analysis of the different data sets used in this study. This includes an interpretation of the preliminary trends that can be discerned. The chapter shall then continue to discuss the results of the diffusion tube interpolations, the R analysis and the SPSS analysis. Each of the sections discusses the results obtained in the context of the other results, thus giving a more complete picture.

4.2 Location of monitoring network and power stations

The results of GIS mapping of data points is shown below, with Figure 4.1 showing the location of the 126 diffusion tubes used and Figure 4.2 showing the fixed monitoring stations and power stations.

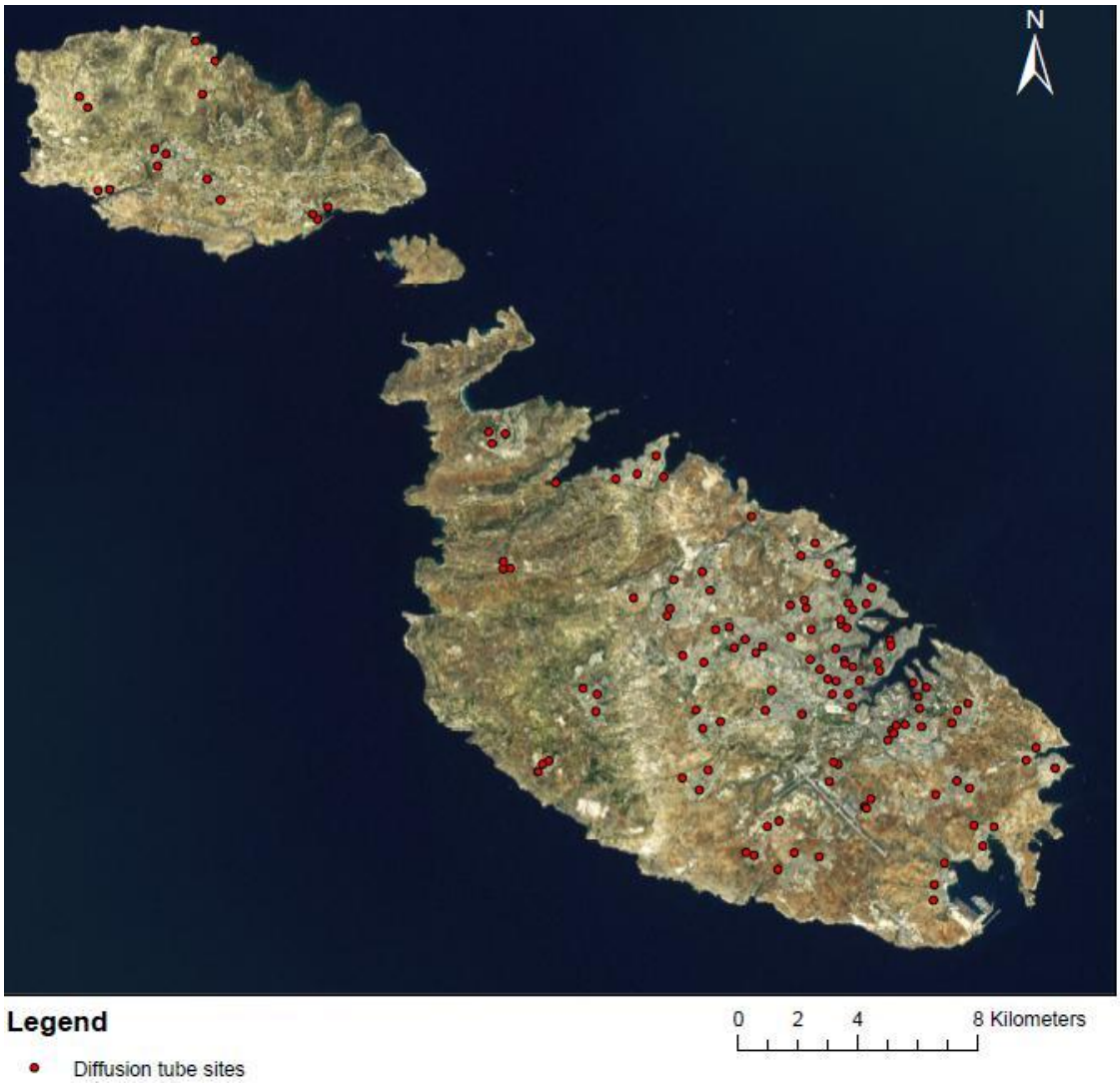

Figure 4.1: Diffusion tube network

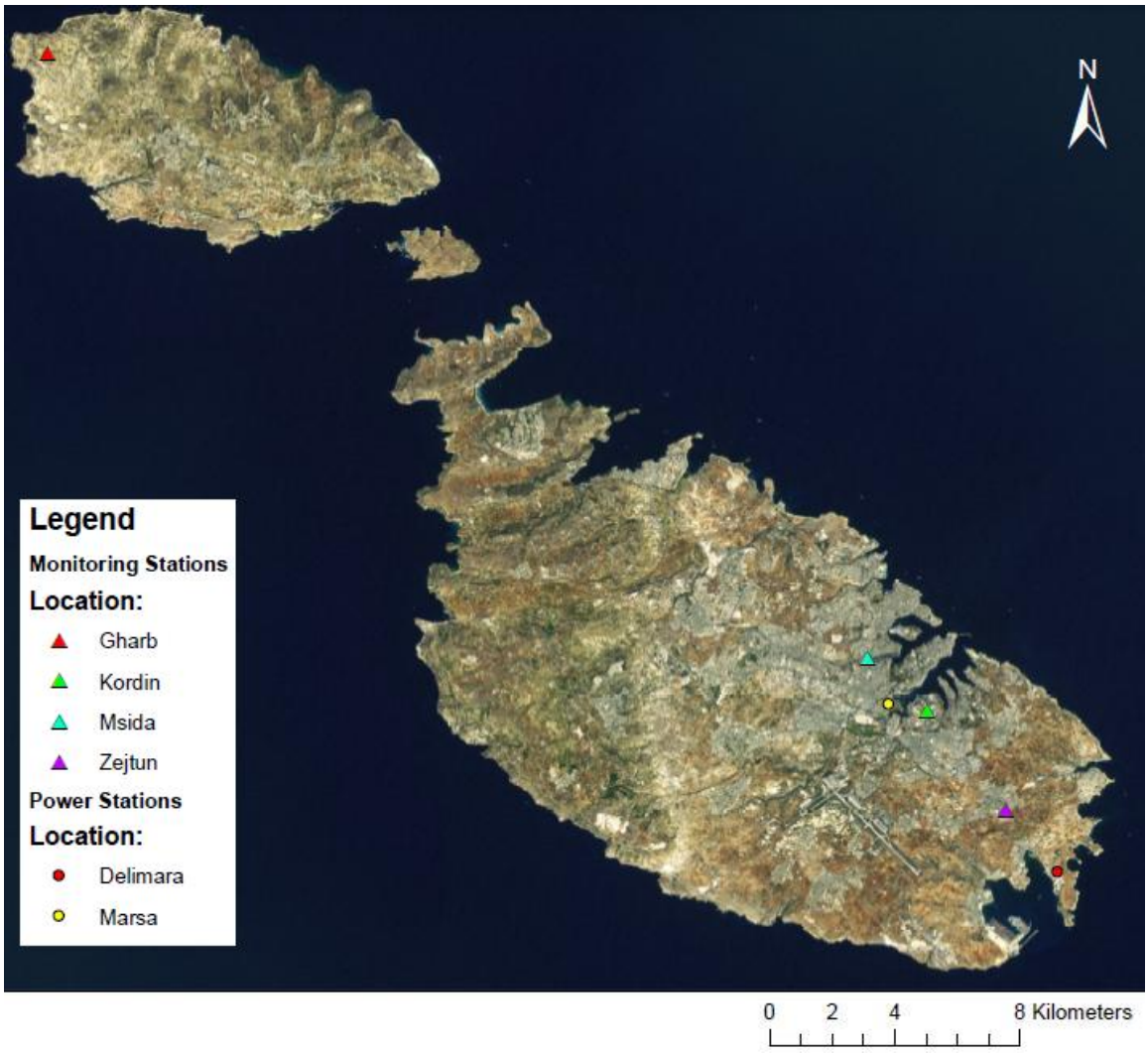

Figure 4.2: Location of monitoring stations and power stations

As can be seen from the figures above, the diffusion tube network is distributed across Malta and Gozo, with a higher concentration of diffusion tubes in the central part of Malta, which has a higher population density (NSO, 2012) and coincides with the Valletta-Sliema agglomeration (Stacey & Bush, 2002). The three monitoring stations in the agglomeration are located as follows:

1. Żejtun - in a urban background setting in the direction of the prevailing wind from the agglomeration
2. Msida - a traffic site as close as possible to Valletta
3. Kordin - an industrial site which is also close to the point which experiences the maximum ground level concentration from MPS

The fourth station, the one in Għarb is located in a rural area in the Maltese zone and is used to represent an SO_2 rural background reading (MEPA, 2012). The siting of the stations followed the recommendations suggested by Stacey and Bush (2002).

4.3 General numerical analysis

4.3.1 Wind data

All of the data obtained from the different sources was then statistically analysed using R, starting with the wind data; the results of which are displayed in the tables below:

Location	Period	Mean wind direction (º)
Għarb	01/01/2008 00:15 - 31/12/2010 10:00	227.0
Kordin	01/01/2007 00:00 - 31/12/2011 23:00	173.1
Marsa	15/05/2010 00:00 - 31/12/2010 23:00	216.1
Msida	01/01/2008 00:00 - 31/12/2010 23:00	216.1
Żejtun	01/01/2007 00:00 - 31/12/2011 23:00	210.2

Table 4.1: Wind data analysis (part 1)

Location	Minimum wind speed (m/s)	Maximum wind speed (m/s)	Mean wind speed (m/s)
Għarb	0.0	30.2	5.6
Kordin	0.0	16.7	3.5
Marsa	0.0	32.2	9.1
Msida	0.1	14.3	2.5
Żejtun	0.0	16.7	3.7

Table 4.2: Wind data analysis (part 2)

The above results show that, overall, wind varied between 0.0 and 32.2 m/s depending on location. The data shows that Msida had the lowest mean wind speeds at 2.5 m/s, followed closely by Kordin (3.5 m/s) and Żejtun (3.7 m/s). Higher wind speeds were recorded at Għarb, with the mean wind speed being 5.6 m/s and a maximum wind speed of 30.2 m/s, one of the highest speeds recorded. Both the highest mean wind speed (9.1 m/s) and highest wind speed (30.2 m/s) were recorded at Marsa. However, with regards to the mean wind speed, it should be noted that the period examined is shorter than that of the other locations, hence deviations may be present.

4.3.2 Monitoring station data

As above, the monitoring station data available was statistically analysed using R, producing the results displayed in the tables below:

Location	Period	Minimum SO_2 reading ($\mu g/m^3$)	Maximum SO_2 reading ($\mu g/m^3$)
Għarb	01/06/2007 00:00 - 31/12/2010 23:00	0.0	89.0
Kordin	01/01/2007 00:00 - 31/12/2010 23:00	0.0	368.8
Msida	01/01/2007 00:00 - 31/12/2010 23:00	0.0	401.2
Żejtun	01/01/2007 00:00 - 17/12/2010 15:00	0.0	295.5

Table 4.3: Monitoring station data analysis (part 1)

Location	Mean SO_2 reading ($\mu g/m^3$)	75 percentile reading ($\mu g/m^3$)	95 percentile reading ($\mu g/m^3$)	99 percentile reading ($\mu g/m^3$)
Għarb	1.8	1.8	6.4	15.7
Kordin	9.1	9.5	30.1	91.5
Msida	3.6	3.0	8.7	48.6
Żejtun	5.1	5.6	15.6	44.5

Table 4.4: Monitoring station data analysis (part 2)

Note that histograms representing the distribution of the data sets have been added in the Appendix (Figures A.1-A.4). The results indicate that the monitoring station data was quite consistent with regards to the period available and minimum readings. The analysis has shown that Għarb has the lowest SO_2 concentrations, both as a maximum value (89.0 $\mu g/m^3$) and mean value (1.8 $\mu g/m^3$). Additionally 75% of the readings are lower than 1.8 $\mu g/m^3$, which is equal to the mean value, with 99% of the readings being lower than 15.7 $\mu g/m^3$. These values clearly show that the maximum value of 89.0 $\mu g/m^3$ was an outlier.

Msida and Żejtun were found to have higher SO_2 readings than those of Għarb; with Msida having a lower mean reading (3.6 µg/m^3) than that of Żejtun (5.1 µg/m^3). However, Msida had the highest recorded SO_2 concentration reading (401.2 µg/m^3) whereas Żejtun had a far lower maximum reading of 295.5 µg/m^3. Furthermore, although the 95th percentile of Żejtun (15.6 µg/m^3) was higher than that of Msida (8.7 µg/m^3), the trend is reversed in the 99th percentile with Żejtun being 44.5 µg/m^3 and Msida being 48.6 µg/m^3. This shows that although Msida generally had lower readings than Żejtun, Msida experienced occasional spikes in SO_2 concentration (approximately 1% of readings), which were higher than those registered at Żejtun. As with Għarb, the majority of readings (75%) occurred quite close to the mean value.

Kordin exhibited the highest mean reading of 9.1 µg/m^3, with the highest reading being 368.8 µg/m^3, which was the second highest concentration reading of the stations. Like the other stations, 75% of readings occurred very close to the mean value. With the 95th percentile being 30.1 µg/m^3 and 99th percentile being 91.5 µg/m^3, Kordin also demonstrated a tendency for SO_2 concentration peaks. As with Msida, exceptionally high peaks accounted for less than 1% of the total readings. At this stage it should also be noted that there were only two occasions when the 350 µg/m^3 hourly limit of Directive 2008/50/EC was exceeded. These are shown in the table below:

Time	SO_2 reading (µg/m^3)	Location
29/05/2008 01:00	401.2	Msida
28/08/2010 13:00	368.8	Kordin

Table 4.5: Occurrences of SO_2 limit exceedance

Although there were times when the 350 µg/m^3 hourly limit value was exceeded, the frequency was far below the allowance of 24 exceedances per year. Despite this, it should be noted that these are hourly averages, hence there may have been brief instances when the concentration of SO_2 was higher. However, for the purposes of air quality standards, Malta was in compliance with Directive 2008/50/EC for the period evaluated.

4.3.3 Emissions data

The statistical analysis of the MPSs emissions data is displayed in the table below. Additionally, a histogram representing the distribution of the data set may be found in the Appendix (Figure A.5).

Period	01/08/2009 01:00 - 01/03/2012 00:00
Minimum emission (g/hr)	127.5
Maximum emission (g/hr)	1554.5
Mean emission (g/hr)	817.5
75 percentile emission (g/hr)	1029.1
95 percentile emission (g/hr)	1199.8
99 percentile emission (g/hr)	1459.4

Table 4.6: Emissions data analysis

The table shows that the range of emission rates was quite large, between 127.5 to 1554.5 g/hr. Moreover, the mean of the emissions rate was 817.5 g/hr with the majority of readings (75%), being slightly above the mean rate (1029.1 g/hr). The 99th percentile (1459.4 g/hr) was found to be quite close to the maximum rate, showing that around 1% of the total values were close to the maximum emission rate.

4.3.4 Diffusion tube data

The statistical analysis of the diffusion tubes data is displayed in the table below:

Year	Minimum SO_2 concentration ($\mu g/m^3$)	Maximum SO_2 concentration ($\mu g/m^3$)	Mean SO_2 concentration ($\mu g/m^3$)
2004	0.0	34.6	12.1
2005	0.0	24.5	9.0
2006	0.0	15.9	5.4
2007	0.0	20.0	7.4
2008	2.0	15.7	6.4
2009	1.5	24.1	5.0
2010	1.5	23.5	4.7

Table 4.7: Diffusion tube data analysis (part 1)

Year	75 percentile SO_2 concentration ($\mu g/m^3$)	95 percentile SO_2 concentration ($\mu g/m^3$)	99 percentile SO_2 concentration ($\mu g/m^3$)
2004	14.2	25.3	29.7
2005	10.7	17.7	22.5
2006	6.6	12.7	14.4
2007	9.6	13.2	19.2
2008	7.8	12.9	15.5
2009	6.3	9.4	13.5
2010	5.3	10.8	17.0

Table 4.8: Diffusion tube data analysis (part 2)

Note that histograms representing the distribution of the data sets have been added in the Appendix (Figures A.6 –A.12). The analysis results showed an overall decrease in the mean SO_2 concentration readings in the diffusion tube network between 2004 and 2010 (from 12.1 to 4.7 $\mu g/m^3$). The only exception was the year 2007, in which an increase in the mean concentration of SO_2 was recorded compared to 2006 (5.4 to 7.4 $\mu g/m^3$).

It should also be noted that despite this overall mean decrease, maximum recorded values increased in 2009 (24.1 µg/m^3) and 2010 (23.5 µg/m^3) compared to 2008 (15.7 µg/m^3). Nevertheless, both the 75th percentile and 95th percentile decreased compared to those of 2008, showing that 95% of the recorded values have decreased. However, the 99th percentile of 2010 (17.0 µg/m^3) is higher than that of 2008 (15.5 µg/m^3), showing that there were localised areas where SO_2 concentrations may have increased significantly (approximately 1% of locations, equivalent to about 1 diffusion tube).

4.4 Diffusion tube interpolation

The results of the diffusion tube network interpolation produced using IntaMap are shown in Figures 4.3 – 4.9 below. The results can be seen to be in concordance with the results of the study by Vella *et al.* (1996), with higher SO_2 concentrations near the MPS area, particularly to the South East of the power station (refer to Figure 2.12). However, compared to the 1996 research, the area of high concentration was seen to be significantly more localised following 2008 (Figure 4.7 – 4.9).

Additionally, the results help to illustrate the trends obtained from the numerical data analysis presented in Section 4.3.4. In fact, the same overall decreasing trend in SO_2 concentration was witnessed, with the means of the diagrams (see part (b) of Figures 4.7 - 4.9) decreasing during the examined period (with the median value decreasing from 16.9 to 8.8 $\mu g/m^3$). As with the numerical analysis the exception was 2007, exhibiting a median increase from 2006 (from 7.9 to 9.0 $\mu g/m^3$). Conversely, there wasn't any significant difference in the values seen in 2008 (15.2 $\mu g/m^3$), 2009 (15.7 $\mu g/m^3$) and 2010 (15.7 $\mu g/m^3$). Yet, as was found in the numerical analysis, the majority of the areas measured a lower level of SO_2 in 2009 and 2010 compared to 2008. Notably, a significant decrease in SO_2 was witnessed in the towns surrounding the MPS, especially to the West of the MPS. A trend which was not evident in the numerical analysis was the increase in SO_2 concentrations witnessed in Northern Gozo in 2008 and 2009. This might have been caused by the emergence of a new SO_2 source which would warrant further research.

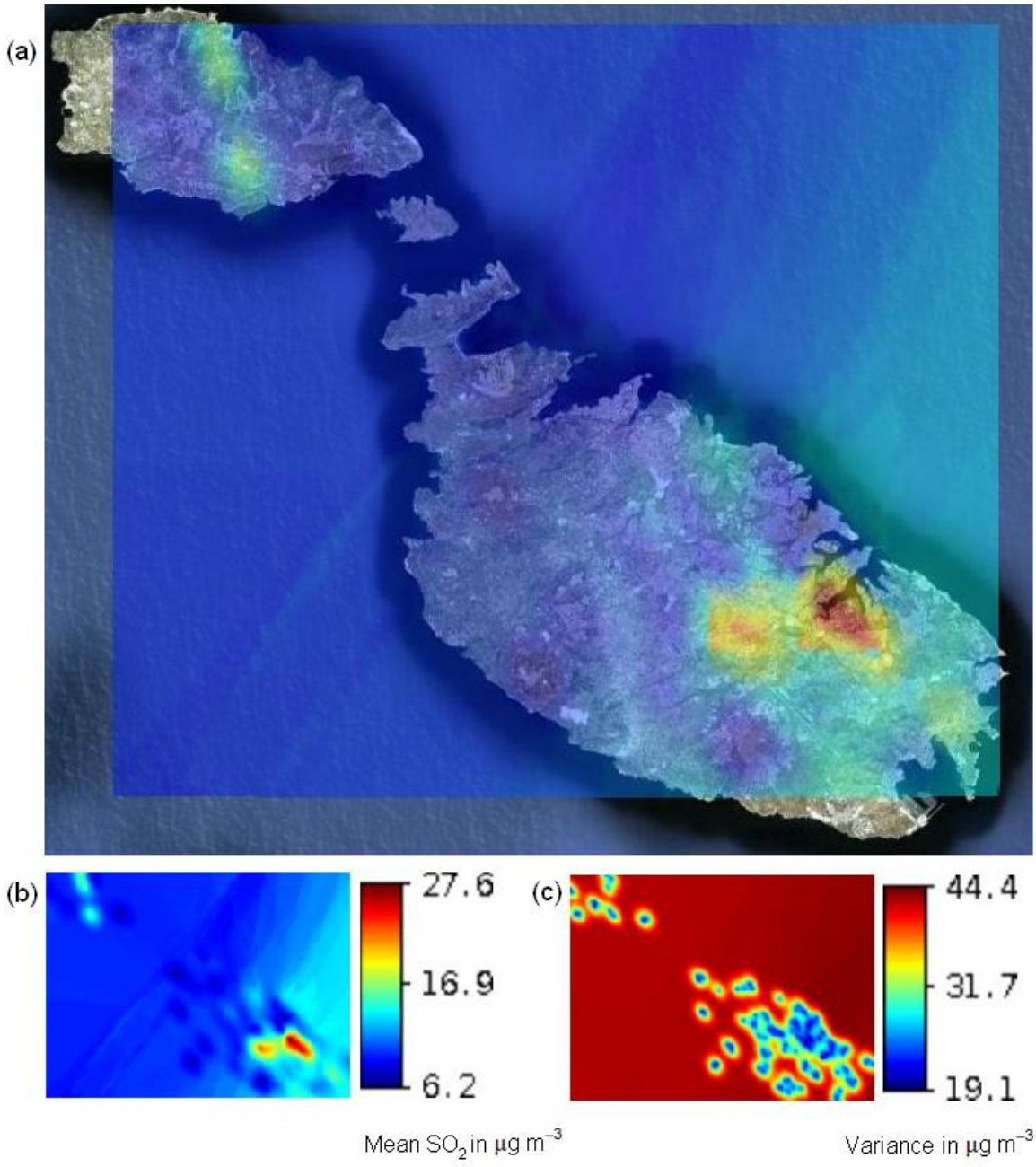

Figure 4.3: Diffusion tube interpolation for 2004 averages

Where (a) is the mean SO_2 concentration, i.e. (b), corresponding to geographical location and (c) is the variance in (b).

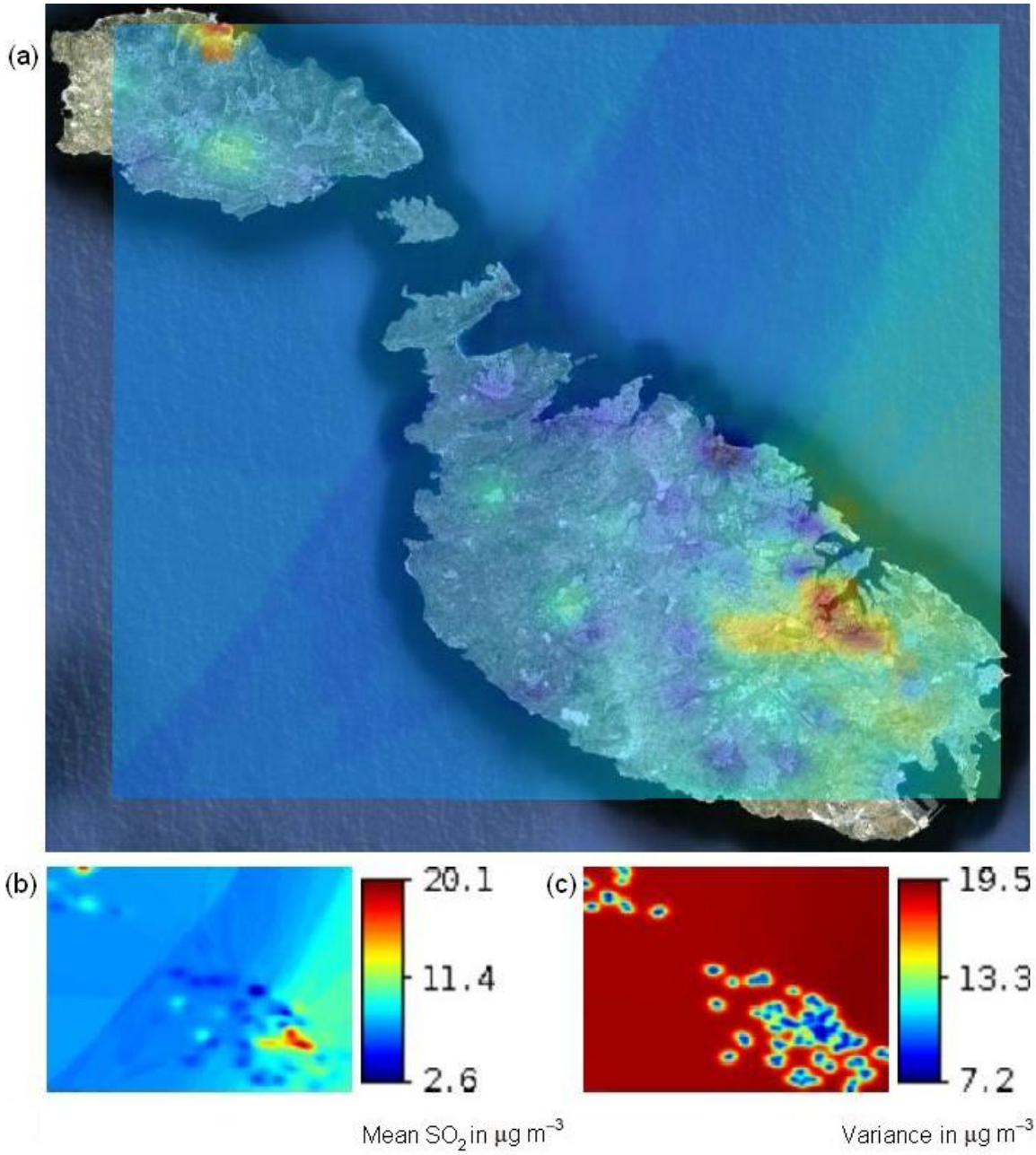

Figure 4.4: Diffusion tube interpolation for 2005 averages

Where (a) is the mean SO_2 concentration, i.e. (b), corresponding to geographical location and (c) is the variance in (b).

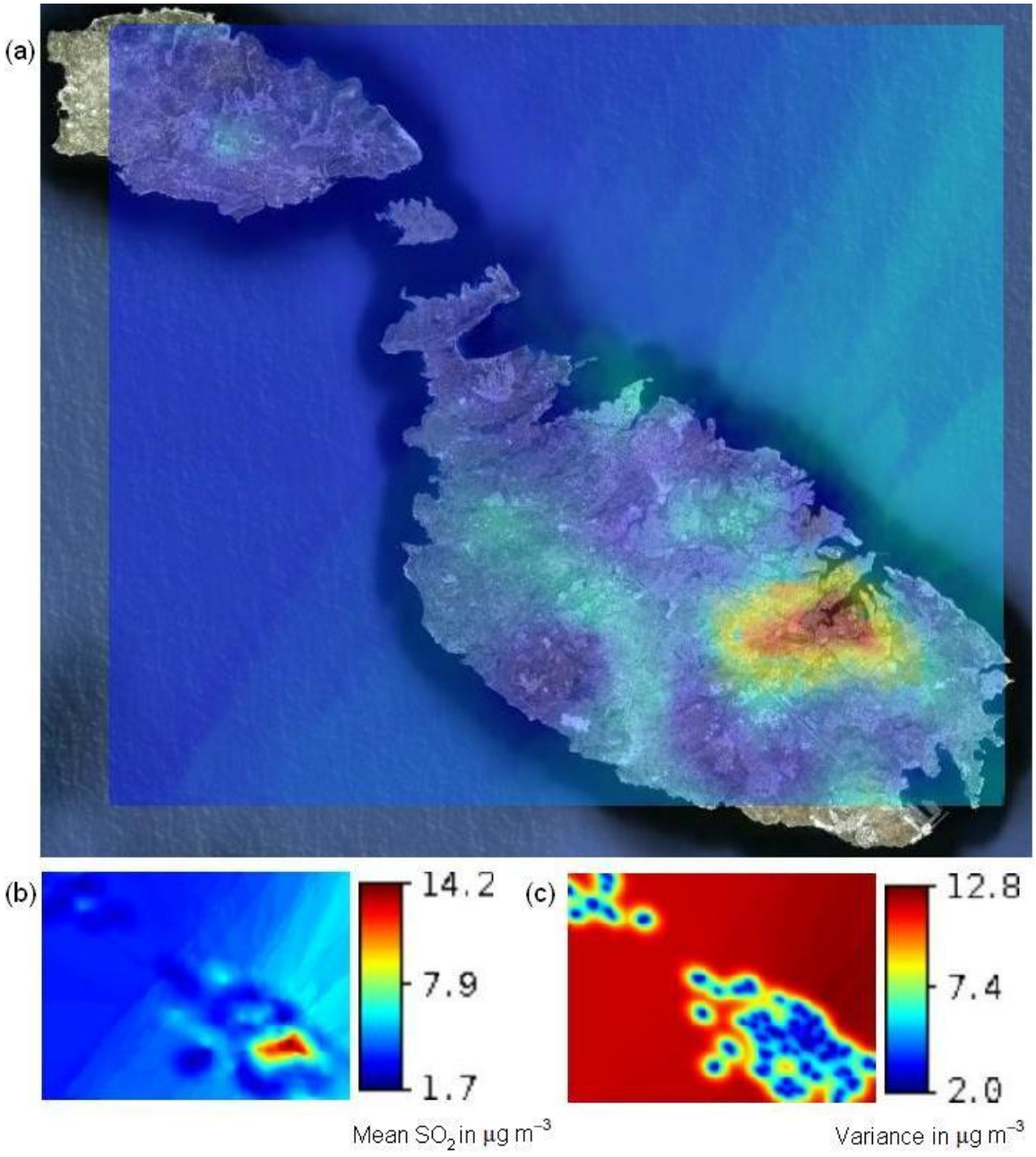

Figure 4.5: Diffusion tube interpolation for 2006 averages

Where (a) is the mean SO_2 concentration, i.e. (b), corresponding to geographical location and (c) is the variance in (b).

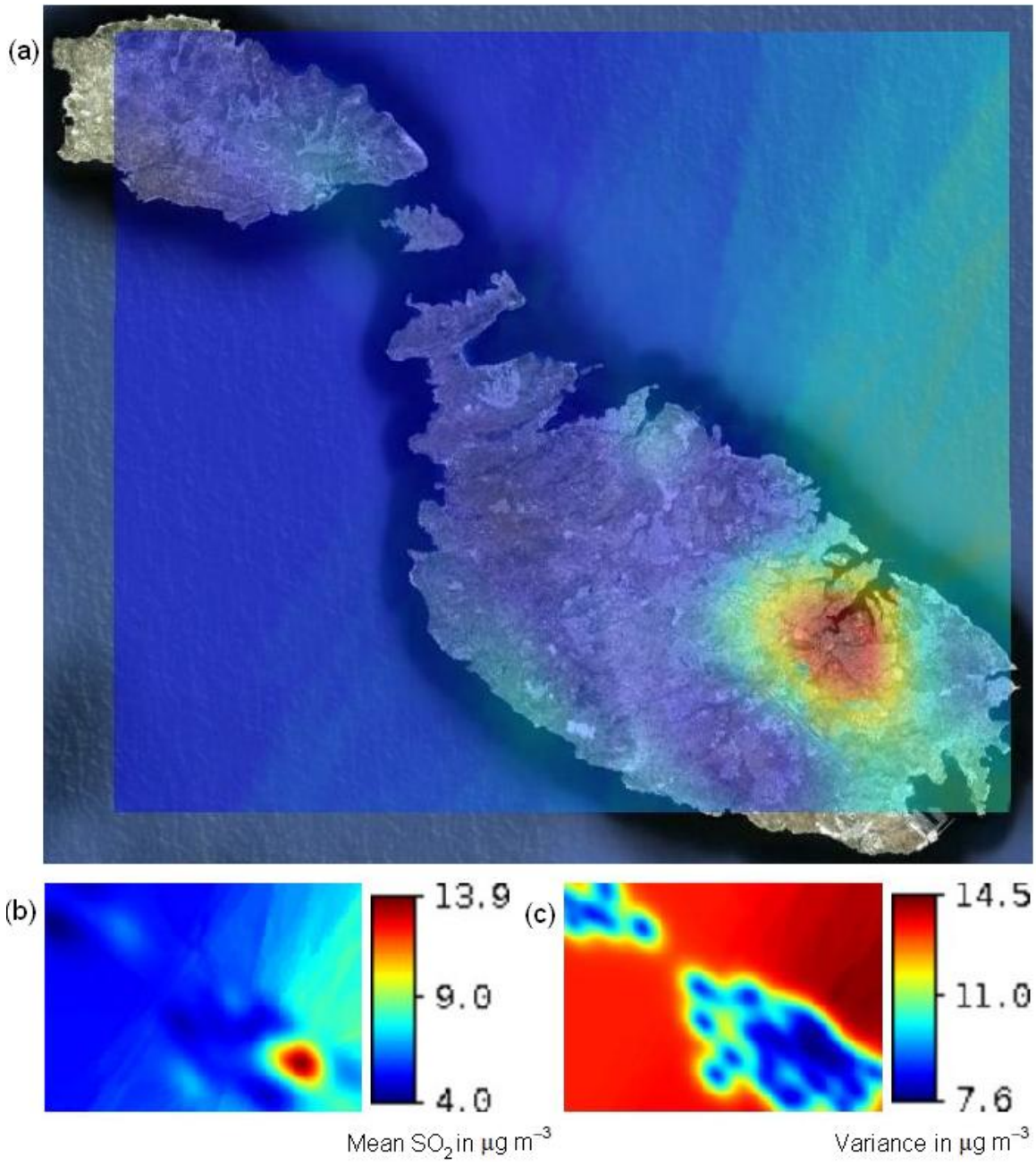

Figure 4.6: Diffusion tube interpolation for 2007 averages

Where (a) is the mean SO_2 concentration, i.e. (b), corresponding to geographical location and (c) is the variance in (b).

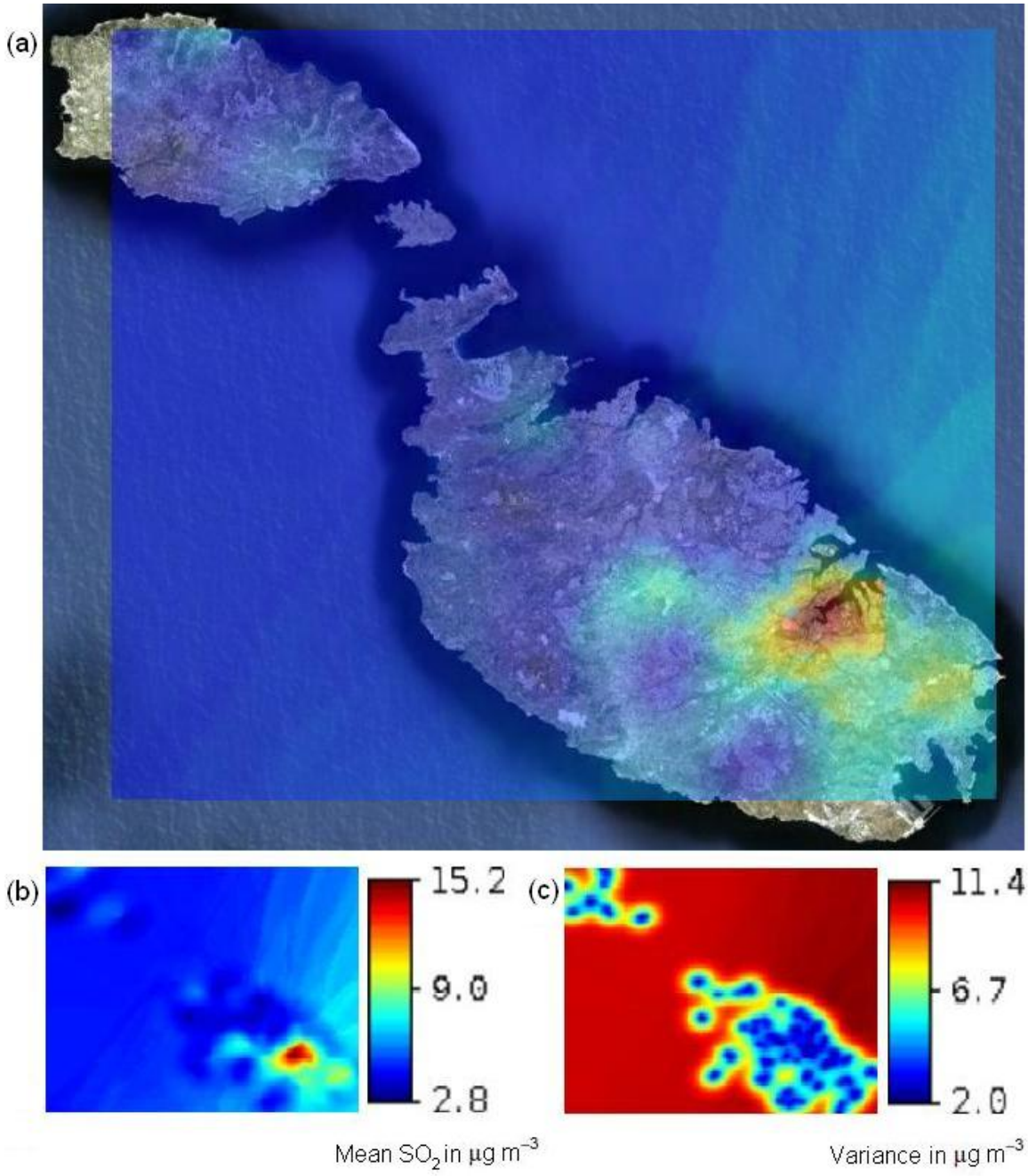

Figure 4.7: Diffusion tube interpolation for 2008 averages

Where (a) is the mean SO_2 concentration, i.e. (b), corresponding to geographical location and (c) is the variance in (b).

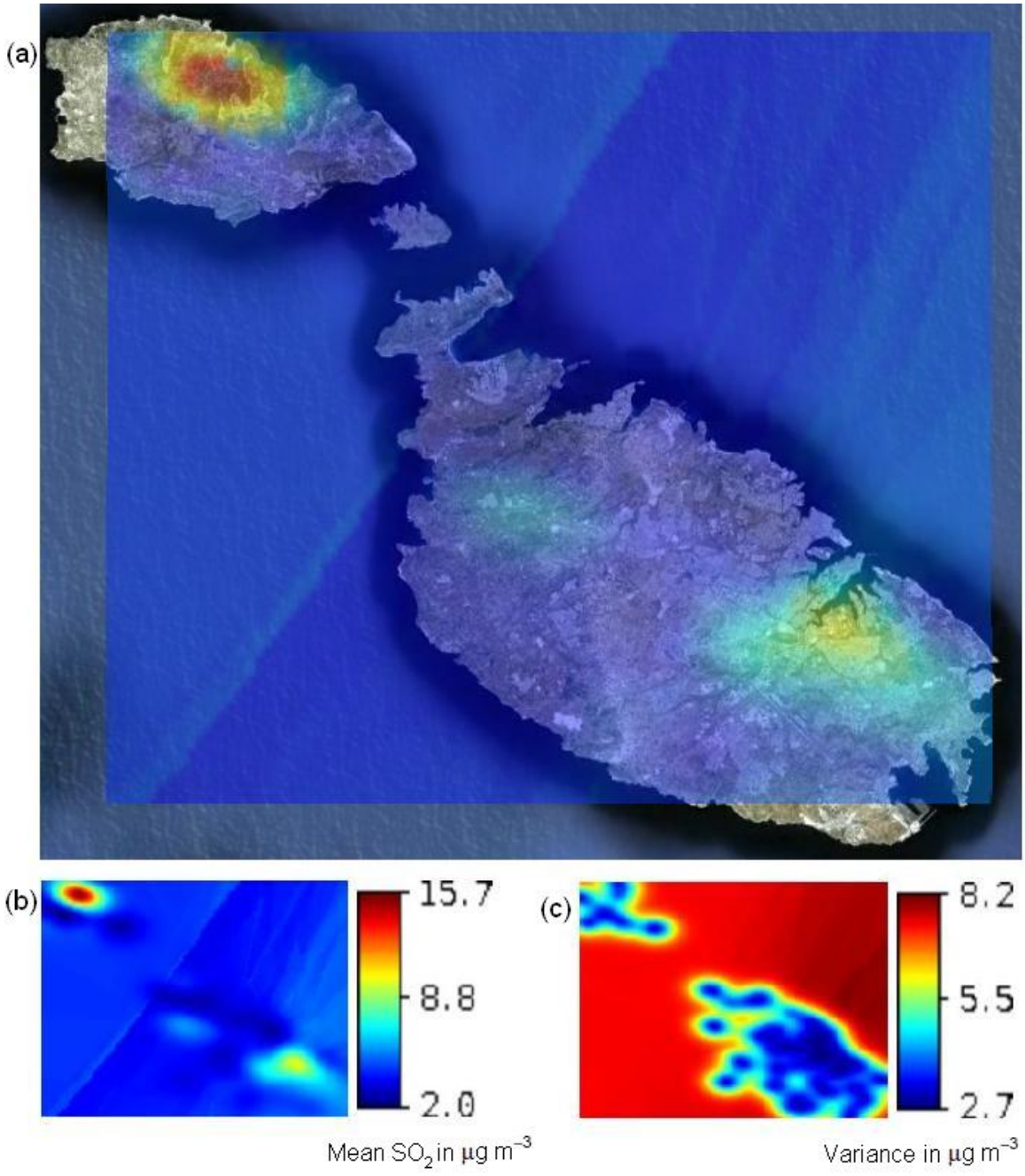

Figure 4.8: Diffusion tube interpolation for 2009 averages

Where (a) is the mean SO_2 concentration, i.e. (b), corresponding to geographical location and (c) is the variance in (b).

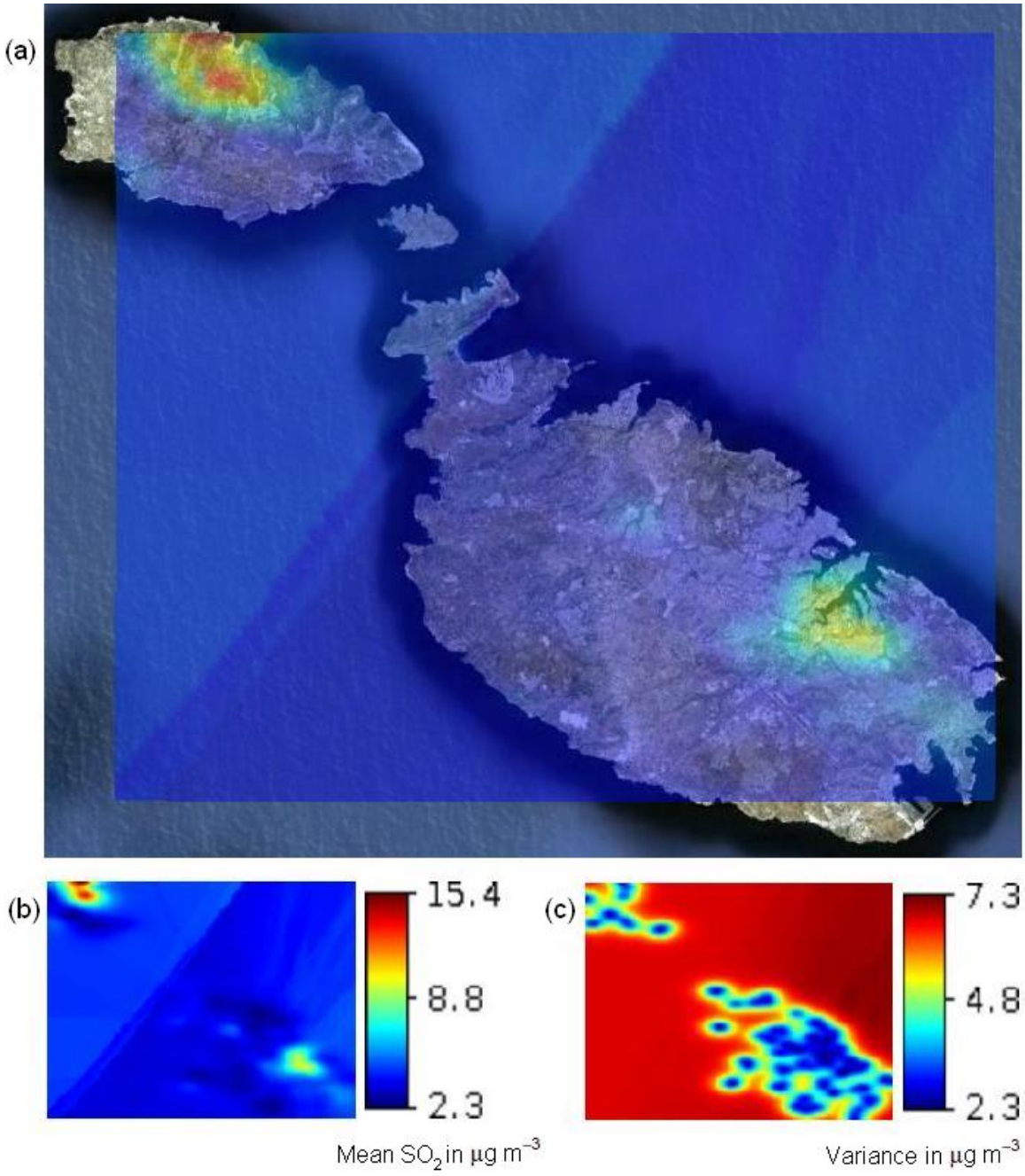

Figure 4.9: Diffusion tube interpolation for 2010 averages

Where (a) is the mean SO_2 concentration, i.e. (b), corresponding to geographical location and (c) is the variance in (b).

4.5 R analysis

4.5.1 Wind data

The wind roses obtained for the MEPA monitoring stations and MPS are shown in Figures 4.10 and 4.11. Consistent with the numerical analysis of Section 4.3.1, the wind roses in Figure 4.10 show that of the MEPA monitoring stations, Għarb experienced the highest wind speeds. This was expected due to the Għarb station being located relatively far from buildings and urbanised areas (Barratt, 2001). The wind roses also show that Kordin and Żejtun experienced lower wind speeds, with a large proportion of the speeds in the 3-6 m/s wind speed category. Msida was found to have the lowest wind speeds, with a large proportion of the readings in the 0-3 m/s wind speed category. As noted in the numerical analysis, Marsa was observed to have the highest wind speeds. This may have been due to the smaller data set available or due to the higher altitude of the sensor.

Consistent with the work of Galdies (2011), almost all of the stations experienced a predominance of North Westerly winds (more than 25%). The notable exception being Msida, with more that 40% of the wind occurrences being oriented in an East to West (or *vice versa*) direction. This could be explained by the fact that Msida is part of a valley system, which may have influenced direction of wind flow. In general, the wind roses are consistent with what was reported in previous work by Galdies (2011).

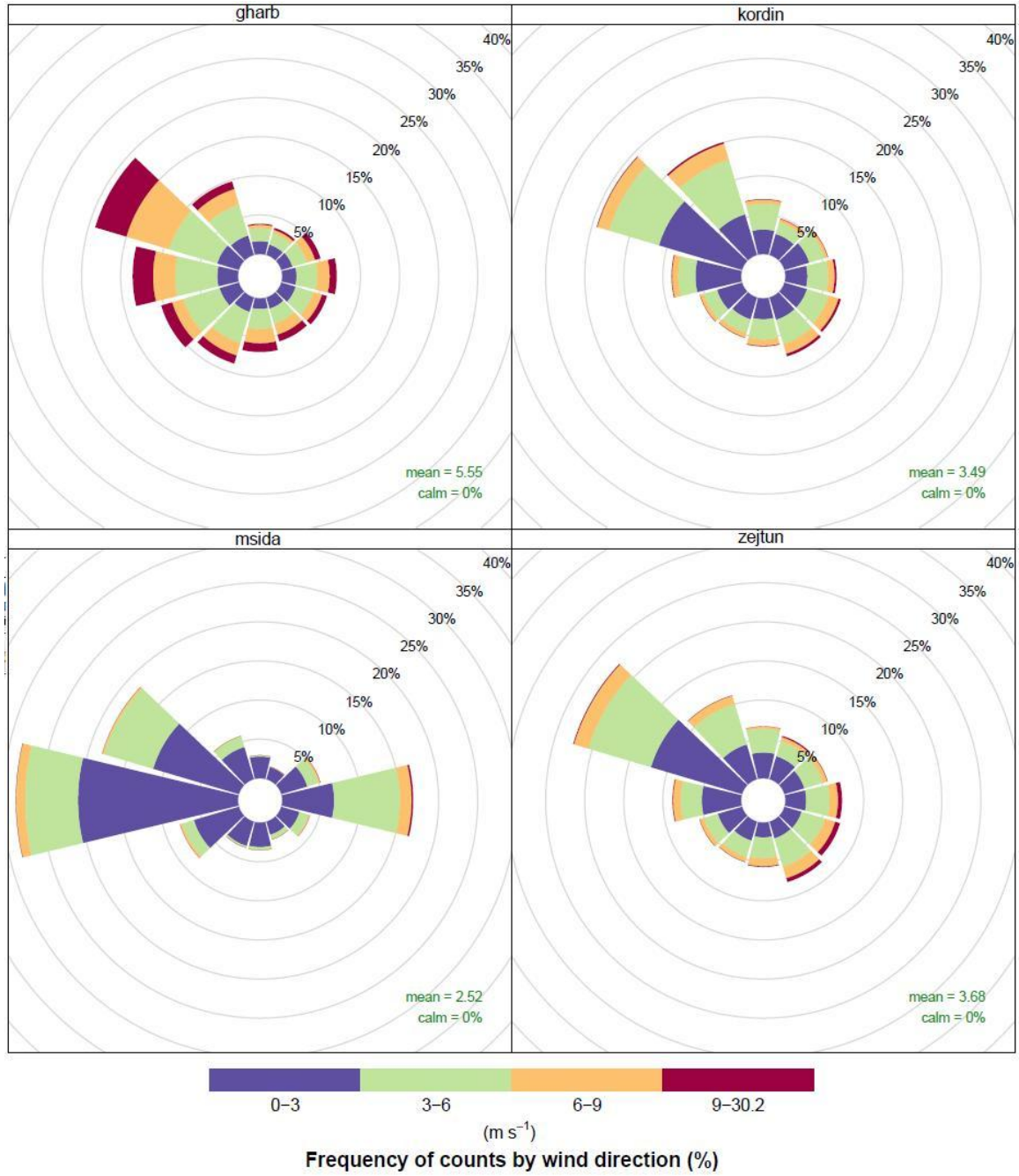

Figure 4.10: Monitoring stations wind roses

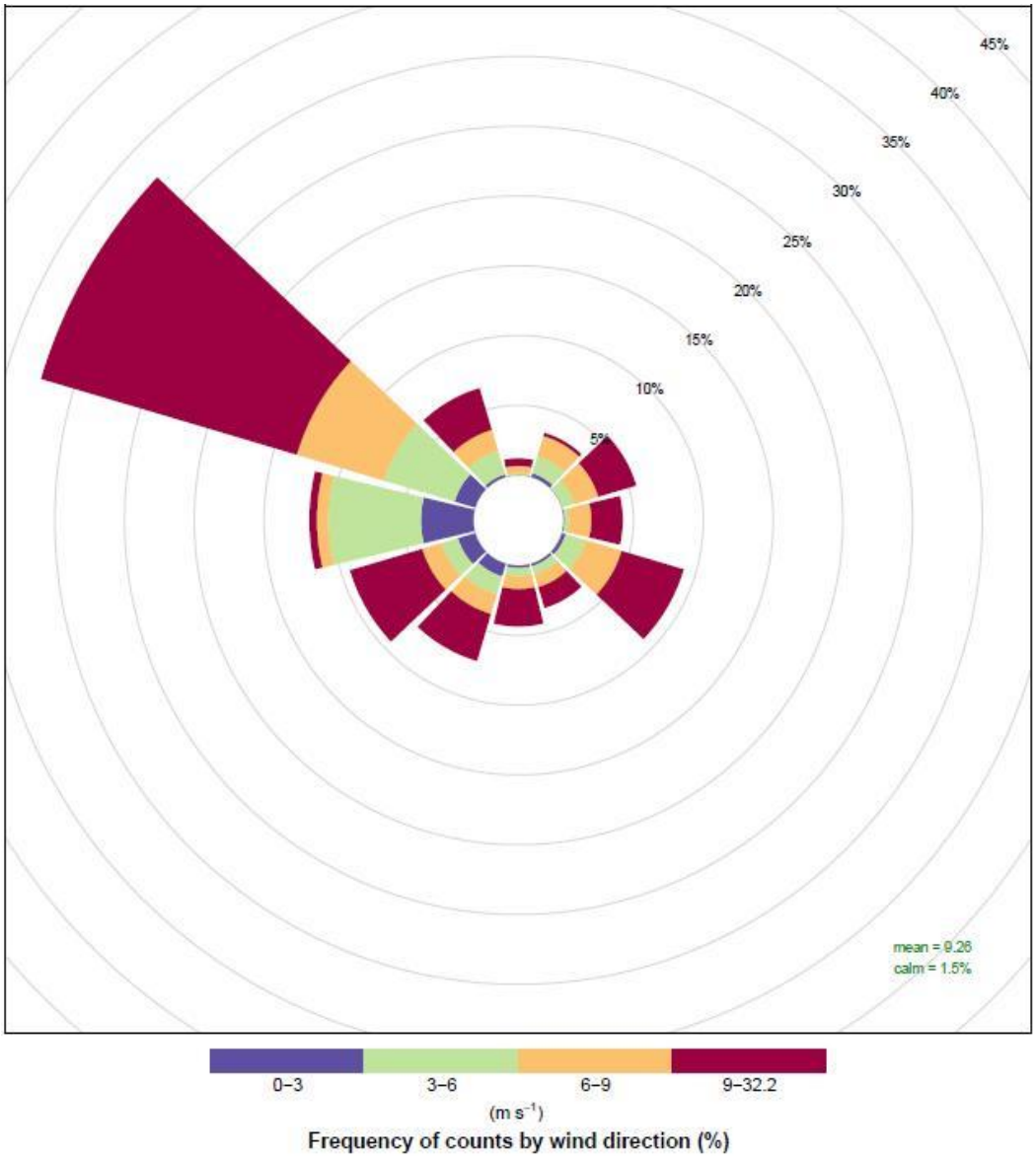

Figure 4.11: MPS wind rose

4.5.2 Marsa power station emissions

The timePlot, trendLevel and timeVariation plots produced for the MPS emissions data set are shown in Figures 4.12 – 4.16. Figure 4.12 shows the overall emissions plot of the analysed period. Consistent with the results of the numerical analysis in Section 4.3.3, the emission rates can be visually interpreted as being quite variable. To facilitate the detection of trends, timePlots with average monthly and yearly values were also produced (Figures 4.13 and 4.14 respectively).

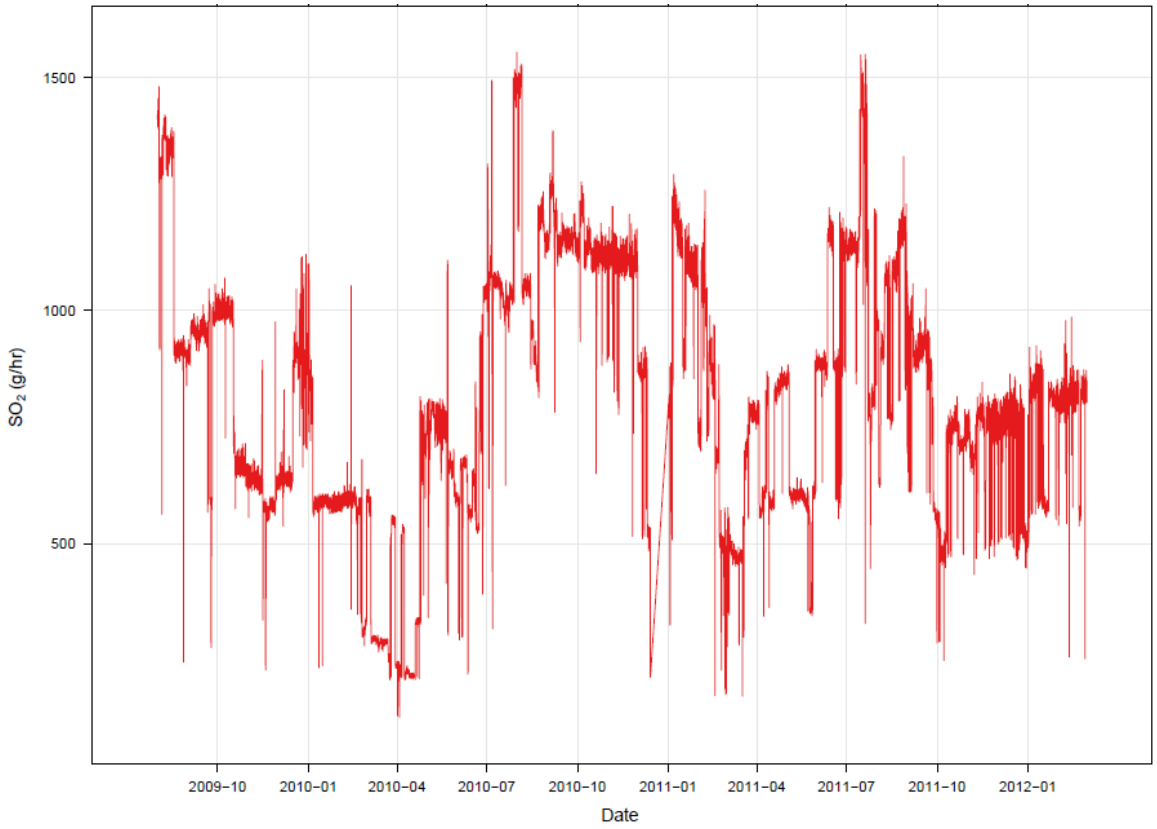

Figure 4.12: Marsa emissions timePlot

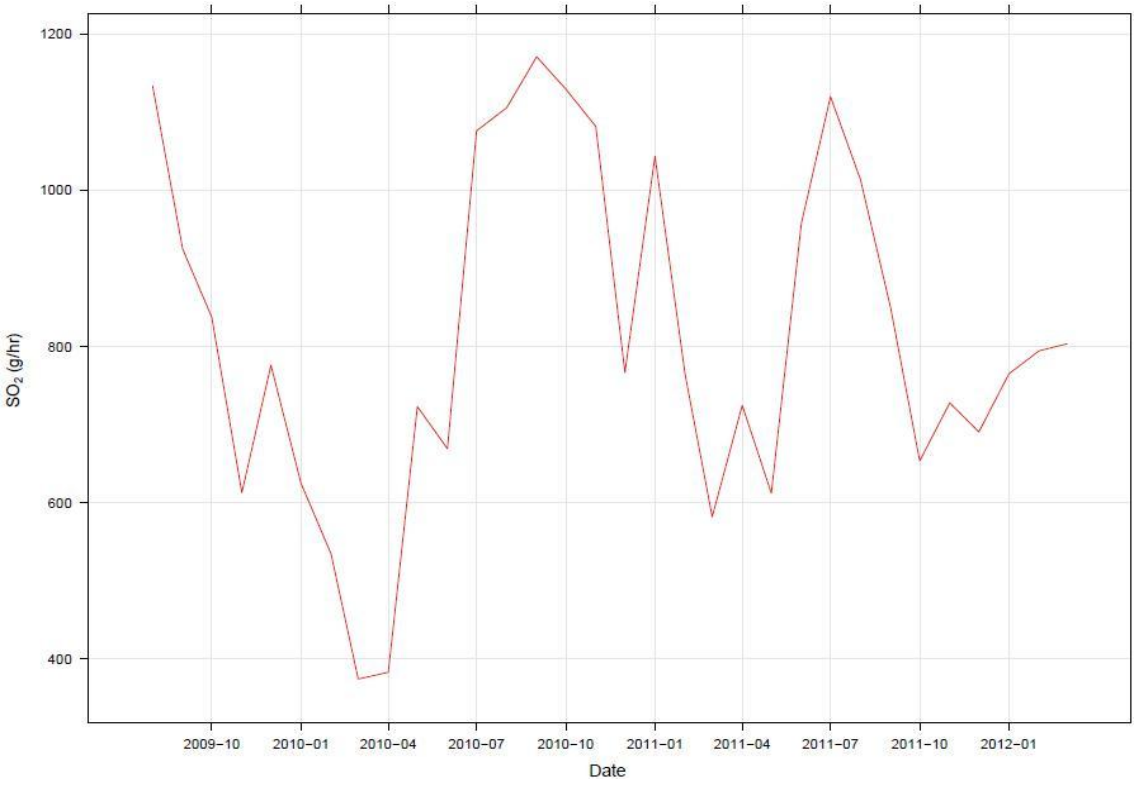

Figure 4.13: Marsa emissions timePlot averaged by month

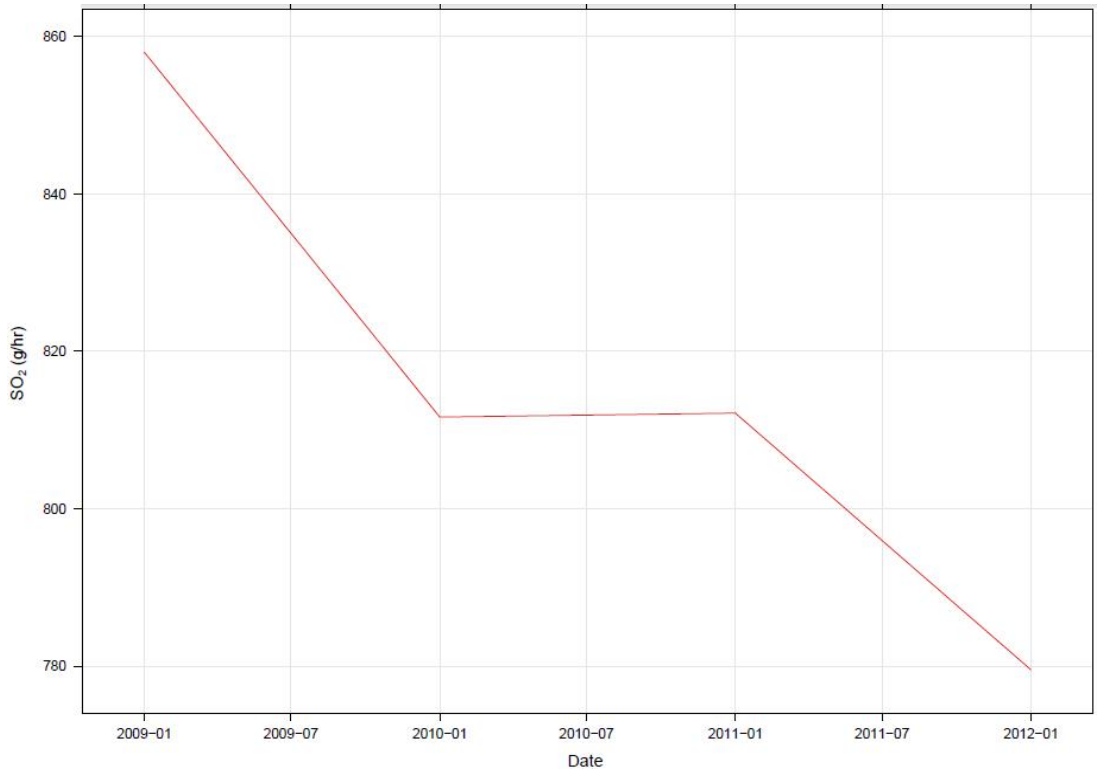

Figure 4.14: Marsa emissions timePlot averaged by year

Figure 4.13 reveals that each year, emissions tended to peak around the month of July. This is consistent with Maltese National Statistics Office data (period 2000-2006), which shows that power generation was found to peak in July and August each year. As power generation increased, emissions produced from the MPS also increased (NSO, 2012). The plot also indicates that the lowest emissions were recorded around March.

Figure 4.14 shows that yearly averaged emissions decreased from approximately 858 g/hr to 780 g/hr over the period. However, it should be noted that the years 2009 and 2012 did not comprise data for a complete year, so the average values for these two years may contain significant uncertainty. Nonetheless, the overall indication is that efforts to reduce emissions (see Section 2.4) produced some positive results. The exact extent of their success is not discernible from Figure 4.14 due to uncertainty issues.

The plot resulting from the trendLevel analysis is shown in Figure 4.15. As can be seen, the data is colour coded and categorised by year, month and hour. The plot indicates that the hour of the day did not have significant effect on the emissions generated. This can be seen from the fairly consistent colouring along each column. Consistent with Figure 4.13, the trendLevel plot demonstrates that emissions peaked around July/August and were lowest in the March/April period. The year 2010 was characterised by high emissions from July to November. Concurrently, the lowest monthly emissions were also recorded in 2010, in the months of March and April. This combination of highest and lowest emission readings explains why, despite the fact that 2011 had more moderate emissions than 2010, 2010 and 2011 recorded similar yearly averages (see Figure 4.14). Another

anomaly that can be detected from the plot is the high level of emissions produced in January 2011. The above observations illustrate the fact that SO_2 emissions are variable since power demands change with time and are dependent on a large number of variables (such as technological developments and climate). To supplement the above results, the timeVariation function was used to generate plots (Figure 4.16) of emissions categorised by time of day, weekday and month.

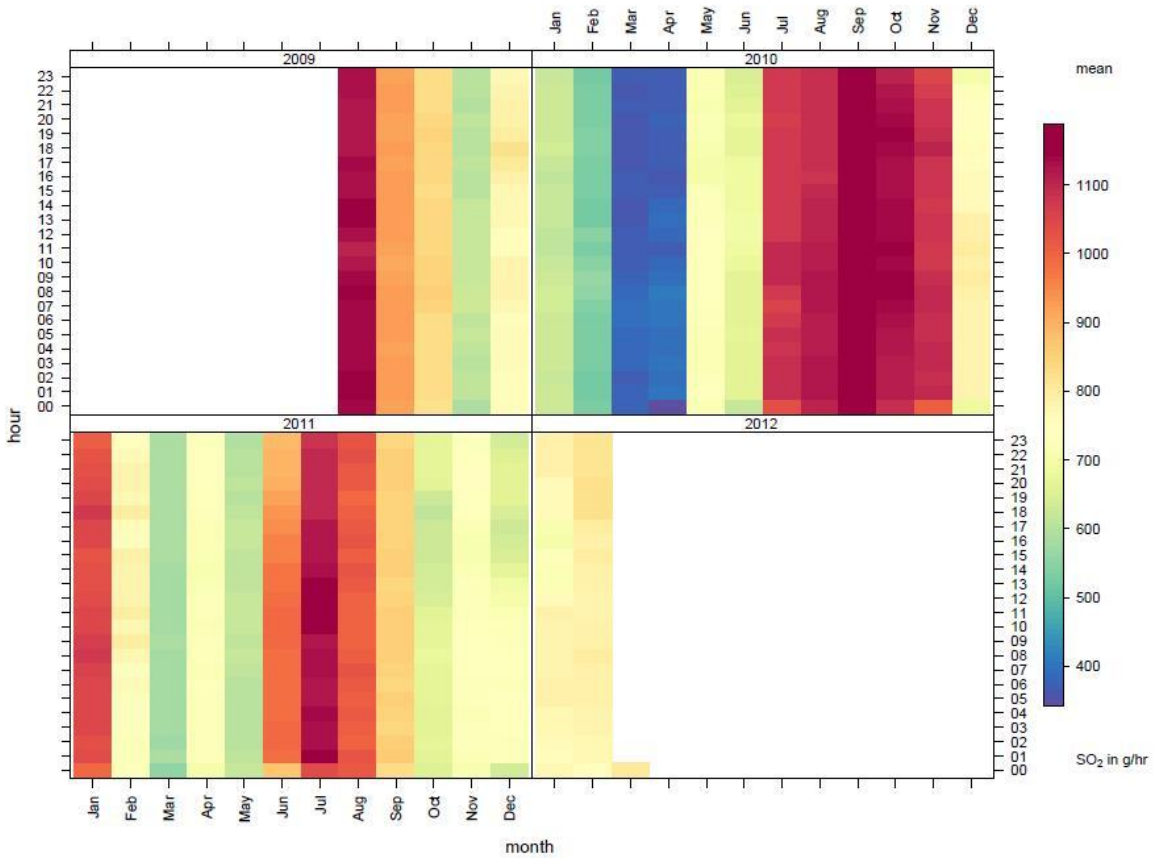

Figure 4.15: Marsa emissions trendLevel plot

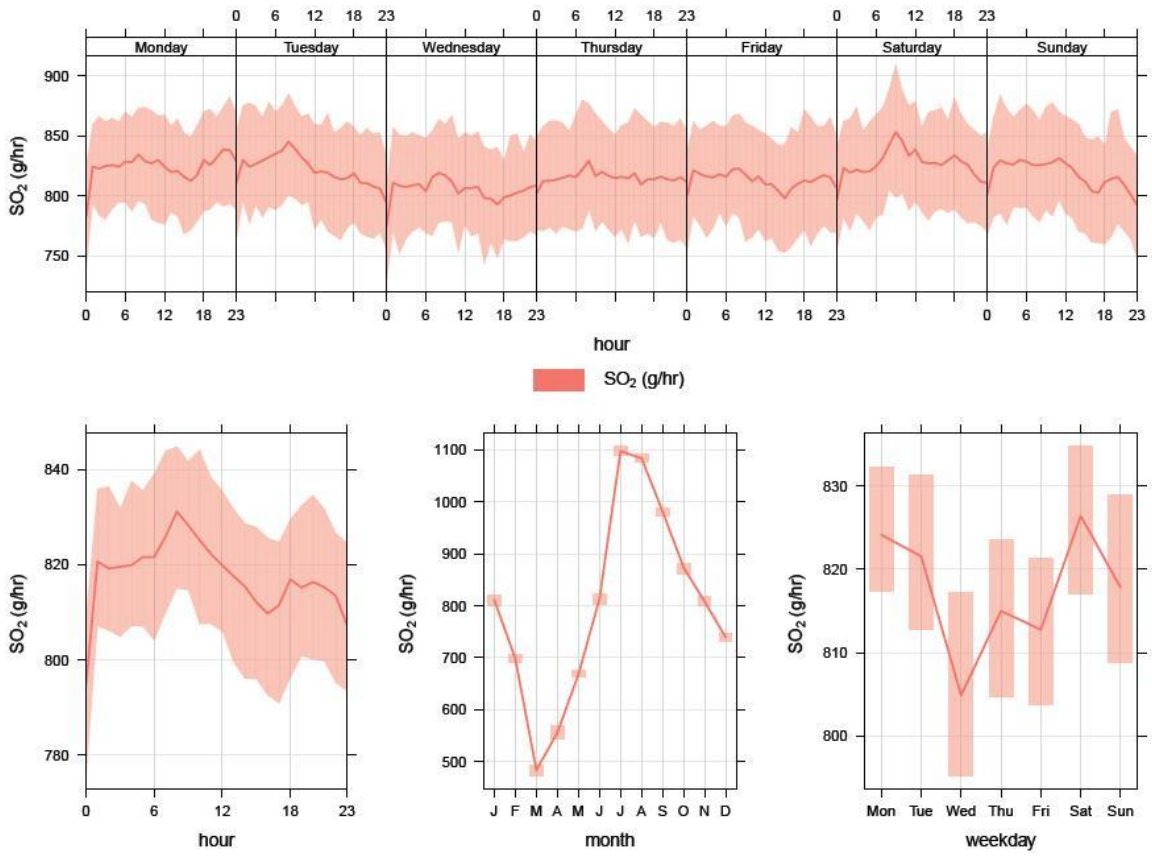

Figure 4.16: Marsa emissions timeVariation plot

The topmost plot of Figure 4.16 shows the overall emission averages in a typical week. This plot shows that there was a trend for emissions to fluctuate around 820 g/hr during each daily cycle during the week. This can be more clearly seen in the bottom left plot, which shows the average amount of emissions during a typical 24 hour period. In a typical period, variability is shown to be of the order of around +/- 20 g/hr. Hence the uncertainty is such that on some days the peak emissions, which are shown to be around 8:00 AM, may have occurred at other times. This level of uncertainty may be the cause of the disagreement between the timeVariation and the trendLevel results, since the trendLevel results showed that emissions did not vary according to time of day. Being a

more rigorous function, the timeVariation shows that there were variations in time of day; however the uncertainty is such that the trends may be reversed.

The bottom-middle plot of Figure 4.16 shows the average monthly emissions over the whole period. Consistent with the trendLevel and timePlot results, emissions were found to peak in July/August and were lowest in March/April. Since all of these results are consistent, it can be concluded that emissions were lowest in early Spring (March/April) and highest in mid-Summer (July/August).

The final plot (bottom right of Figure 4.16) demonstrates the average daily emission levels in a typical week. As with hourly emissions, there is significant uncertainty, with the possibility of trends being reversed in certain periods. The plot suggests that Monday, Tuesday, Saturday and Sunday were found to have higher emissions than Wednesday, Thursday and Friday. Particularly, Saturday was found to have the highest emissions, while Wednesday had the lowest. Although no detailed examination of this phenomenon will be made (since it is outside the scope of this research), a possible cause may have been lifestyle trends e.g. high electricity consumption on Saturday as people were at home using appliances instead of communal facilities at work.

4.5.3 Marsa power station emissions and wind data

Wind speed, wind direction rotated by 180º and the total mass emission rate for MPS were used to produce the inverse pollution rose shown in Figure 4.17 below. The plot shows the amount of pollutant and direction where the pollutant is being transported to as a percentage of total frequency.

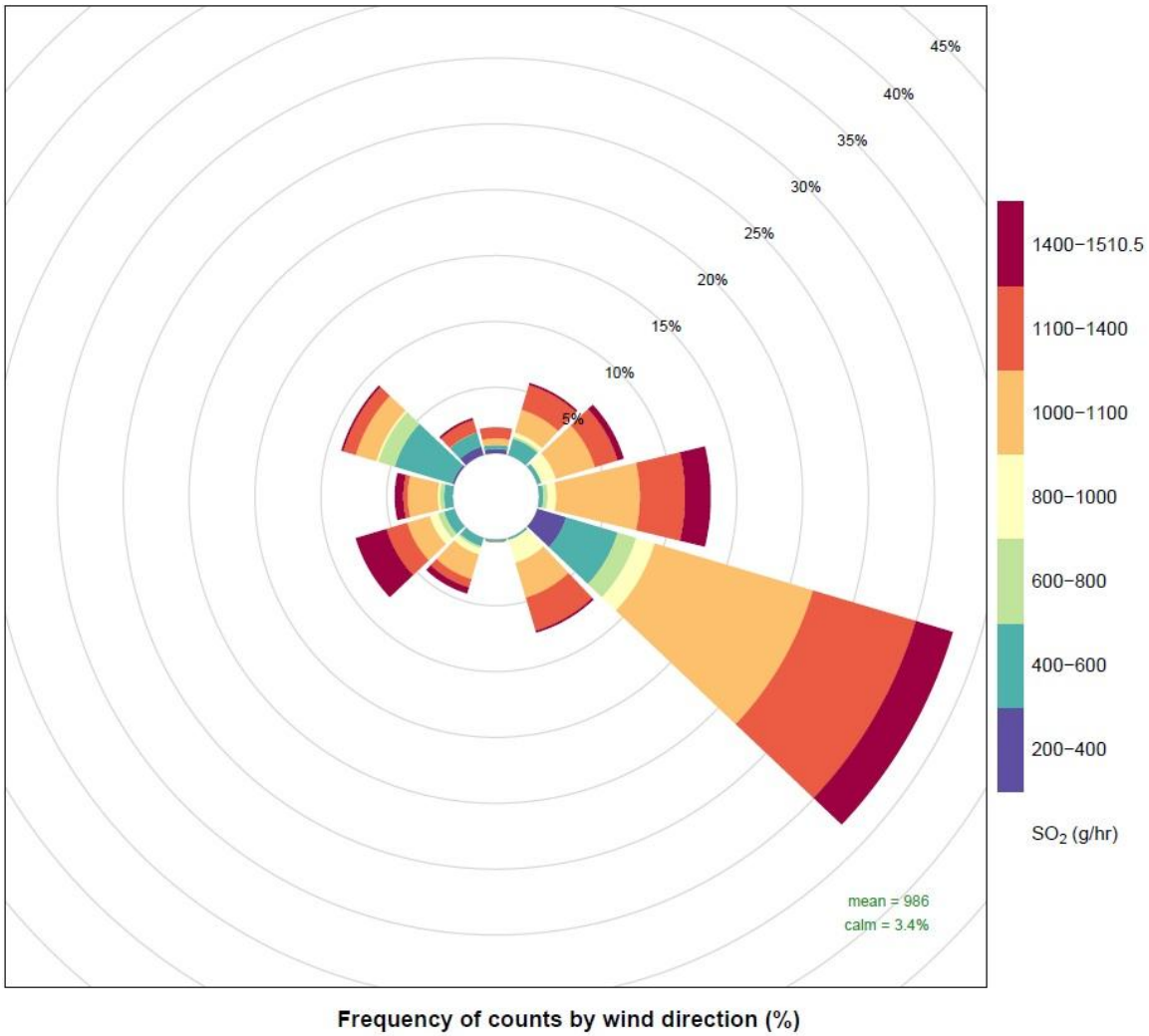

Figure 4.17: MPS inverse pollution rose

The pollution rose shows that due to the prevalence of NW winds, almost 40% (adding the two South East components) of wind readings resulted in emissions in the South East direction. The plot also shows that the higher emission levels (above 1400 g/hr) went mostly in the East, South East and South West directions (about 2.5% of readings in each direction).

It should be noted that the pollution rose does not indicate any significant relationships between emission levels and wind conditions. This was expected since there was no hypothesis linking wind conditions to power use.

4.5.4 Monitoring stations SO_2 data

Trends for SO_2 at the four fixed monitoring stations were also examined. The timePlot, trendLevel and timeVariation plots produced are shown in Figures 4.18 – 4.22. Figure 4.18 shows the mean monthly readings across the different stations. It should be noted that the Kordin station data set had poor data capture due to technical problems. However an analysis of the data gathered by the Kordin station shows that the SO_2 levels were generally higher than those of the other stations. This is in concordance with the results of Vella *et al.* (1996) and also of the diffusion tube network interpolation. Għarb monthly averages show that there were a lesser number of peaks and lower readings than those of the other stations. This was also expected since the Għarb station is considered to be a rural background station (MEPA, 2012). However, the June 2008 period is rather anomalous due to the significantly high SO_2 levels observed in Għarb.

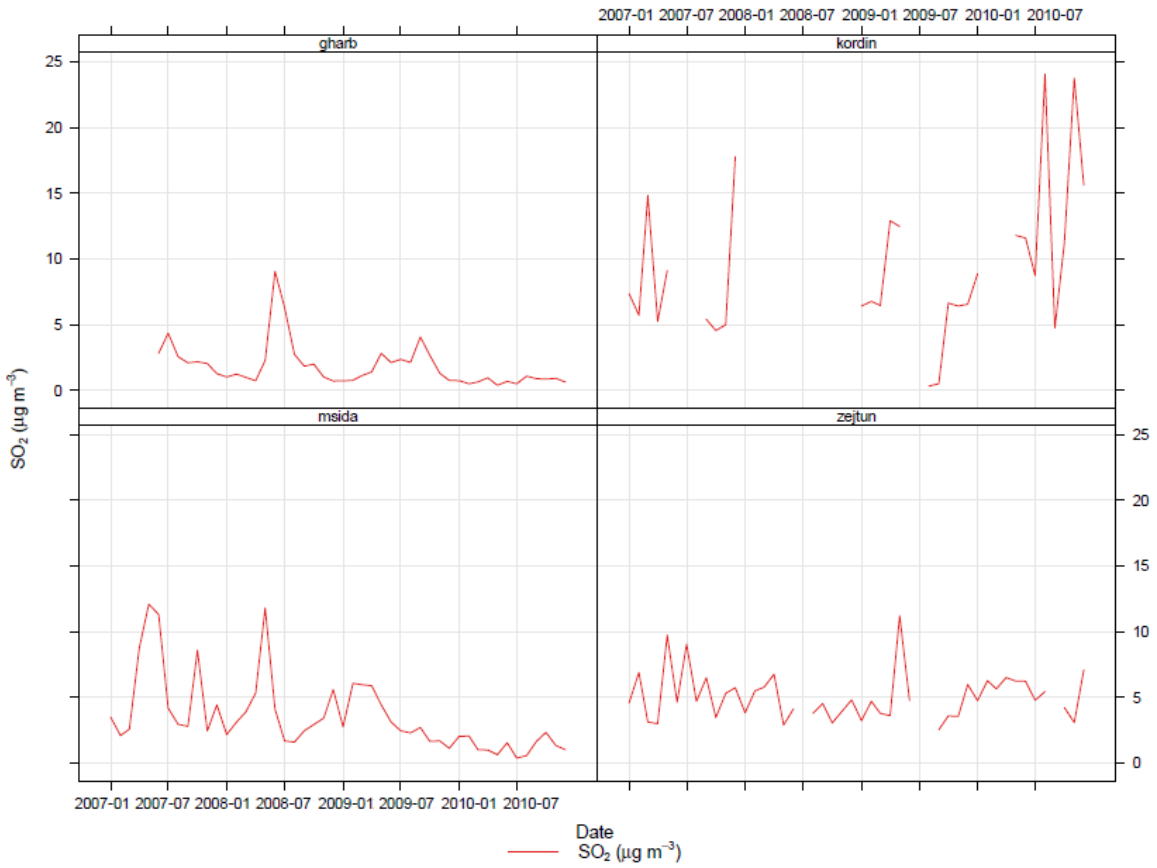

Figure 4.18: Monitoring stations timePlot averaged by month

With regards to the Msida and Żejtun readings, significant monthly variability was observed, with the graphical representation not showing significant trends except for occasional acute peaks. Interestingly, a peak in average SO_2 concentrations around May/June 2008 was also observed in Msida. The fact that such a peak was witnessed in Msida and Għarb around the same period suggests the possible presence of an SO_2 source related to a more Northern geographical location. Unfortunately, data from Kordin, which is relatively close to Msida and may have supported this hypothesis, was not available. Despite these differences, none of the monthly averages in the stations surpassed 25

µg/m^3. The analysis of this data can be supplemented by looking at the yearly averages plotted in Figure 4.19 below.

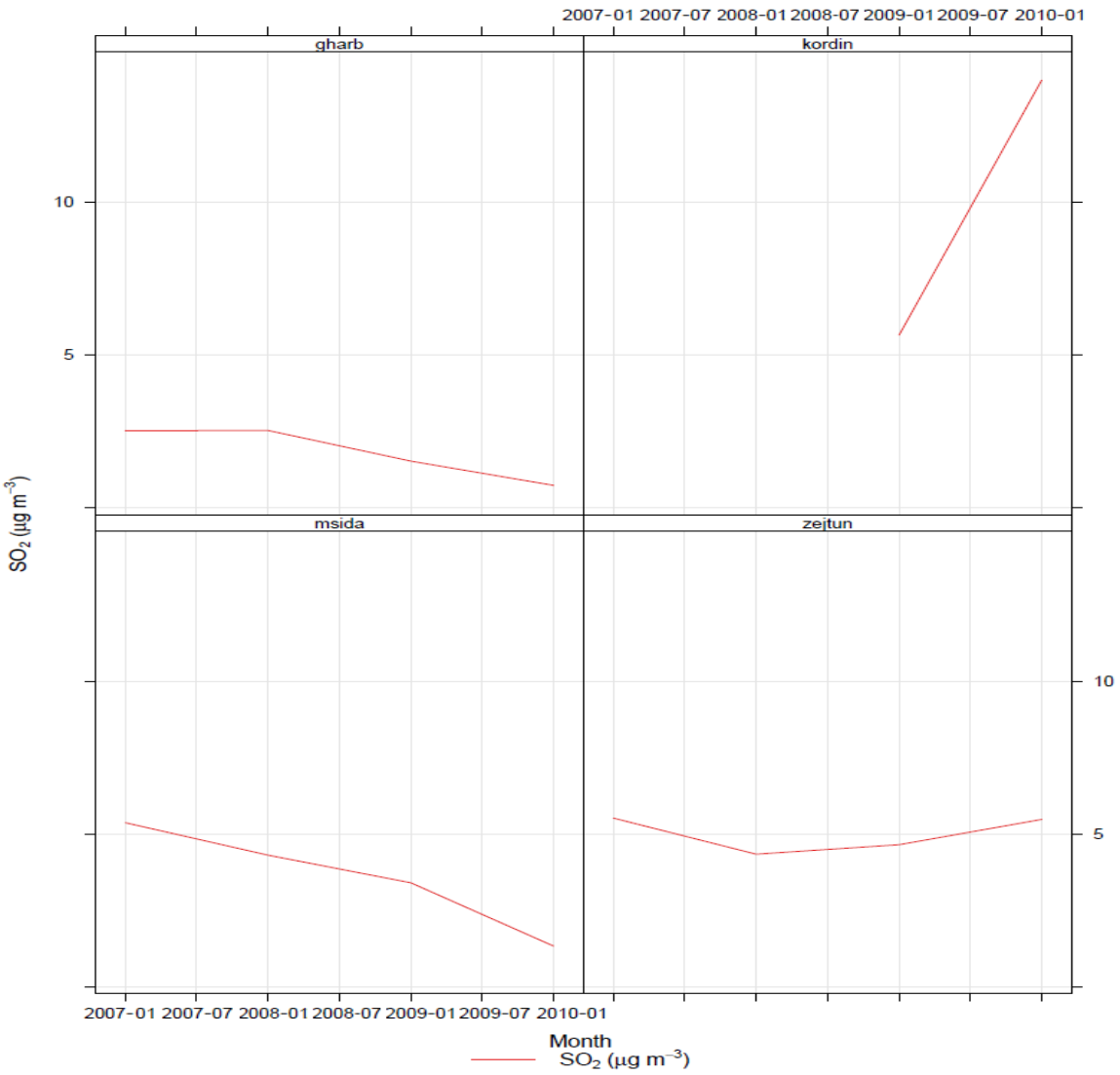

Figure 4.19: Monitoring stations timePlot averaged by year

The above plot shows that Msida and Għarb both experienced decreasing average SO_2 concentration between 2007 and 2010. This is consistent with the diffusion tube interpolation which showed a decrease in the Msida area and low concentration in NW

Gozo. Due to the North-Westerly location of the Għarb station, the increases measured in Northern Gozo by the diffusion tube network after 2008 would not be visible in these measurements.

Kordin showed an increase in yearly average from around 6 to 14 µg/m^3 between 2009 and 2010. However, it should be noted that this value is likely to include significant uncertainty due to missing values. The fact that Kordin SO_2 levels increased while those of Msida decreased shows that the effect of SO_2 emissions from the MPS could have become more localised to the area around the power station. Żejtun showed minimal changes, with a yearly average of around 5 µg/m^3.

Two trendLevel plots were also produced for the comparison of readings across the different monitoring sites. Figure 4.20 compares SO_2 readings classified by station, month and hour of the day while Figure 4.21 compares SO_2 readings by station, month and year. Figure 4.20 shows that there was a difference in readings in the hour of the day that varied according to the month and the effect was different in each station. In the case of the Għarb monitoring station, there was minimal change in readings during the day except for the months of June and July. In these months readings peaked around 8:00 AM. Coincidentally, this is the same time that MPS emissions peak (refer to Section 4.5.2), whether this is coincidental or due to a statistical relationship between Għarb readings and MPS emissions shall be examined in the statistical analysis results of Section 4.6. Kordin results showed significant variability across time of day and month. The data shows that November exhibited relatively high concentrations of SO_2 for 15

hours in an average day, whereas the average day in September had relatively low concentration of SO_2 for most of the day. Peaks in SO_2 occurred around 12:00 – 17:00, with some months having peaks starting earlier, and others lingering later; however, the 12:00 -17:00 period overlapped almost all year round (with the exception of March). This time period suggests a possible link with some form of human activity.

On the other hand, Figure 4.20 shows that both Msida and Żejtun had very little pattern in the daily emissions across the different months. The notable exceptions for Msida were the months of April, May and June. April and May were characterised by an increase in emissions between the hours of 7:00 – 18:00. May also exhibited an unusual peak in emissions in the hours of 23:00 – 1:00. On the other hand, June exhibited an increase in emissions between 11:00 – 19:00. Żejtun also demonstrated a similar pattern in May, with an increase in emissions between 5:00 – 19:00 with peaks at 8:00 and 16:00. Although this may have been coincidental, it should be noted that all of the above peak times have some overlap with times of high emissions from the MPS (refer to Figure 4.16).

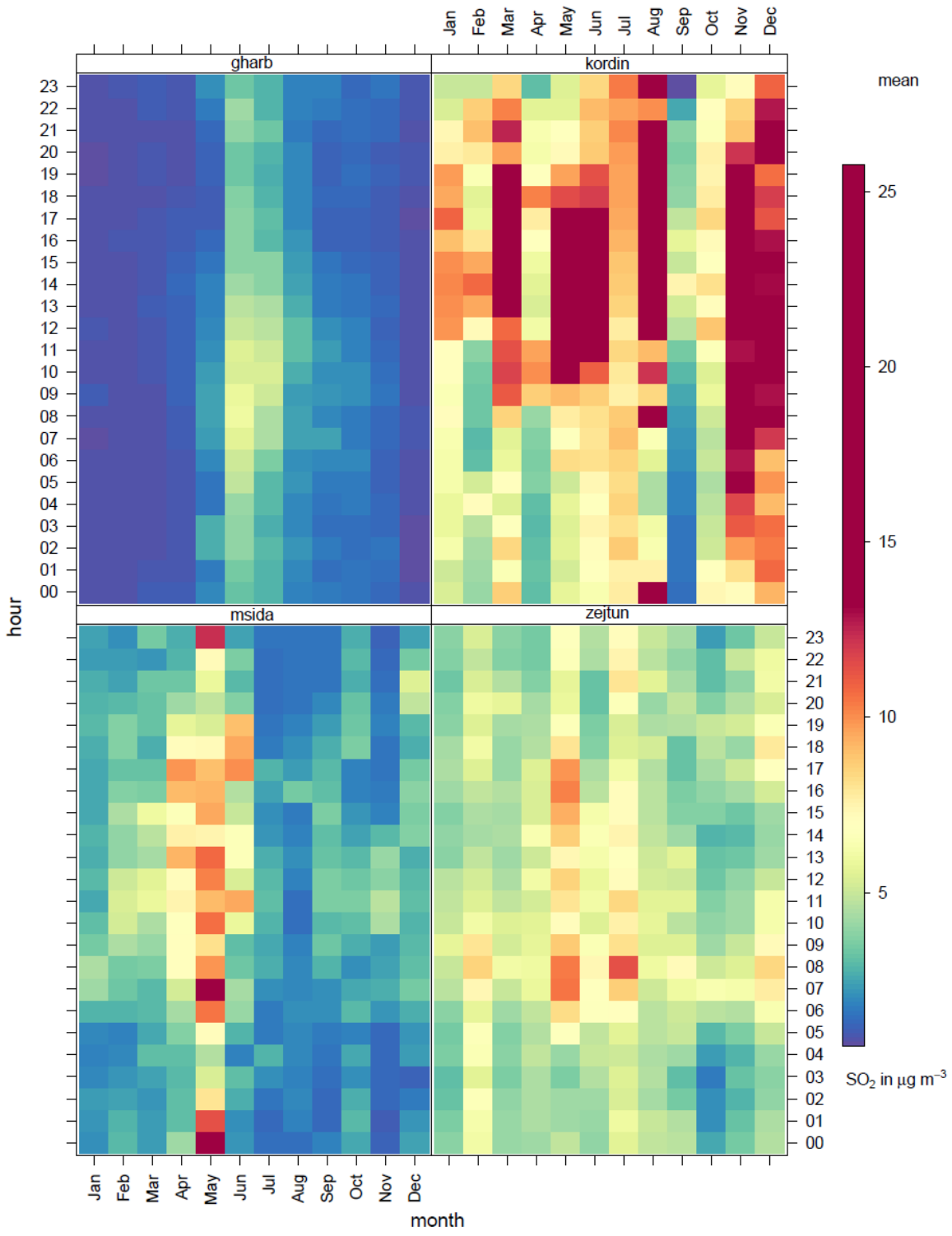

Figure 4.20: Monitoring stations trendLevel plot by month and hour

Alternatively, Figure 4.21 shows the variation in the average monthly SO_2 readings according to station and year. The Għarb results concur with the timePlot findings, showing that average monthly SO_2 levels were generally low, with the exception of June 2008. June 2008 was found to have a relatively intermediate level of SO_2 (when compared to readings of other stations). A corresponding peak was recorded in Msida in May 2008, along with peaks in May and June of 2007, but not in Kordin, due to lack of data. This is a clear indication that as with the previous results, the Kordin data set may not have been comprehensive enough to generate certain statistical trends. On the other hand, Żejtun showed a relatively high peak a year later, in May 2009.

Despite monthly variations; Għarb and Kordin demonstrated a general trend of decreasing SO_2 levels in the years of 2009 and 2010. Żejtun exhibited both an increase in averages and a decrease in the amplitude of monthly peak emissions, which approximates the results of the yearly timePlots, i.e. yearly average SO_2 levels remained the same. Kordin results showed relatively intermediate to high SO_2 levels almost all year round. The year 2010 was calculated to have high SO_2 monthly averages for 7 months of the year. The reason for this increase cannot be clearly established with the data available, especially since Figure 4.14 indicated that emissions from the MPS were decreasing. Hence, a more thorough investigation of this would be required.

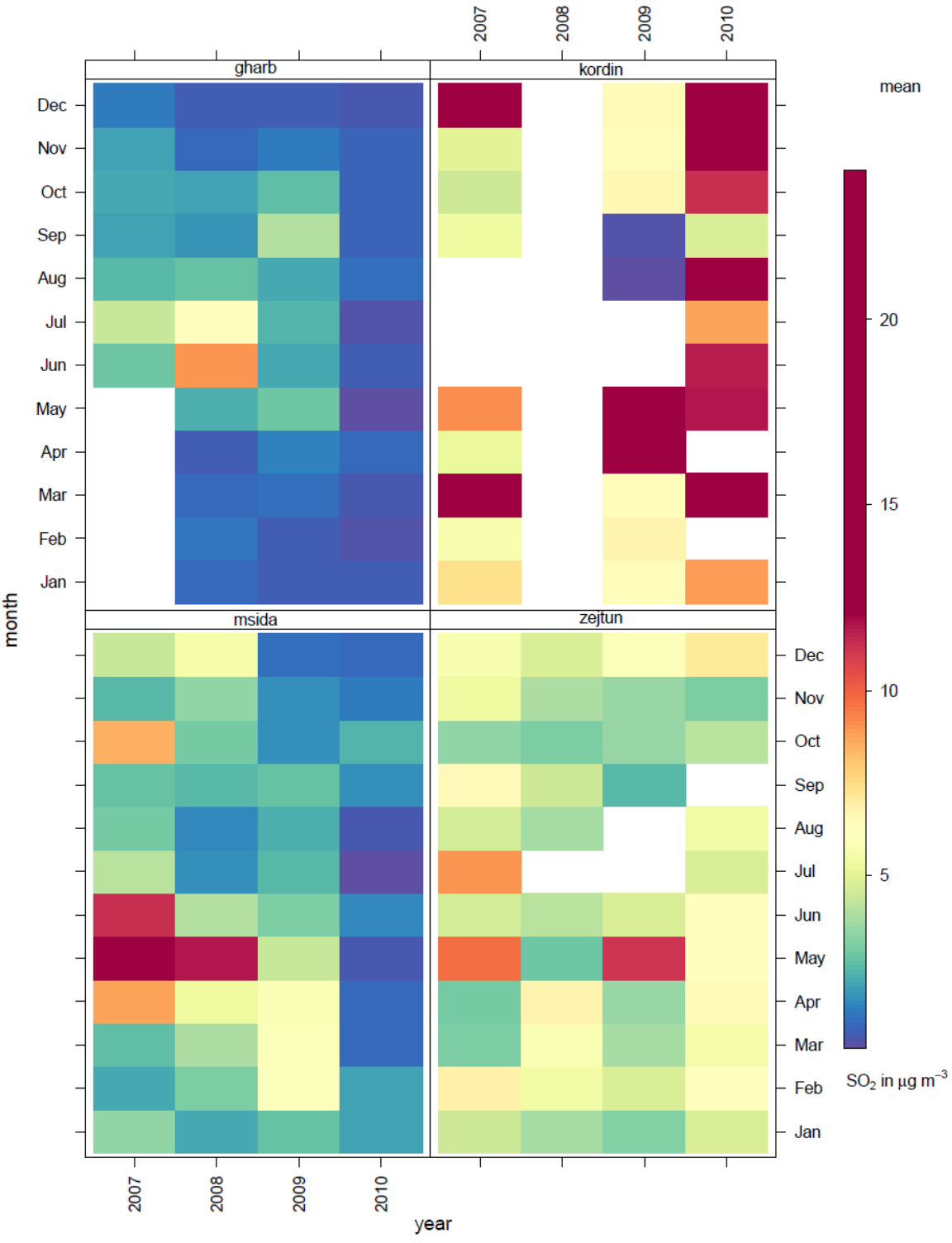

Figure 4.21: Monitoring stations trendLevel plot by month and year

To complement the above results, the timeVariation function was used to generate plots (Figure 4.22) of SO_2 levels categorised by time of day, weekday and month. For comparative reasons, the different stations were plotted on the same axes. The topmost plot shows the overall SO_2 concentration outlook for a typical week. This plot clearly shows that the Kordin station experienced significantly higher readings than the other stations (although one should note the high level of uncertainty in the values). In general Żejtun had higher levels than those of Msida, although Msida was seen to have instances when peak concentrations surpassed SO_2 levels in Żejtun. As expected, Għarb had the lowest average SO_2 concentrations, which were fairly stable. In this regard, one can comment on the fact that the uncertainty level in Għarb readings was very small compared to that of the other stations (less than +/- 1 $\mu g/m^3$; as opposed to the approximately +/- 2 $\mu g/m^3$ of Żejtun and Msida and the +/- 5 $\mu g/m^3$ of Kordin).

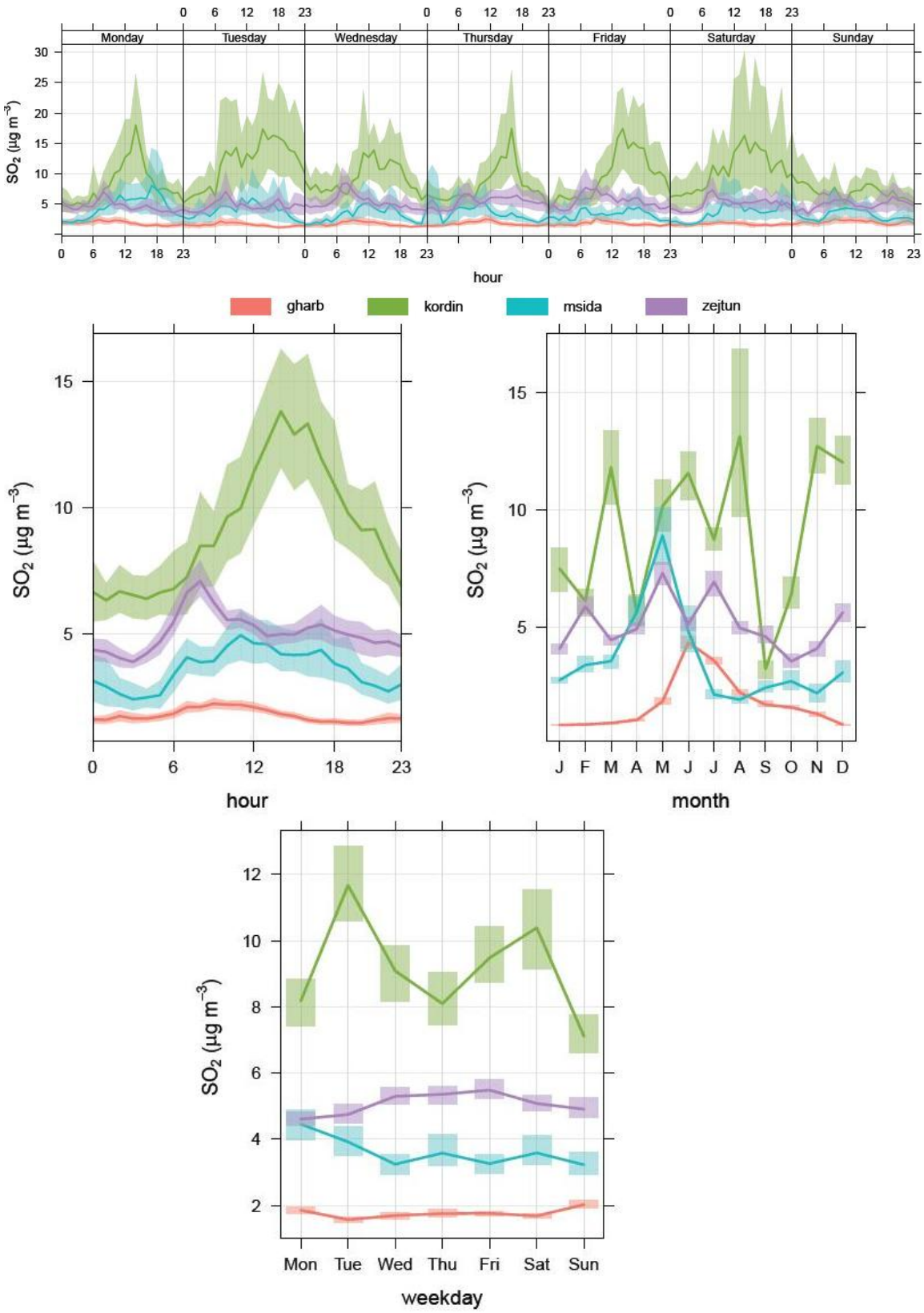

Figure 4.22: Monitoring stations timeVariation plot

The typical daily variation plot (middle-left plot) shows the calculated average SO_2 concentrations in an average 24 hour period. The plot shows that, as above, Għarb had the lowest average daily SO_2 concentrations, which were fairly stable. The average day in Żejtun had higher levels than those of Msida. Both these stations experienced a similar pattern of reduction in SO_2 in the early hours of the morning (before 6:00), an increase in SO_2 after 8:00 and a decrease after 18:00. This indicates that SO_2 levels at these locations were linked to daytime, possibly due to an increase in power demands and/or human daytime activities. Conversely, Kordin experienced significant SO_2 peaking around 15:00 - 16:00. Hence, peak SO_2 levels were reached a number of hours after Żejtun and Msida. This phenomenon is quite unexpected due to the relative proximity of Msida and Kordin. Further experimental examination of this anomaly may be required to identify a possible cause for this phenomenon.

The middle-right plot shows the average monthly SO_2 readings over the whole period. Unlike Figures 4.20 and 4.21, the results show that there was a more prominent monthly change in the Għarb readings. Peaking can be seen in the months of June and July, which may have been partly due to the abnormally high readings of June and July 2008. If that is the case, a typical year in Għarb would not have such peaking. Conversely, a typical year in the Żejtun station included several peaks oscillating around 5 $\mu g/m^3$, in agreement with the timePlot results. Meanwhile, the Msida results were characterised by significant SO_2 increases in April, May and June, with concentration of SO_2 decreasing by about 2.5 $\mu g/m^3$ in the following months. It should be pointed out that this decrease makes the average SO_2 readings in Msida in July and August lower than those of Għarb.

Contrasting with the above trends, the results for Kordin were fairly haphazard, with sharp peaks followed by deep troughs (see August and September). This abnormal pattern, in conjunction with high uncertainty (approximately +/- 3 $\mu g/m^3$ in some months) may indicate that lack of data may have distorted the results of the monthly plot.

The final plot (bottom) demonstrates the average daily emission levels in a typical week. Interestingly, this plot shows no overlap between the different locations, with highest concentrations present at Kordin, followed by Żejtun, Msida and finally by Għarb. Għarb again showed fairly stable results, with daily concentrations being within less than 1 $\mu g/m^3$ of each other. Monday concentrations of Żejtun and Msida were found to be similar, however during the following days, Żejtun concentrations increased and those of Msida decreased (both by approximately 1 $\mu g/m^3$). This pattern can be seen to be quite different from the weekday pattern of emissions (refer to Figure 4.16). It is possible that certain factors may have resulted in SO_2 accumulating in Żejtun, following the high emissions experienced in the beginning of the week. Alternatively, the results may be purely coincidental, a product of wind patterns (and other environmental factors) over the examined periods. On the other hand, the Kordin results resemble those of the emission patterns. Monday and Tuesday were found to produce an increasing trend in SO_2 emissions, decreasing on Wednesday and Thursday before increasing again towards the end of the week. This may lead to the conclusion that the close geographical proximity of the Kordin monitoring station to the MPS may make it particularly susceptible to overall emission patterns from the power station.

4.5.5 Monitoring stations SO_2 data and wind

When looking at air quality monitoring data, it is often useful to look at the pollutant concentrations in conjunction with wind data which helps to elucidate the origins of the pollutant. The results of this analysis are shown in Figures 4.23 – 4.32. The first two plots, Figures 4.23 and 4.24 were produced using the pollutionRose function.

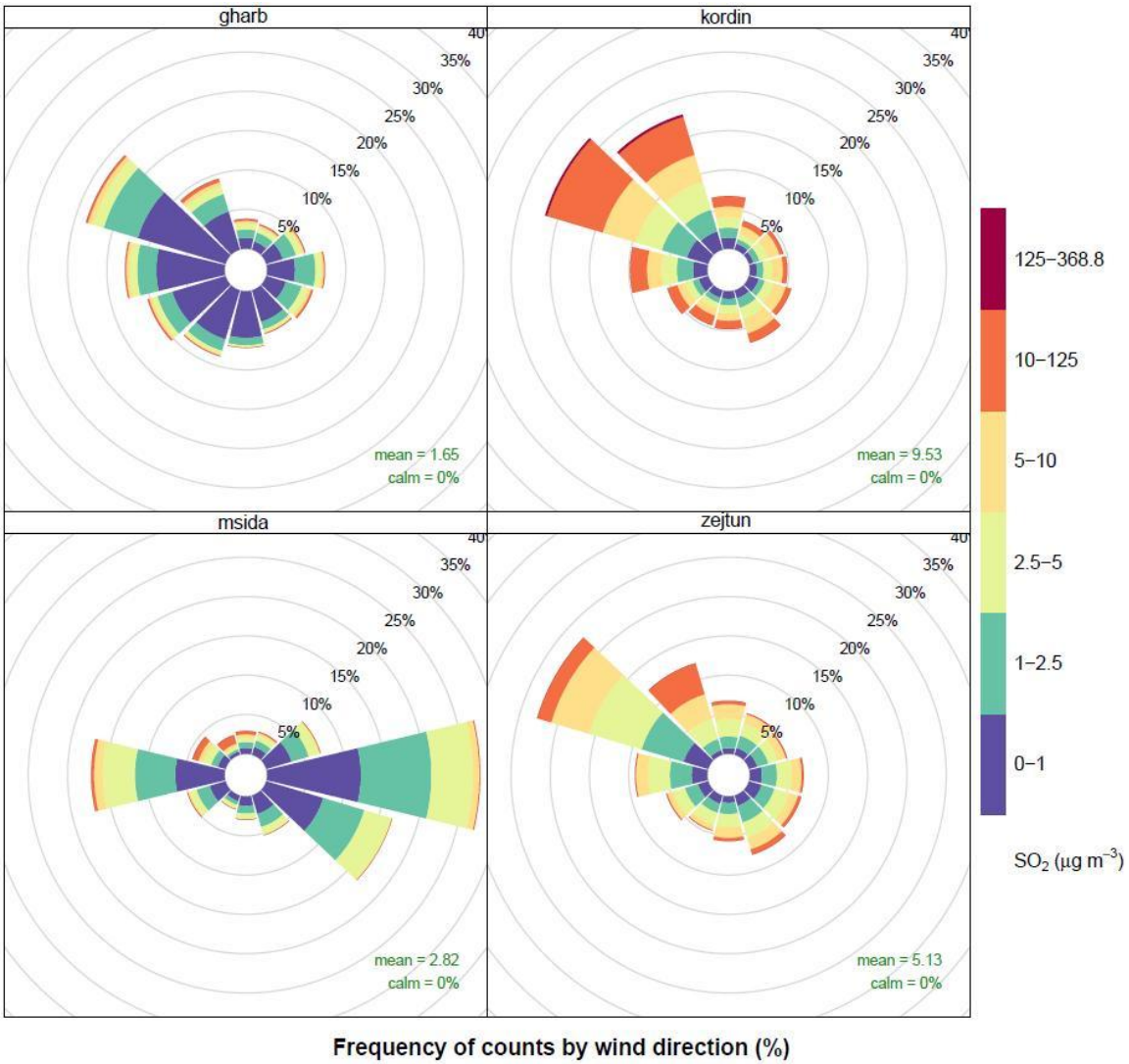

Figure 4.23: Monitoring stations pollution roses

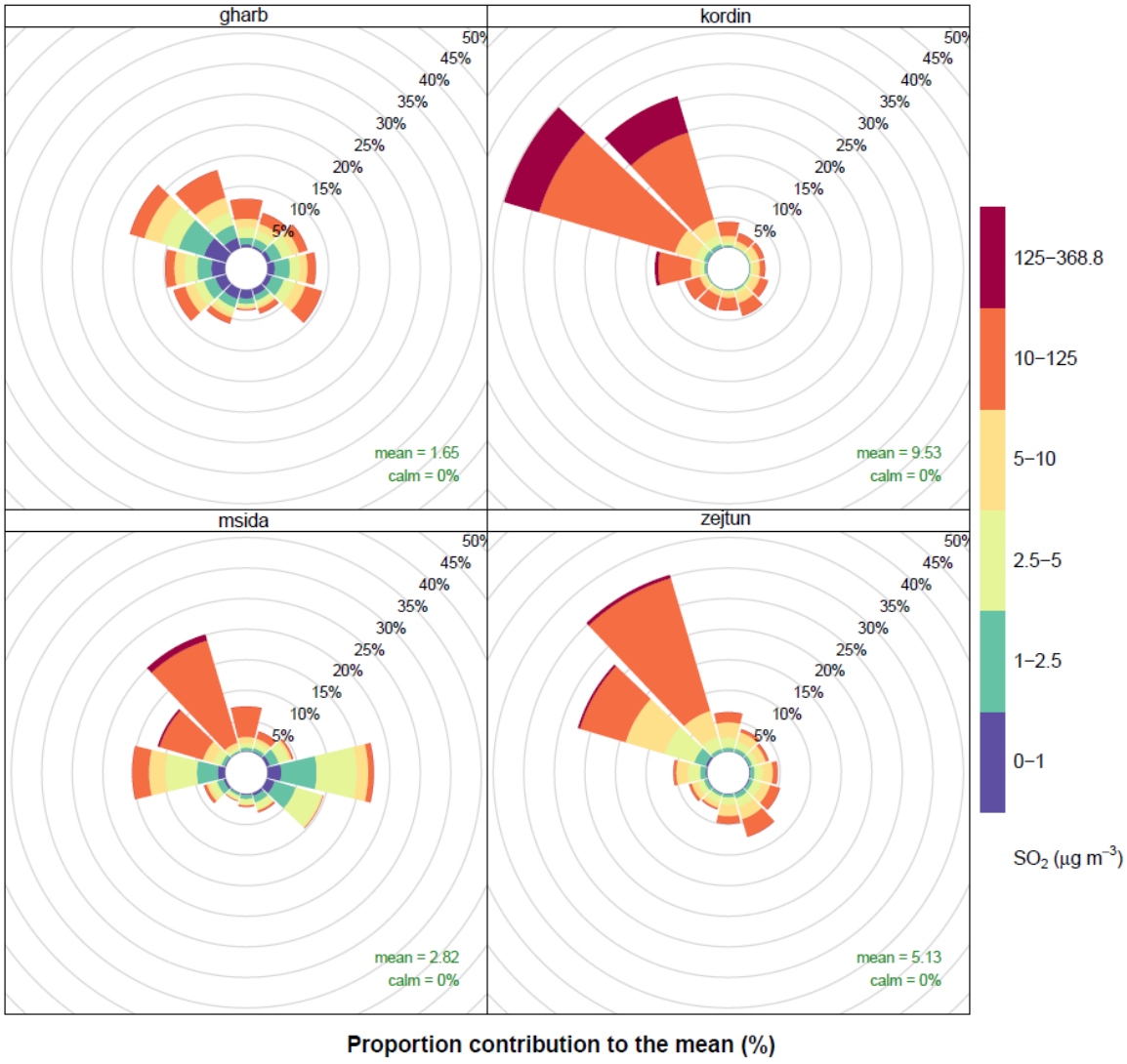

Figure 4.24: Monitoring stations pollution roses with weighted mean

Three of the monitoring station pollution roses in Figure 4.23 resemble the wind roses produced in Section 4.5.1, with the exception being Msida. The reason for this similarity is that the plots produced in Figure 4.23 are based on wind direction frequency, hence they should concur. Although Msida still showed a West-East direction predominance, the predominant direction is shown as East in Figure 4.23. The reason for this difference

is that overlap between the wind dataset and the Msida monitoring station data set was smaller than the complete wind dataset, resulting in distortion of results. What can also be noted from this plot is that for Kordin, Msida and Żejtun, the largest proportion of SO_2 concentrations above 10 µg/m^3 were recorded when the wind was from the NW direction.

This can be elaborated further through Figure 4.24. This plot shows the proportion each wind direction contributed to the final value of the mean. As shown in the diagram, the NW wind direction contributed a relatively large proportion to the mean value of the Kordin and Żejtun stations (60% and 50% respectively). For Msida the NW wind direction contributed 30% of the mean value and the East-West axis accounted for about 32%. In the case of Għarb, there did not seem to be any significantly large contributor, although the Northern wind directions seemed to contribute more to the mean than the Southern wind directions.

Another useful way of looking at the distribution of the readings distribution is shown in Figure 4.25. The percentileRose, is a bivariate plot of wind direction and SO_2 readings, with the percentile levels shown as a colour coding. This plot can be used to determine the distribution of readings (especially the outliers) with respect to wind direction. In this case, the Għarb results were found to agree with the pollution roses above, with 99.5% of readings distributed across all directions, with slightly higher readings from the Northern directions. However, when looking at the higher concentrations (top 0.5%), higher SO_2 readings were recorded with wind from the South East direction. It can also be noted that Għarb was the only location that had 100% of the readings below 100 µg/m^3.

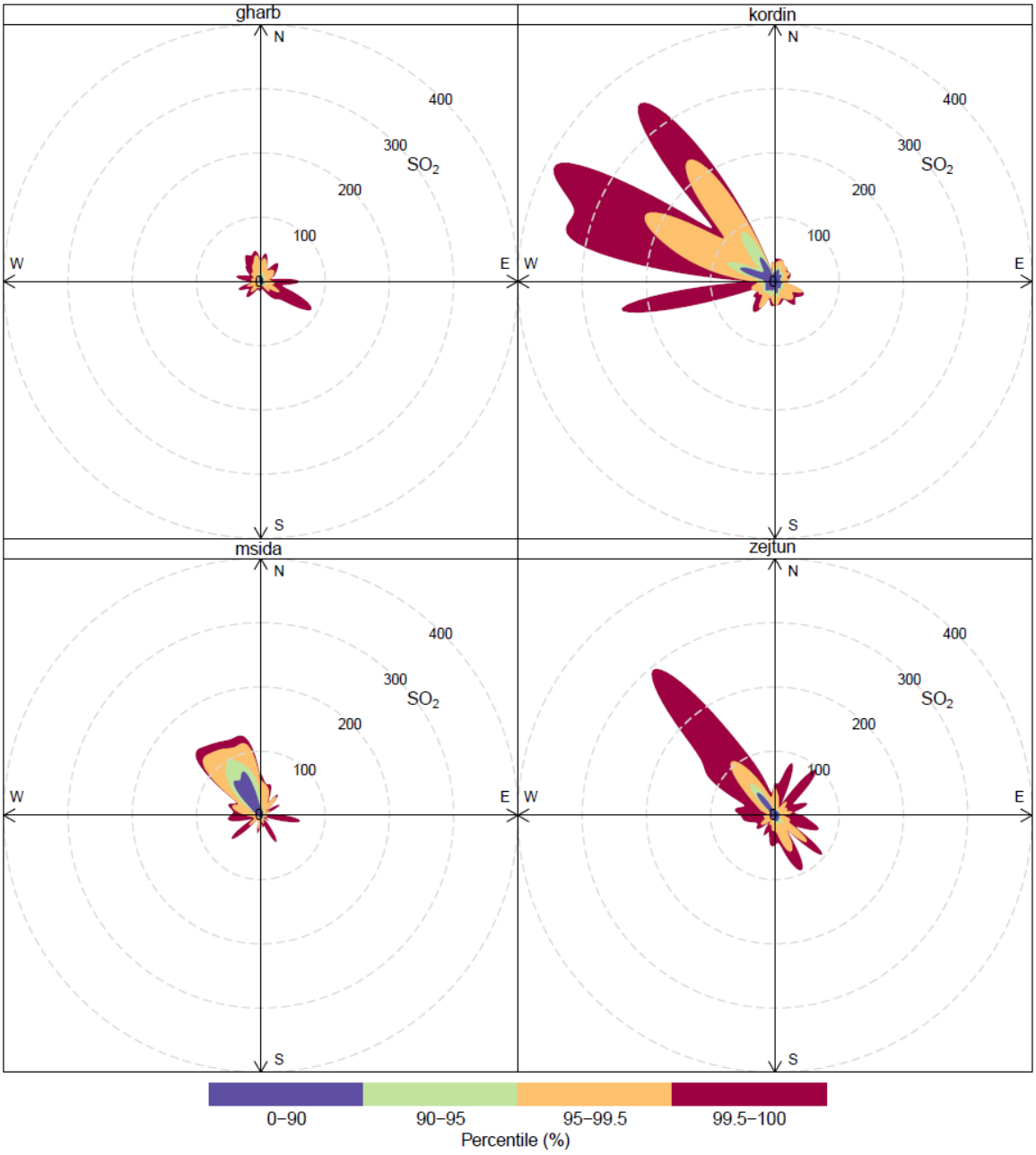

Figure 4.25: Monitoring stations percentile roses

Also in agreement with the pollution roses, Kordin and Żejtun had the majority of the higher SO_2 readings occurring with a NW wind. The plot also illustrates that a significant proportion of the top 0.5% of readings for Kordin were larger than 200 µg/m^3 while those of Żejtun were mostly smaller than 200 µg/m^3. Kordin readings also had the most

outliers, with a significant proportion of the top 5% of readings being larger than 100 µg/m^3. Msida generally had readings lower than 100 µg/m^3 however had some outliers (in the top 5% of readings) occurring with a NW wind that went beyond100 µg/m^3 but not as high as those of Żejtun or Kordin. However, this may have been partly attributable to the loss of data in the data integration stage, since Msida was shown to have the highest recorded SO_2 reading of 401.2 µg/m^3 in the numerical analysis (see Section 4.3.2). Notwithstanding, this value was merely an outlier and the trends demonstrated in the percentile rose above may still be of value.

Building on what has been discussed in the above plots, polar plots that link wind speed, direction and SO_2 concentration were produced. The resultant plots are shown in Figures 4.26 - 4.30 below. In particular, Figure 4.26 shows the polar plot for Msida. The plot indicates that the relatively higher concentrations of SO_2 were (on average) recorded with a N to NW wind direction and a wind speed between 5 and 10 m/s. From a direction perspective, this corroborates the findings of the weighted mean pollution rose (Figure 4.24). The fact that these readings were recorded with higher wind speeds may indicate a source which was further away from the monitoring station, in the N-NW direction. Hence, in the case of Msida, the hypothesis that the MPS was the main contributor of SO_2 seems to be unlikely. To test whether this result could have been caused by outliers, a second polar plot showing the uncertainty of the polar plot calculation was produced (Figure 4.27).

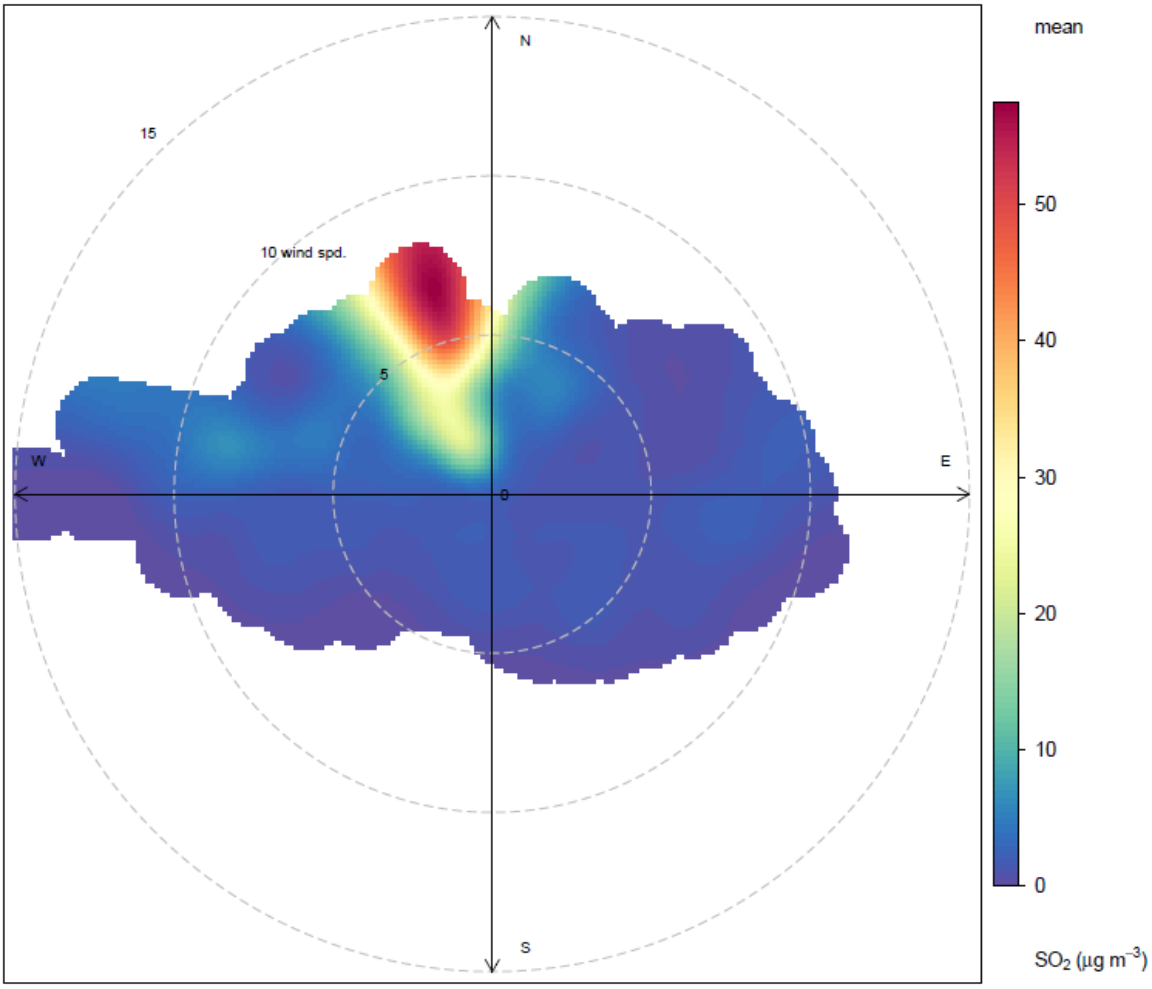

Figure 4.26: Msida polar plot

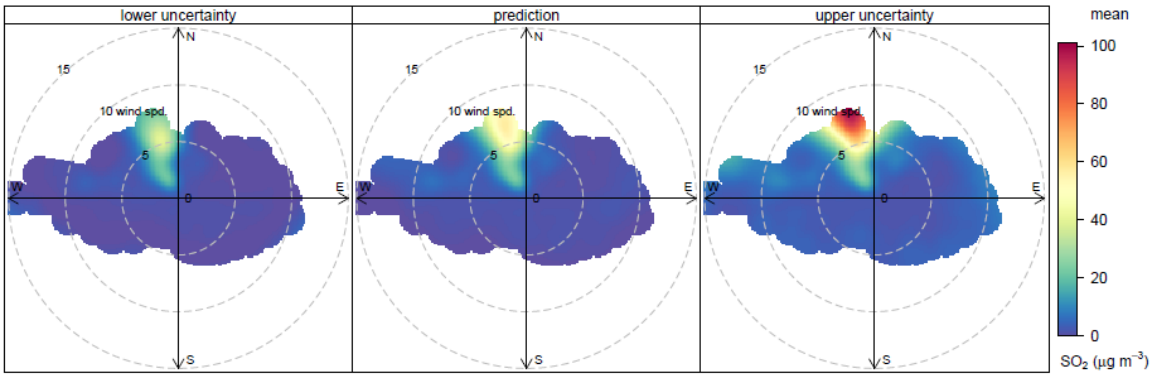

Figure 4.27: Msida polar plot uncertainty range

Figure 4.27 shows that even at the lower ranges of uncertainty, a higher than average SO_2 reading was obtained with N-NW wind at 5-10 m/s speed. This indicates that the result was unlikely to be caused by outliers, and that there could be a specific source from that direction. Hence, it would be prudent to examine the results of other stations before discussing possible sources.

Similar to Msida, the other stations show that the higher readings were registered with N or NW wind. In the case of Żejtun (Figure 4.28) it was predominantly from NW wind, of speed between 2 – 10 m/s.

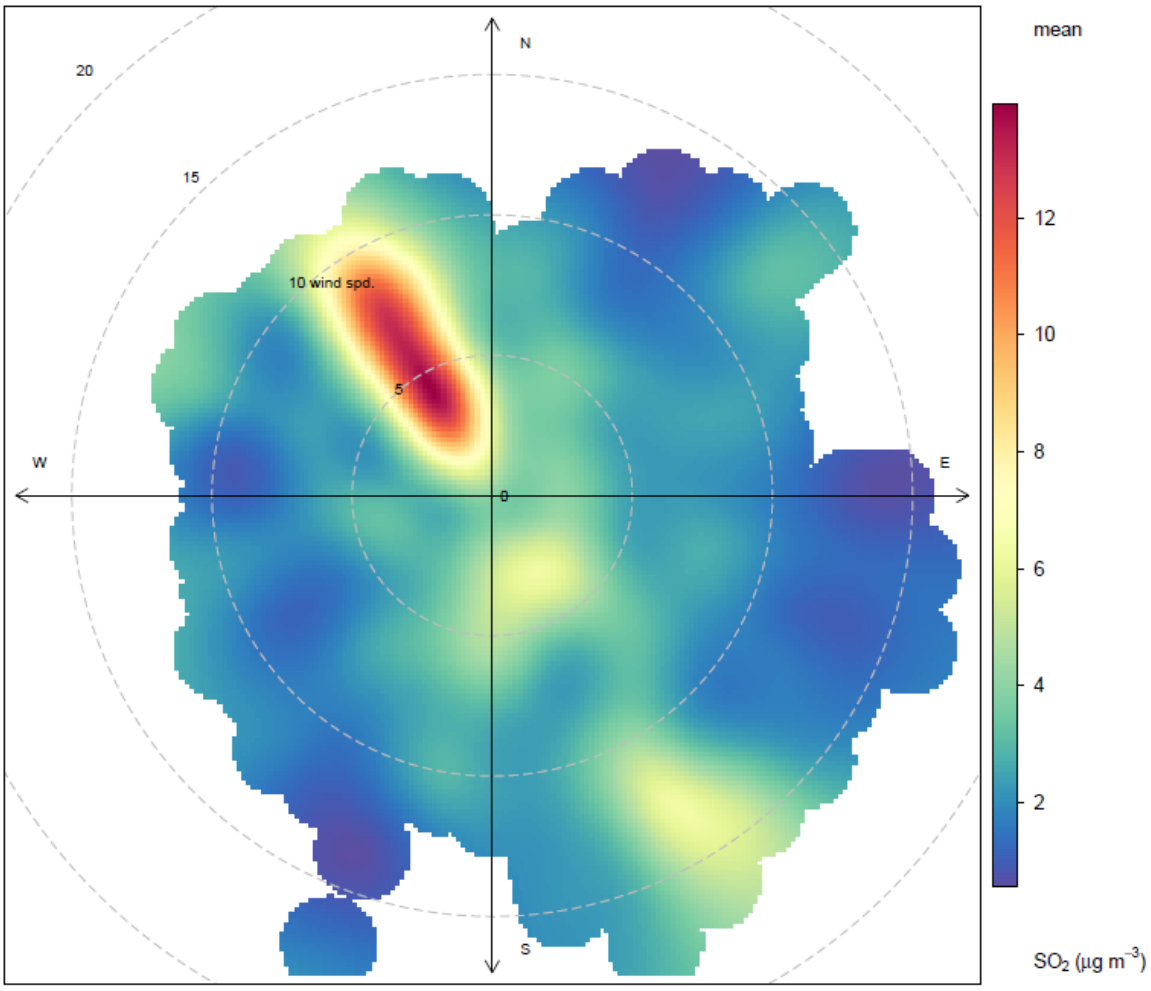

Figure 4.28: Żejtun polar plot

It should be noted that this wind speed covered a large proportion of the average wind speed range observed in the NW direction. This indicated a source that exerted effect independent of wind speed, which could denote a relatively close source. Additionally, the Żejtun polar plot shows that there were relatively intermediate SO_2 readings recorded with wind from a SE direction.

Although Kordin (Figure 4.29) also recorded high readings with NW winds, these were recorded at wind speeds greater than 10 m/s. This might indicate that the source was further away from the station.

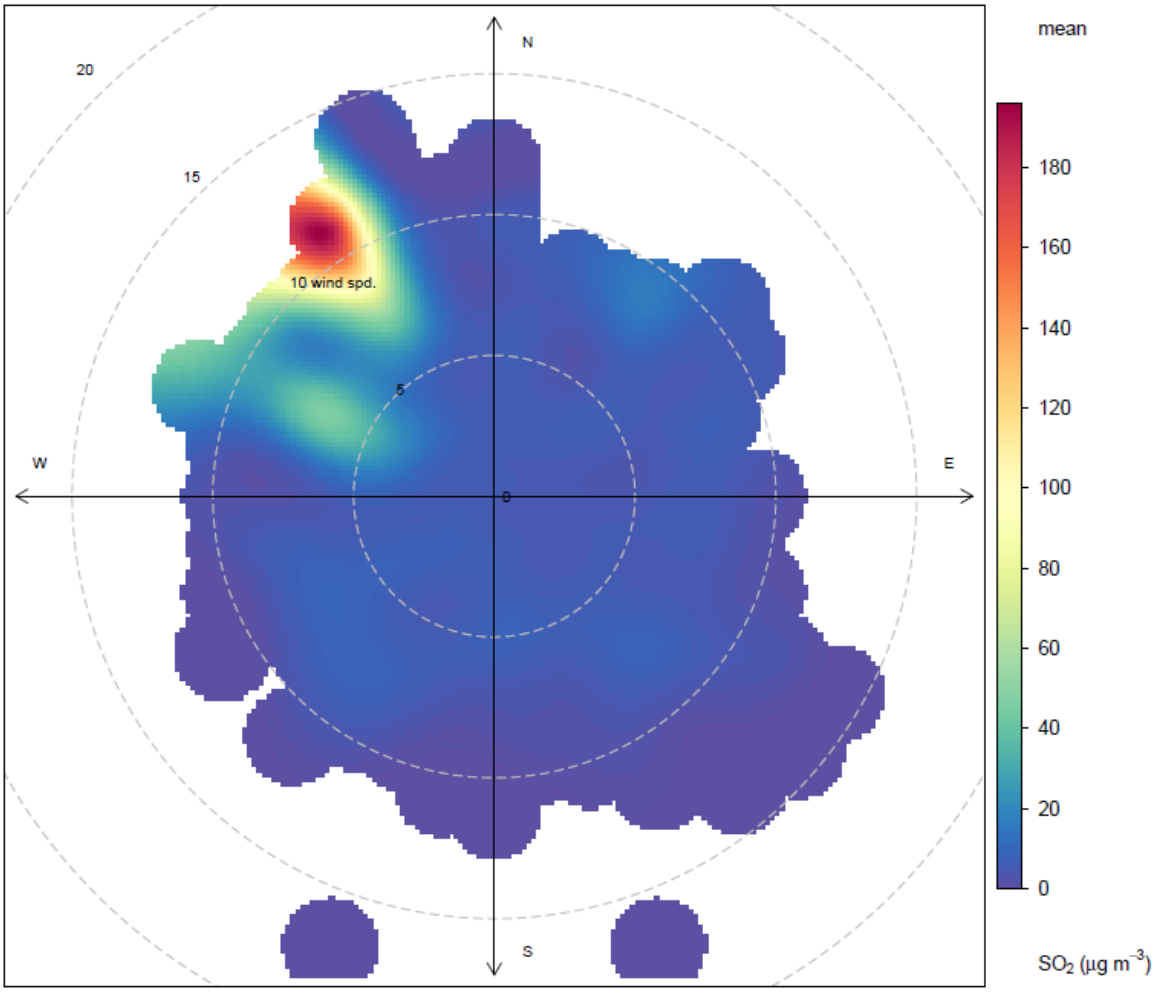

Figure 4.29: Kordin polar plot

Like Msida, Kordin was also characterised by the fact that relatively low emissions were generally recorded outside of the NW quadrant. This was not the case with the Għarb readings, which had higher readings with Northern winds of less than 5 m/s speed coupled with relatively intermediate readings with SE wind (virtually independent of speed), as seen in Figure 4.30.

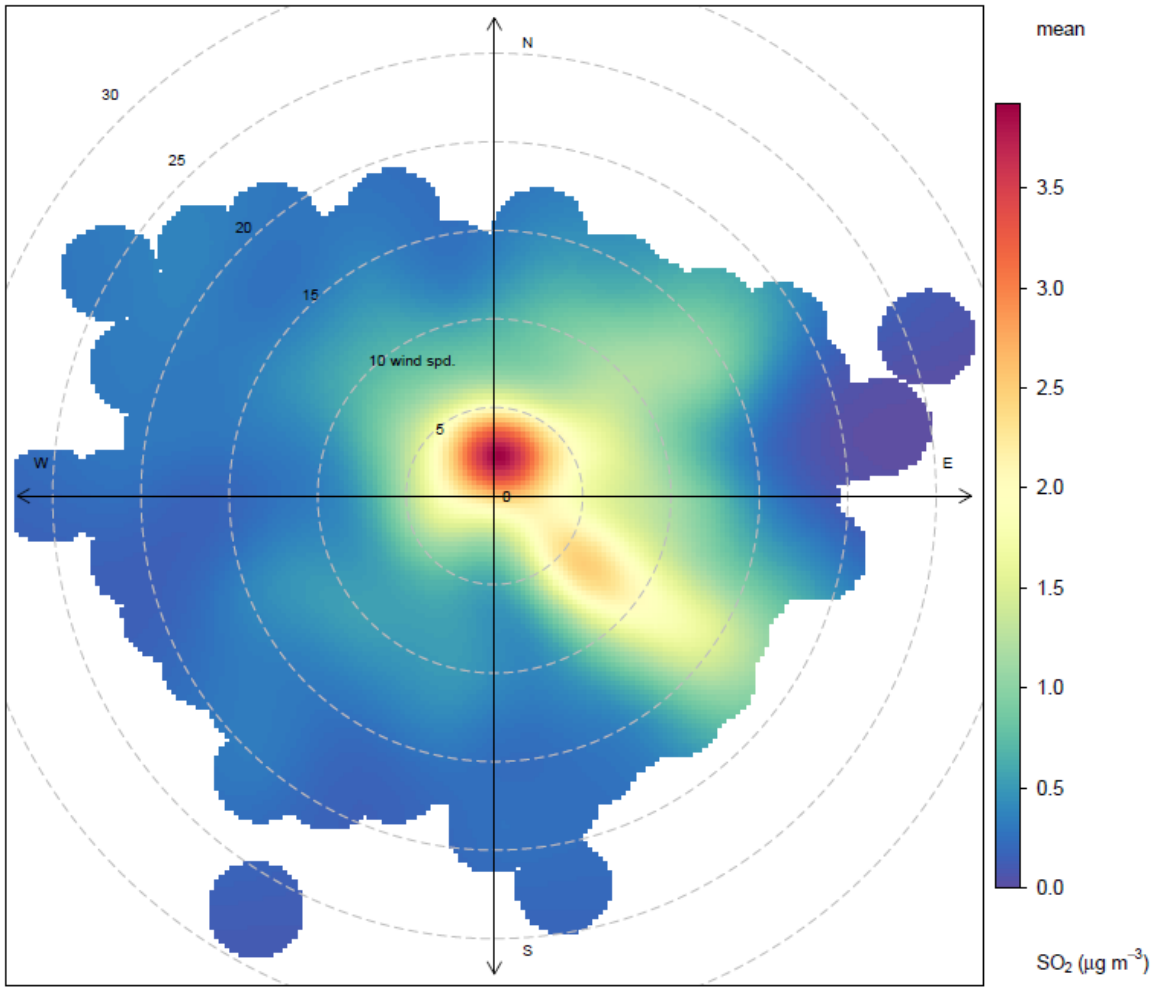

Figure 4.30: Għarb polar plot

The fact that all the above trends were relative should be emphasised. In fact, looking at the different scales used in each polar plot, one can easily determine that the higher

readings at Kordin were around 50 times larger than those of Għarb. Hence, it would be prudent to also examine the polar plots on a comparative scale as shown in Figure 4.31, thus adding some context to these results. This clearly shows that despite relative differences within readings of the same station, the majority of readings in Għarb, Msida and Żejtun were very low compared to those of Kordin.

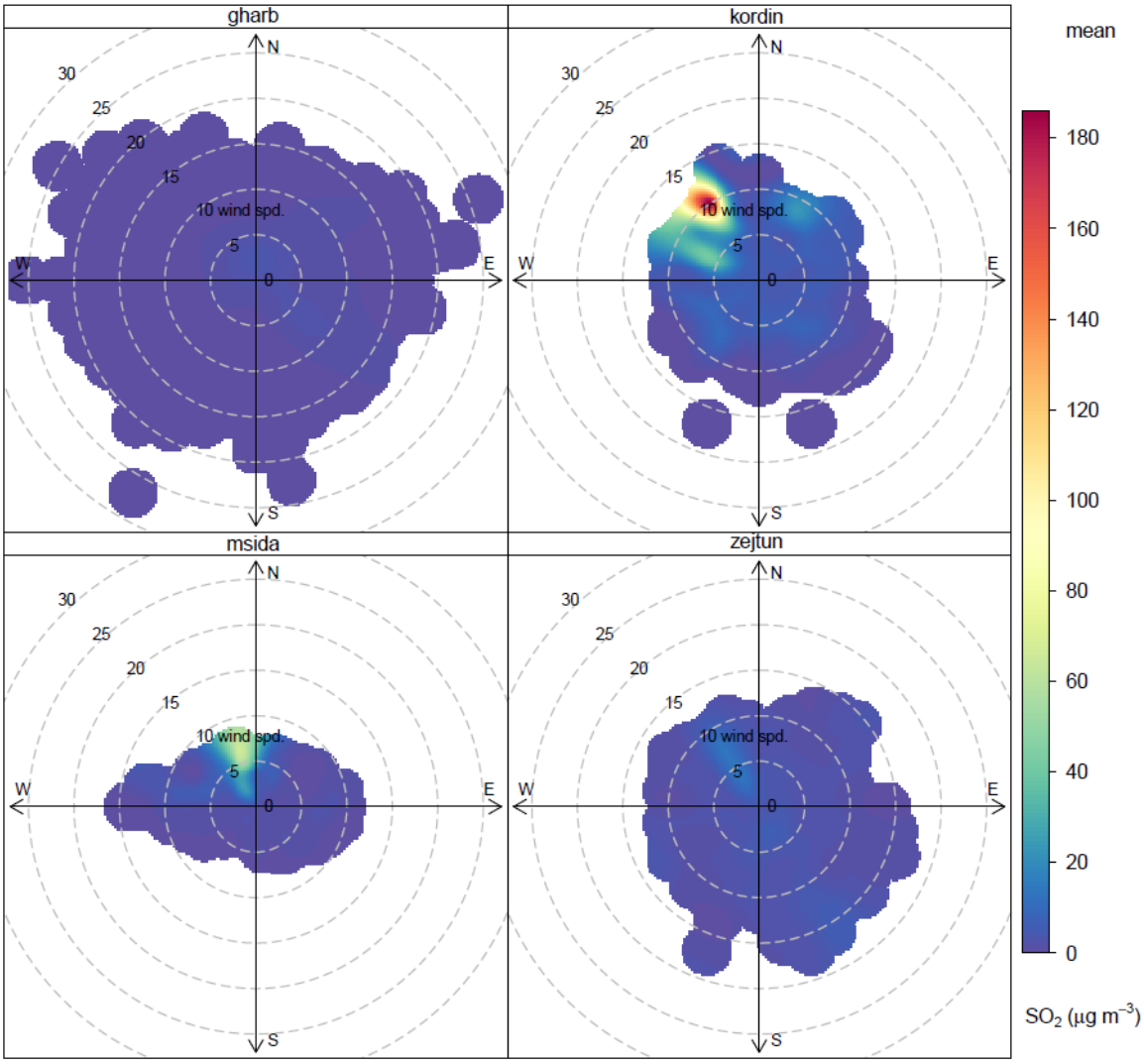

Figure 4.31: Joined polar plot

In fact, the polar plot of Kordin is very similar to Figure 4.29 with high readings for NW winds at wind greater than 10 m/s. Of the others, only Msida was calculated to have intermediate concentrations, with Northern winds, while Għarb and Żejtun had low concentrations throughout the whole plot. Nevertheless, in view of the findings of Figures 4.26-3.30, the wind directions that resulted in relatively high or intermediate concentrations were extrapolated on a map as shown below:

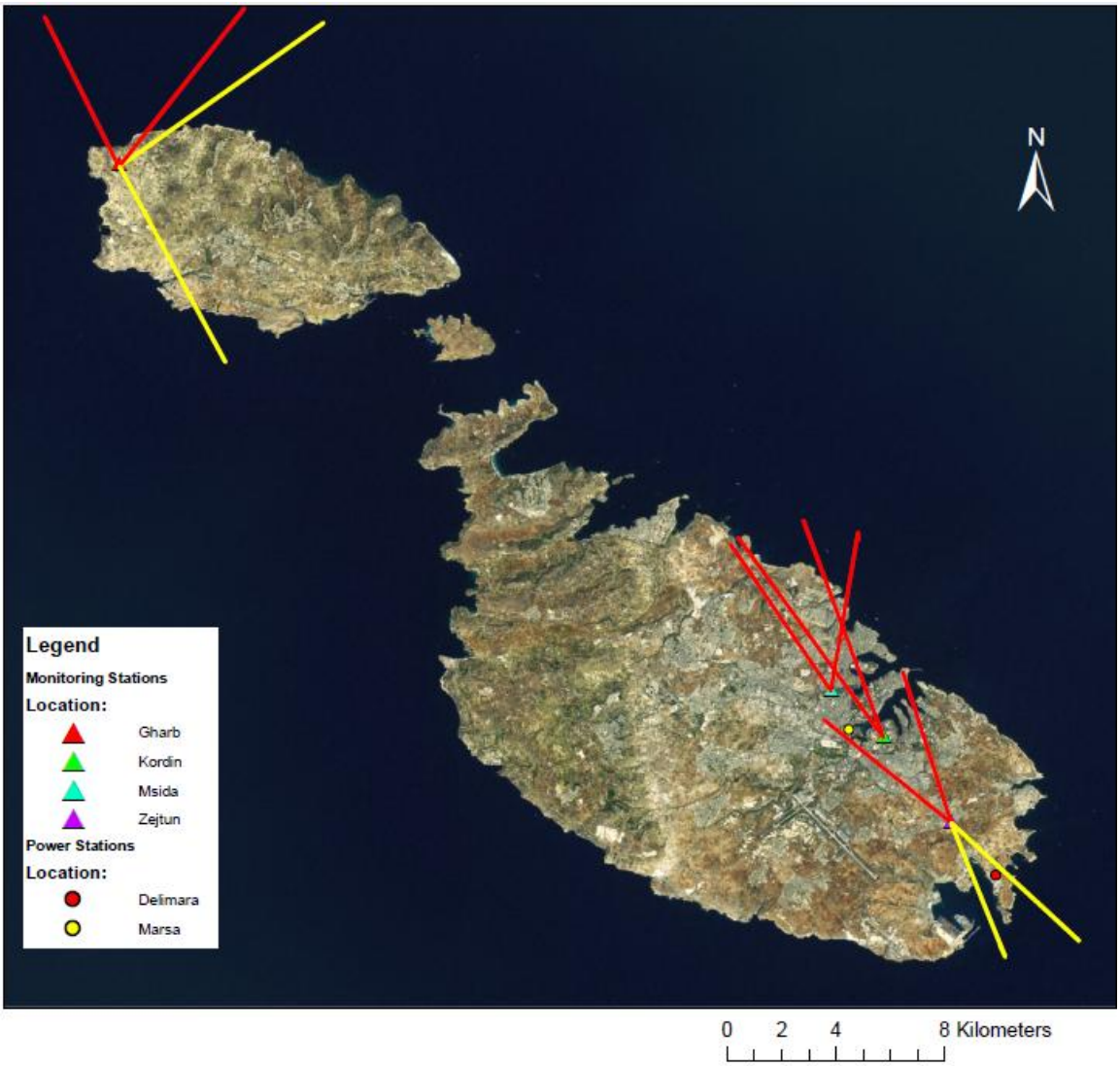

Figure 4.32: SO_2 origin extrapolation

Where lines show wind direction giving high (red) or intermediate (yellow) readings

Figure 4.32 shows a consistent overlap with regards to the high SO_2 levels recorded with a N to NW wind at all the stations. In the case of the Msida and Kordin stations, both polar plots indicated a source which was likely not close to the stations. In view of the directionality of the higher concentrations, a plausible source would have been marine traffic off the coast of Malta. However, with limited data, other sources (even land based) cannot be excluded.

The direction of the higher readings in Żejtun overlap with those of Msida and Kordin, hence the same source could have resulted in the readings. The polar plot for Żejtun showed that readings were almost independent of wind speed, which could indicate more than one source. The fact that the direction includes the MPS signifies that it could also be a possible source of SO_2. This conclusion seems to be bolstered by the fact that intermediate readings in Żejtun were recorded with winds coming from the direction of the Delimara power station. Yet, one could argue that the area also overlaps with a busy port area, which would support the view that marine vessels were the source.

Possible sources may also be listed for the Għarb station, with possibilities for intermediate concentrations being land-based sources in Malta and Gozo or marine traffic between the islands. Marine traffic could also have resulted in the higher concentrations from the Northern winds, however, the low winds speeds coupled with high concentrations suggest a more localised source. In this regard, biogenic sources could have resulted in higher than normal readings of SO_2. Alternatively, it was discovered that a sewage outflow in Wied il-Mielaħ, which has now been closed, was still operational in

the examined period (The Times, 2011; Wied il-Mielaħ, 2012). This was located roughly one kilometre to the North of the Għarb station and could have been (at least) partly responsible for a localised increase in SO_2 levels. Although not necessarily emitting SO_2 directly, species such as hydrogen sulfide emitted from sewage may be oxidised in air in the presence of aerosols, water or radicals (Cox & Sandalls, 1974; Kellogg *et al.*, 1972). If this outflow was the source, future analysis of the area should show a reduction of SO_2 readings associated with the Northern winds.

To corroborate these hypotheses, hourly polar plots were produced for each of the stations (Figure 4.33 – 4.36). In the case of Għarb (Figure 4.33), a localised source seems to again be the most plausible explanation for the polar plot trends. This can be inferred from the low wind speeds in conjunction with higher readings and also by the lack of a specific temporal trend.

Although the previous polar plots showed an overlap in directionality of the Msida and Kordin stations, Figures 4.34 and 4.35 show some differences. Higher readings in Msida were generally registered between 06:00 - 10:00 while of those of Kordin between 13:00 - 16:00. Additionally, the higher readings occurred with wind speeds around 5 m/s for Msida and around 10 m/s for Kordin. This might indicate two possibilities. One possibility is that the Msida and Kordin monitoring stations were detecting SO_2 from different sources. Otherwise, the source is closer to Msida, which would cause both the wind speed and the temporal differences.

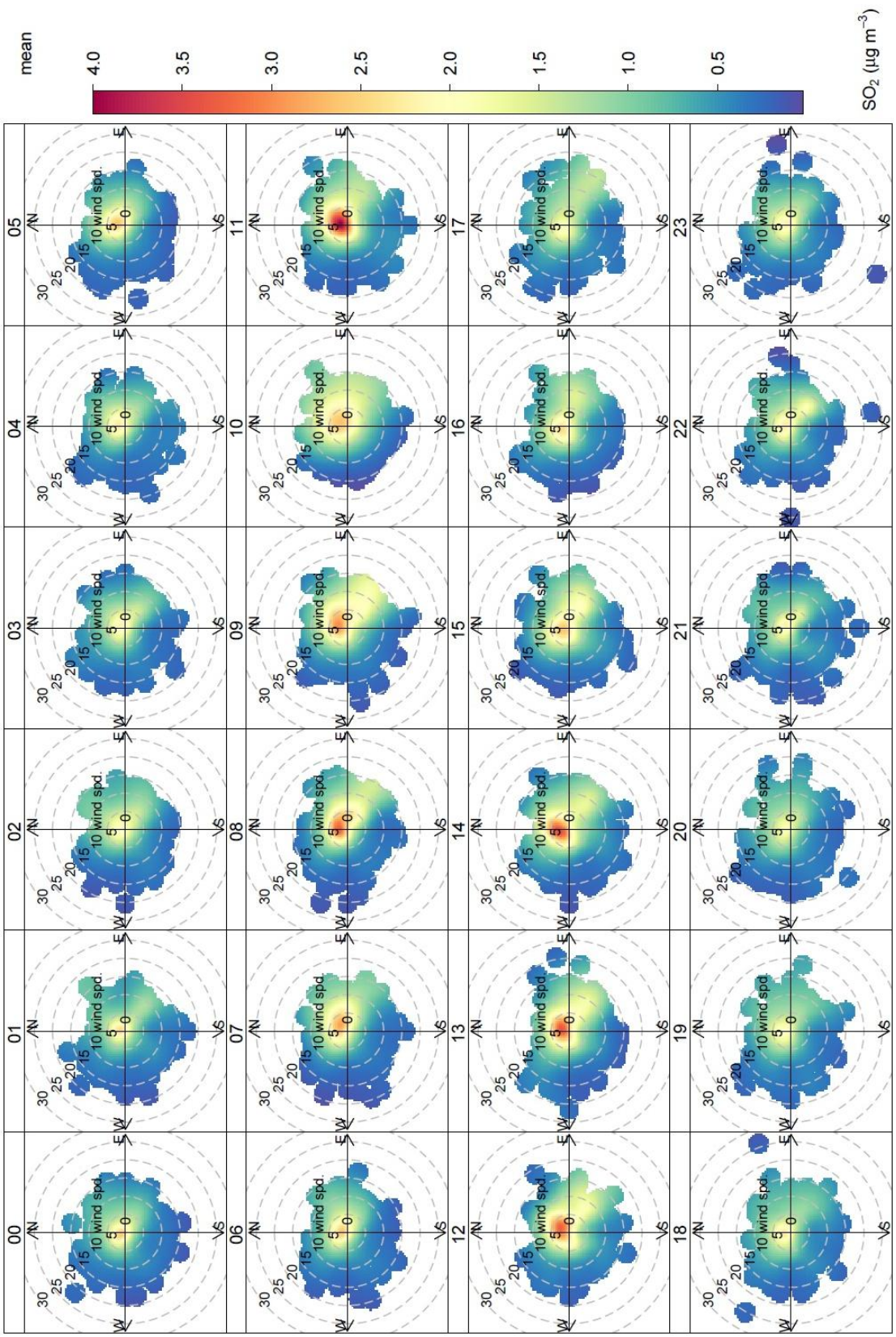

Figure 4.33: Għarb hourly polar plot

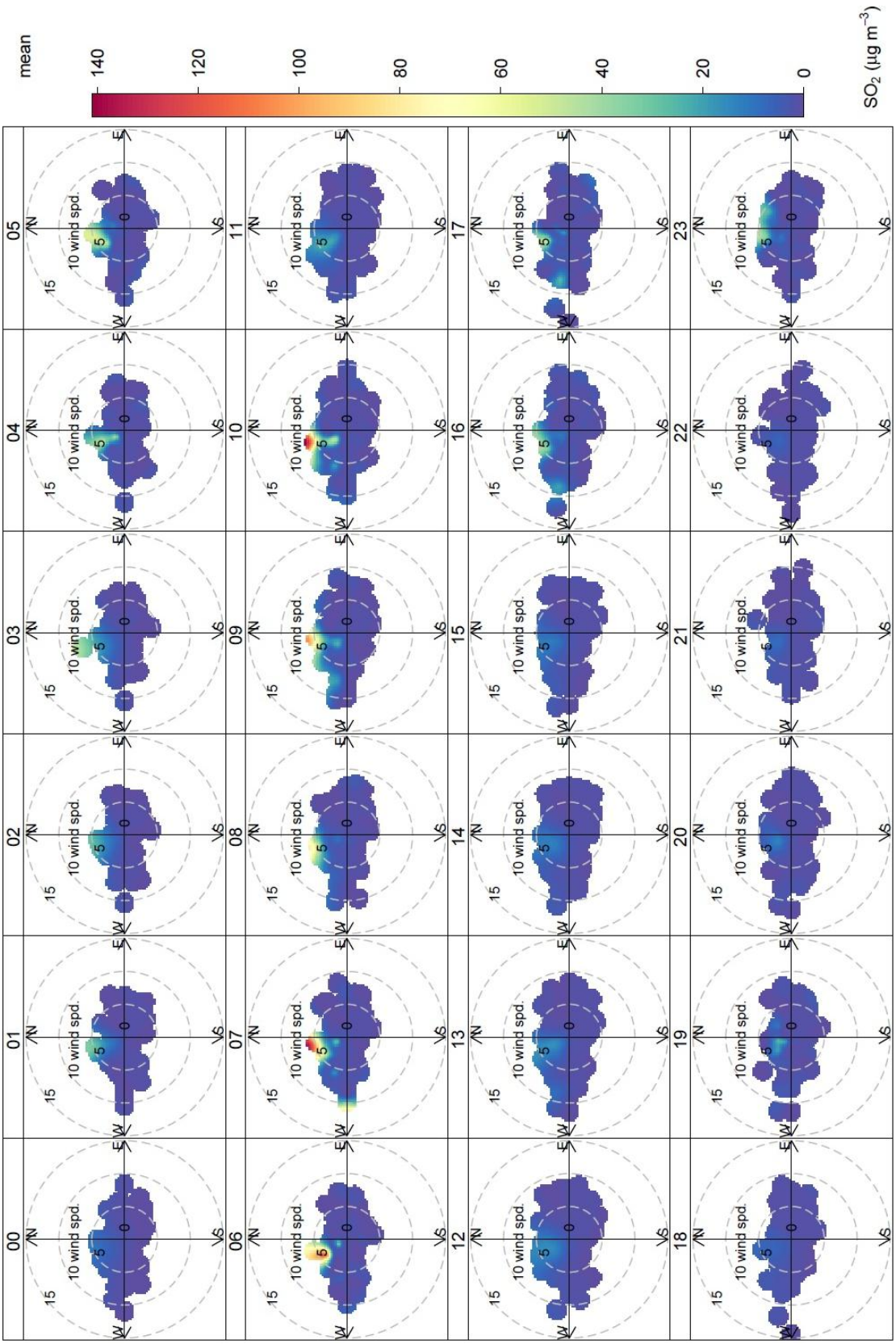

Figure 4.34: Msida hourly polar plot

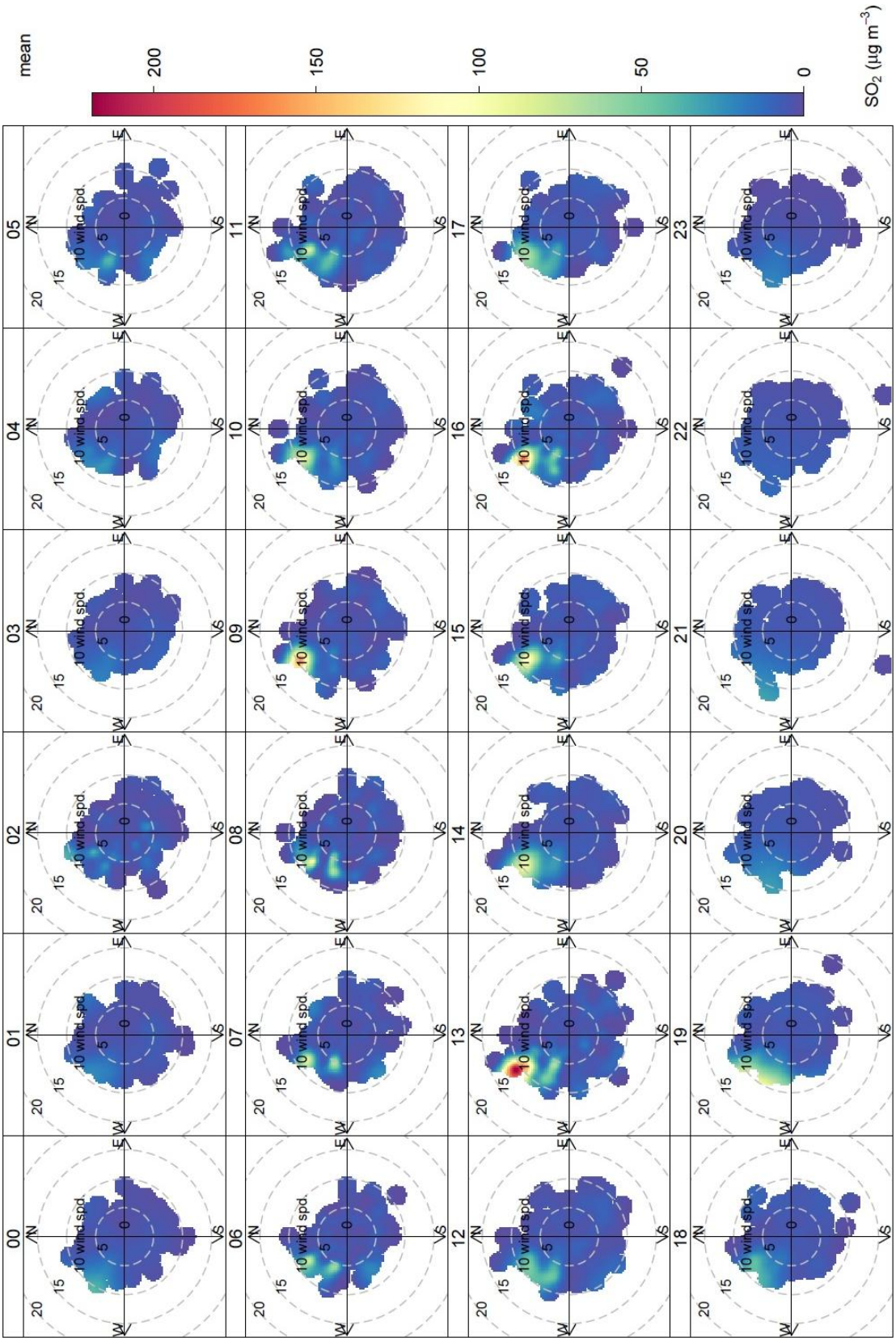

Figure 4.35: Kordin hourly polar plot

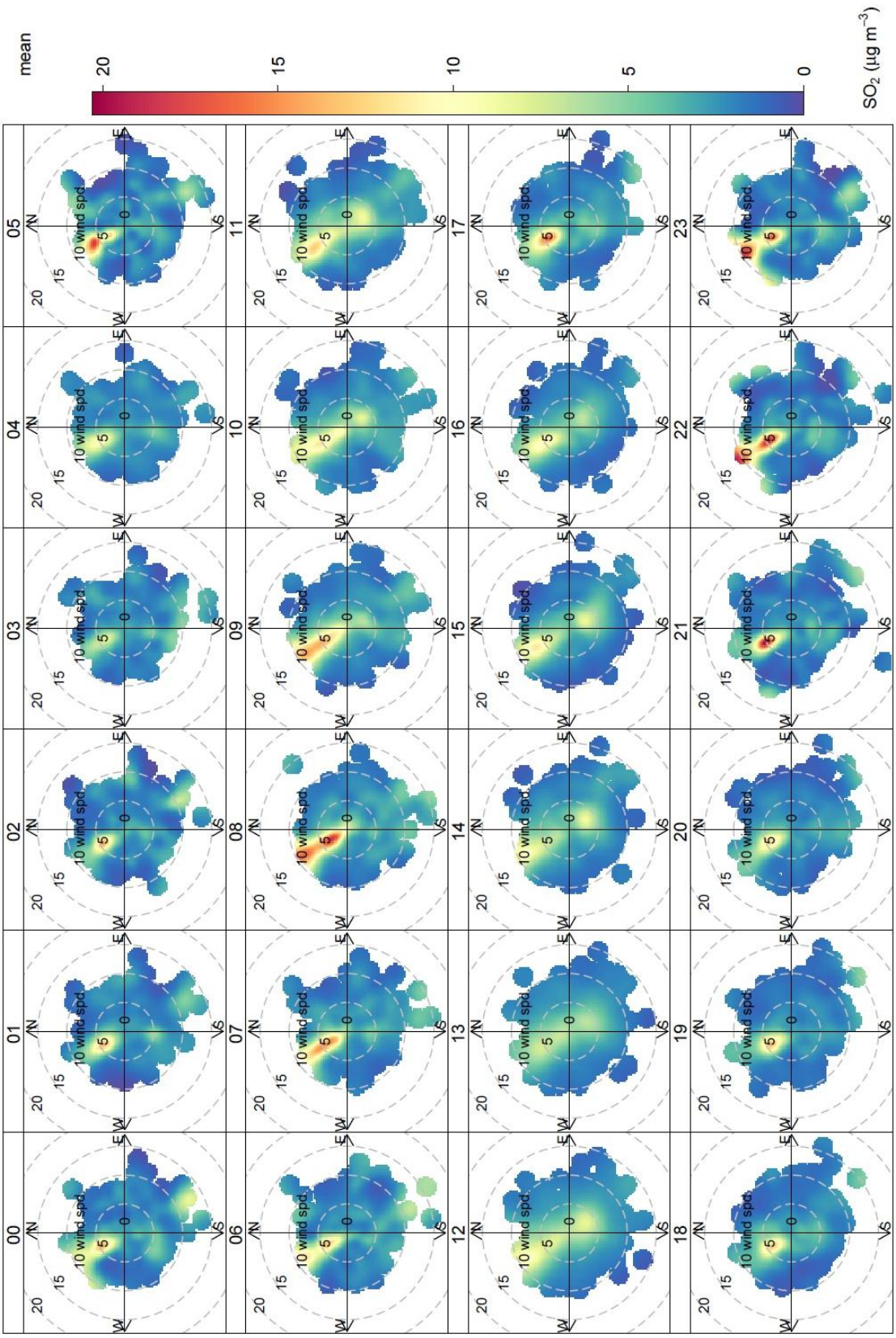

Figure 4.36: Żejtun hourly polar plot

The hourly polar plot of Żejtun indicated that the higher SO_2 concentrations from the NW direction were generally present at every hour, with higher concentrations at 05:00, 07:00 - 09:00, 17:00 and 21:00 - 23:00. This pattern does not rule out any of the sources mentioned, nor does it confirm them, since the temporal pattern doesn't seem to follow a specific trend. However, at any time of day, higher readings in Żejtun were mostly independent of wind speed. This again suggests that there might have been more than one source.

Interestingly, the results indicate an overall diversion from the hypothesis that the MPS was the most significant contributor of SO_2 during the examined period. The fact that the R analysis and the diffusion tube data have shown an overall decrease in SO_2 readings across the islands coupled with decreasing emissions from MPS might have resulted in a shift from the MPS being the most significant contributor (as was concluded by Vella *et al.*, 1996) to other sources that were previously being masked by high emissions from Marsa.

It should be noted that these are merely hypotheses, and proper identification of sources would require a thorough investigation beyond the scope of this study. Therefore, although no conclusive results could be obtained, this analysis helps to highlight potential areas of investigation for future research.

4.6 SPSS analysis

An SPSS analysis using the ANCOVA model was used to analyse the monitoring station and wind data to determine the statistical relationship between the "Reading" (the dependent variable) and the predictors. In this case, the predictors were considered to be "Wind direction" (being a factor i.e. categorical), "Wind speed" and "Emissions" (being covariates i.e. metric). Additionally, an attempt to produce a predictive model for each monitoring station was made, the results of which shall be discussed below.

Analysing the Kordin data, it was found that all three predictors were statistically significant variables ($p = 0.000$ for all three); with Wind speed being found to be the best predictor of Reading since it had the largest F-value (276.115) which can be interpreted as having the largest significance. This was followed by Emissions (90.537) and Wind direction (57.251). The three predictor model obtained for the Kordin monitoring station is shown below:

Model 1:

$$\text{Reading} = -10.962 + 0.655\,W1 - 0.184\,W2 - 2.721\,W3 - 2.635\,W4 - 1.561\,W5 + 1.489\,W6 + 10.805\,W7 + 0.011\,(\text{Emissions}) + 2.458\,(\text{Windspeed})$$

Note that W1 – W7 represent Wind direction as illustrated in Figure 3.1. Depending on Wind direction, the corresponding sector variable is set to 1, whereas the other sector

variables are set to 0. For example if Wind direction is 1, W1 is equal to 1, while W2-W7 are equal to 0. Hence predicted value becomes:

$$\text{Reading} = -10.962 + 0.655 + 0.011\,(\text{Emissions}) + 2.458\,(\text{Windspeed})$$

In this case, the three predictor model for the Kordin station had an r-squared value of 0.116, meaning that the model explains 11.6% of the total variance in Reading. The fact that this value is low, coupled with the three predictors being significant leads to the conclusion that there are missing predictors in this model.

All three predictors were also found to be statistically significant in the Għarb analysis ($p = 0.000$ for all three). Like Kordin, Wind speed was found to be the best predictor of Reading since it had the largest F-value (299.074). This was followed by Wind direction (76.798) and Emissions (44.918). The fact that Emissions is significant, but not majorly so, sheds doubt on the presence of a relationship between peaks in MPS emissions and the Għarb station readings, both occuring at 8:00 AM in June and July (see Section 4.5.4). The resultant three predictor model obtained for the Għarb monitoring station is shown below. It should be noted that Model 2 was found to have an r-squared value of 0.103, explaining 10.3% of the total variance in Għarb Reading.

Model 2:

$$\text{Reading} = 1.250 + 0.419\,W1 + 0.148\,W2 + 0.457\,W3 - 0.399\,W4 - 0.450\,W5 - 0.437\,W6 - 0.245\,W7 + 0.0003\,(\text{Emissions}) - 0.071\,(\text{Windspeed})$$

In the case of Msida, only Wind direction (p = 0.008) and Emissions (p = 0.008) were found to be statistically significant. This result is interesting since this was not clearly evident from the polar plots (Figure 4.27) or previous results for Msida. However, because of this result, a two predictor model was used for this location rather than the three predictor model used above. The two predictor model showed that the Msida reading is largely dependent on Wind direction (F-value = 160.651) and somewhat dependent on Emissions (F-value = 8.629). The model shown below was found to have an r-squared value of 0.132, explaining 13.2% of the variance in Reading.

Model 3:

$$\text{Reading} = 7.506 - 5.867\,W1 - 6.889\,W2 - 6.860\,W3 - 6.949\,W4 - 6.645\,W5 - 6.642\,W6 - 4.864\,W7 + 0.0004\,(\text{Emissions})$$

Similarly, the Żejtun analysis also showed a statistical significance for Wind direction and Emissions (p = 0.000 for both). However, this was not surprising, since there were indications of this in the polar plot (Figure 4.28). In this case, the two predictor model showed the significant dependence on both Wind direction (F-value = 119.568) and Emissions (F-value = 106.986). Although this seemed promising, the model itself still had a low r-squared value of 0.097, explaining 9.7% of the total variance in Reading.

Model 4:

$$\text{Reading} = 9.835 - 3.886\,W1 - 3.828\,W2 - 4.041\,W3 - 3.824\,W4 - 4.292\,W5 - 4.763\,W6 - 3.724\,W7 - 0.002\,(\text{Emissions})$$

Although no reliable predictive model could be obtained using these three variables, it can be concluded that all models indicated that predictors were missing from the analysis. This may have included other non-emission related factors such as temperature; however, it is likely that significant emission sources were missing from the models.

A second analysis similar to the above was attempted, with a significant difference: "Wind speed" was omitted as a predictor and only measurements originating from the quadrant representing the MPS were included. The purpose of this analysis was to establish whether, under favourable wind conditions, the MPS was statistically related to SO_2 readings in each of the stations. All the stations resulted in a statistically significant fit for the regression ($p = 0.000$ for all stations). The best fit was obtained for Kordin (r-squared = 0.095), followed by Għarb (0.041), Msida (0.030) and Żejtun (0.009). Despite the statistical fit of the general model, only the Kordin station analysis resulted in MPS emissions being statistically significant ($p = 0.000$).

Hence, it can be concluded that the statistical analysis showed that the Kordin station was the most likely station to be affected by the MPS emissions, while the effect on Msida, Żejtun and Għarb was negligible. This is in agreement with the indications given by the polar plots that there could have been sources such as marine vessels which were missing from the analysis. The agreement of these two analyses would suggest that the hypothesis that the MPS is the major contributor of SO_2 across the islands did not hold true for the examined period.

4.7 Summary

This chapter discussed the results obtained during the course of this study. Sections 4.3 and 4.4 have shown that the effect of the MPS has decreased over the period analysed. The numerical analysis also revealed that there were only two occasions when the 350 $\mu g/m^3$ hourly limit of Directive 2008/50/EC was exceeded.

The R results in Section 4.5 have revealed trends relating higher SO_2 readings in the fixed station network with Northerly/North-Westerly winds. The Kordin station was consistently found to have the overall highest SO_2 readings while Għarb had the lowest. The statistical analysis of Section 4.6 was used to determine the statistical significance of MPS in relation to the readings obtained in each of the fixed monitoring stations. These results shall be elaborated on further in the next chapter which shall discuss the conclusions of this analysis, as well as the overall findings of this study.

CHAPTER 5: CONCLUSION

5.1 Conclusion

At this stage, it would be sensible to look at the important results and re-evaluate them to discuss whether a coherent representation of the facts may be obtained. This section shall highlight the most important of these facts, arriving at an overall conclusion of this study's findings.

It has been determined that the average yearly emissions from the MPS decreased from approximately 858 g/hr to 780 g/hr between 2009 and 2012; with emissions being highest in Summer and lowest in Spring. Because of this, it was expected that a corresponding decrease in the SO_2 concentration in the area would be recorded. In fact, diffusion tube data between 2004 to 2010 has shown an overall SO_2 concentration mean decrease across the islands. However, the results also indicated that there may have been significant increases in SO_2 in small localised areas. This was supported by the fact that increases in SO_2 were detected in diffusion tubes in Northern Gozo and also increases in yearly SO_2 averages in Kordin (although in the case of Kordin, this may have been distorted by data loss). The latter led to the conclusion that the effect of the MPS was still high, but became more localised to the area immediately surrounding the power station.

Although several peaking trends were witnessed in the different analyses, there were only two occasions when the 350 $\mu g/m^3$ hourly limit of Directive 2008/50/EC was exceeded, and no exceedences of the other two limits. Of all the stations, Għarb was repeatedly

shown to have lower SO_2 averages and also a lesser number of peaks. This was expected due to the Għarb station's rural background status. The only exception was the June 2008 period, when higher readings were reported. Although no explanation was found for this phenomenon, it is likely that it was merely an anomaly.

Generally, Kordin was repeatedly shown to have the highest SO_2 measurements, followed by Żejtun, Msida and finally by Għarb. Kordin, Żejtun and Msida were suggested to have patterns of SO_2 concentrations linked to daily activities such as increased power use and transportation. Interestingly, daily peaking in Kordin lagged behind that of Żejtun and Msida by a couple of hours, despite the close geographical position of Kordin and Msida. Weekly SO_2 patterns also differed in stations, with those of Kordin being fairly close to those of the MPS. This, coupled with the diffusion tube results and higher SO_2 readings, pointed to a relationship between MPS emissions and Kordin readings.

Looking at the monitoring station pollution roses, different patterns were identified. It was concluded that the NW wind direction contributed significantly to the mean SO_2 concentrations in Kordin (60%), Żejtun (50%) and Msida (30%). Msida was also found to have significant contributions from the East-West directions (32%), while Għarb did not have any significant sole contributor. The percentile roses revealed more clearly that Għarb had a number of outliers from the SE direction; whereas the percentile roses of the other stations reaffirmed the relationship between higher SO_2 and the NW direction.

Although not totally in agreement with the pollution and percentile roses, the polar plots established that all the stations had higher readings registered with N or NW winds. In the case of the Msida and Kordin stations, both polar plots indicated a source which was to the NW and not immediately close to the stations. It was suggested that this could have been caused by marine traffic off the coast of Malta. The polar plot of Żejtun indicated a similar directionality, although this direction also encompassed the MPS in the case of Żejtun. However, the fact that higher readings were almost independent of wind speed pointed to multiple SO_2 sources. In the case of Żejtun, intermediate readings were also found to originate from the SE direction, which could likewise have been caused by power generation (Delimara) and/or marine traffic. With regards to the Għarb station polar plot, unexpectedly high readings were recorded from the Northern directions. Again, marine sources were suggested, along with biogenic sources and a sewage outflow in Wied il-Mielaħ that was operational at the time.

A 3-predictor statistical analysis with SPSS determined that emissions from the MPS were statistically significant in determining the amount of SO_2 being measured in all of the monitoring stations. It should be noted that Msida and the Żejtun measurements were found to be statistically independent of wind speed. In fact, this was also corroborated by the polar plot in the case of Żejtun. In the case of Għarb and Kordin, Marsa emissions, wind speed and wind direction were all found to be statistically significant in determining SO_2 levels, but the models accounted for relatively little of the variation observed. The results indicated that there were missing variables in the models. This could have been partly the result of the lack of data on Delimara power station emissions; although

without studying other possible sources like marine vessels, a definitive conclusion may not be made. Additionally, a 2-predictor model using only readings registered with wind originating from the MPS direction showed that MPS emissions were only statistically relevant for Kordin. Hence, it can be concluded Kordin was the most likely area to be affected by MPS emissions while the effect on Msida, Żejtun and Għarb was negligible.

All of these results suggest that the *quasi*-direct relationship between SO_2 concentration and the distance from the MPS, as reported in Vella *et al.* (1996), is no longer true. A possible reason for this could be that reduction in emissions from the MPS might have increased the significance of other sources that were previously being masked by high emissions. Hence, although the results have shown that the MPS was still found to be a significant contributor of SO_2 (as proposed by the initial hypothesis of this study), other sources should now start to be monitored as well.

5.2 Further research

The findings of this study contradicted the original hypothesis and were rather surprising. At the outset, it was expected that the influence of MPS would be explicitly seen, especially by the stations in the vicinity of MPS. The polar plots have shown that there might be other source(s) contributing to the levels of SO_2 within the agglomeration. Identifying these sources would be beneficial both from a regulatory as well as an academic perspective. Particular emphasis should be placed on the identification of new

sources to the NW of the Msida and Kordin stations, as well as the source to the North of Għarb monitoring station.

In order to identify the possible sources of these peaks, the effect of the Delimara power station and marine traffic on the trends registered by the different stations needs to be investigated. It is also suggested to investigate whether the signal from both power stations has an effect on the signal registered at the stations.

There should also be an attempt to compile a model to predict annual SO_2 levels. This would require information on the long range transport of sulphur dioxide from Southern Europe as well as Northern Africa, information on shipping activity as well as traffic models (especially for diesel powered vehicles) and activities from other point sources such as industrial boilers and generators. In addition to this, detailed information on wind patterns would be required in order to identify possible effects due to wind recirculation.

With such detailed analyses, the results obtained in this study (such as the timeVariation and trendLevel plots) may be more rationally interpreted. The combination of all of these studies would thus allow a relatively complete understanding of the SO_2 presence in Malta.

APPENDIX

A.1 Monitoring station readings distribution

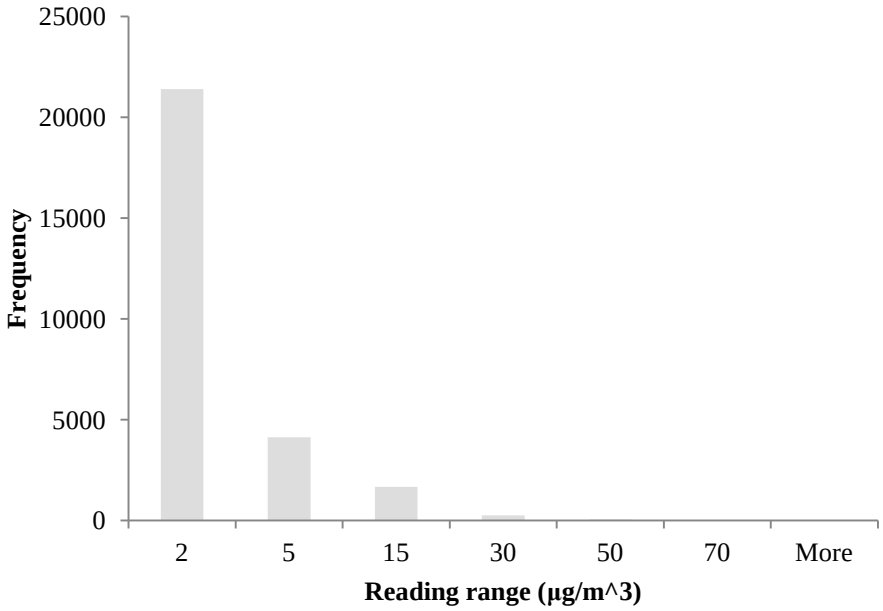

Figure A.1: Għarb monitoring station SO_2 distribution

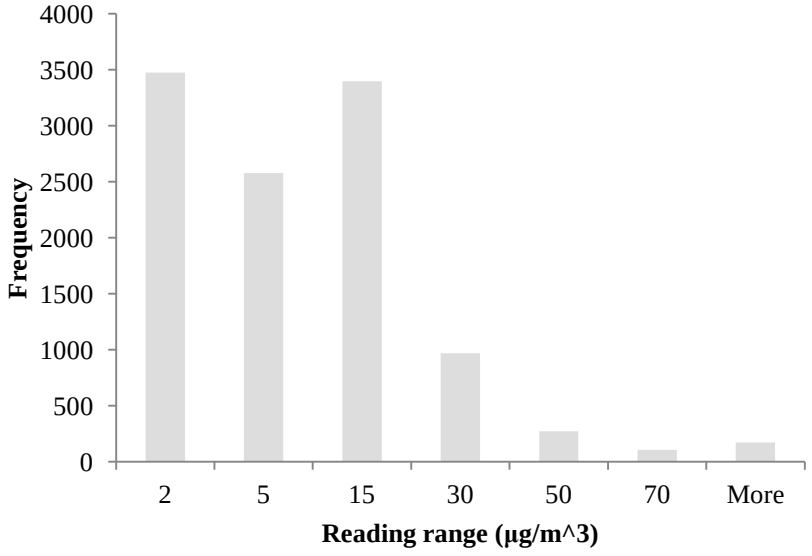

Figure A.2: Kordin monitoring station SO_2 distribution

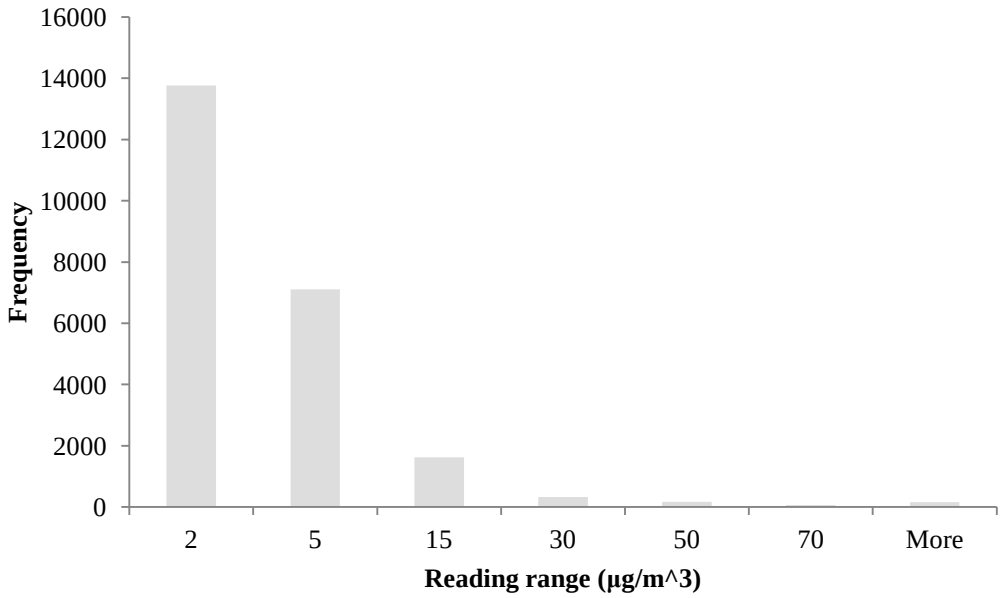

Figure A.3: Msida monitoring station SO_2 distribution

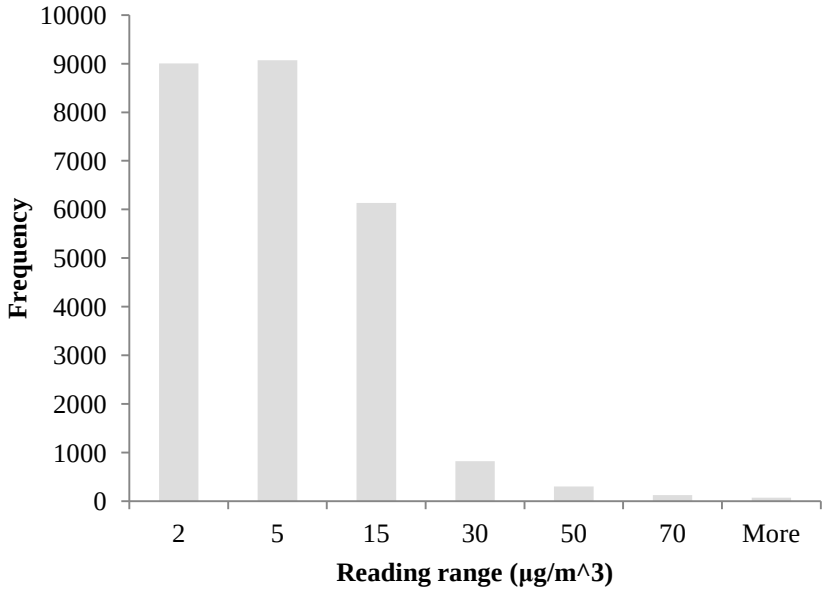

Figure A.4: Żejtun monitoring station SO_2 distribution

A.2 Marsa power station emissions distribution

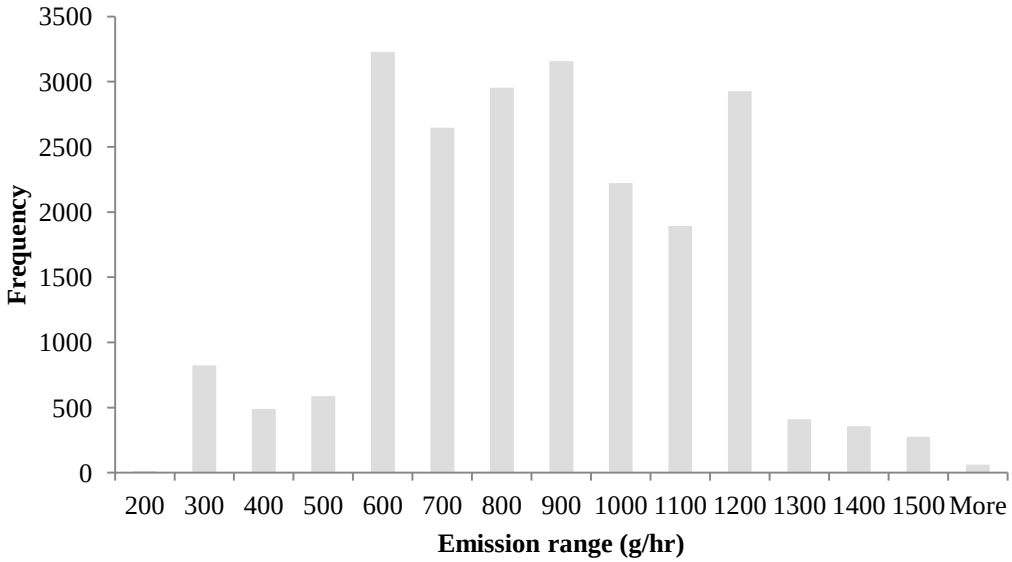

Figure A.5: MPS emissions distribution

A.3 Diffusion tube data distribution

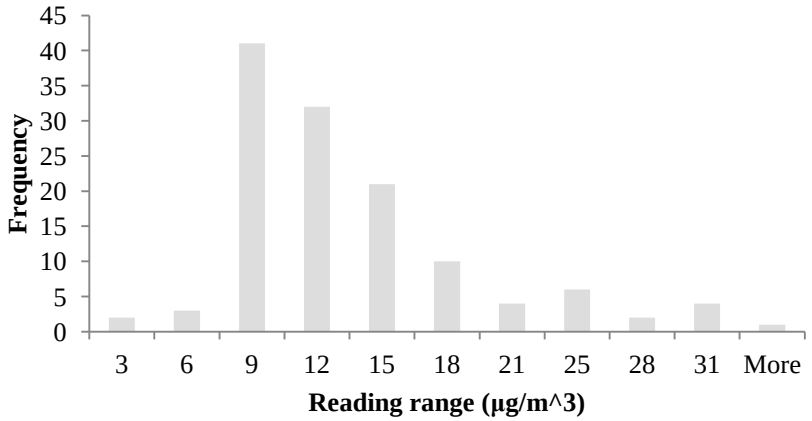

Figure A.6: 2004 diffusion tube reading distribution

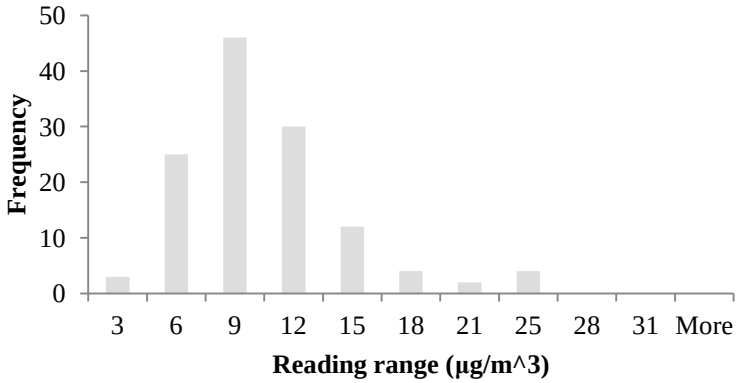

Figure A.7: 2005 diffusion tube reading distribution

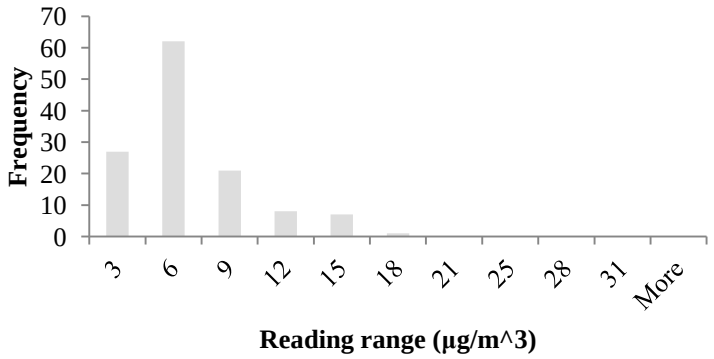

Figure A.8: 2006 diffusion tube reading distribution

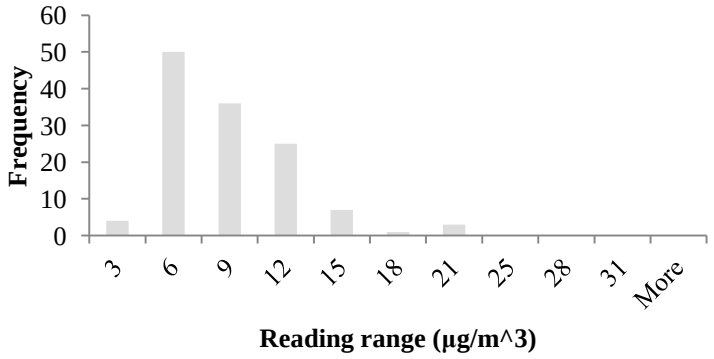

Figure A.9: 2007 diffusion tube reading distribution

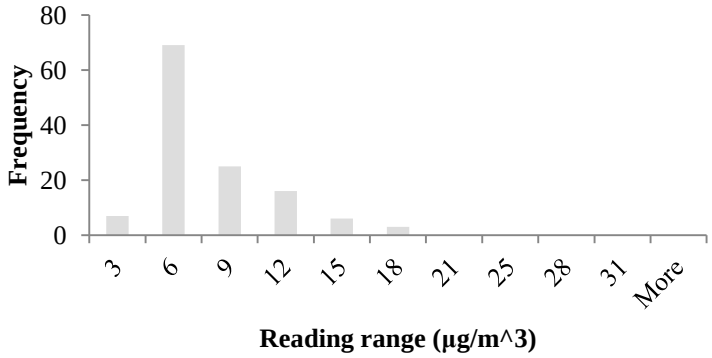

Figure A.10: 2008 diffusion tube reading distribution

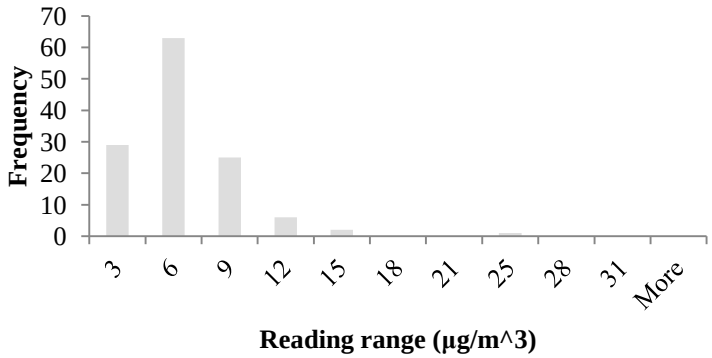

Figure A.11: 2009 diffusion tube reading distribution

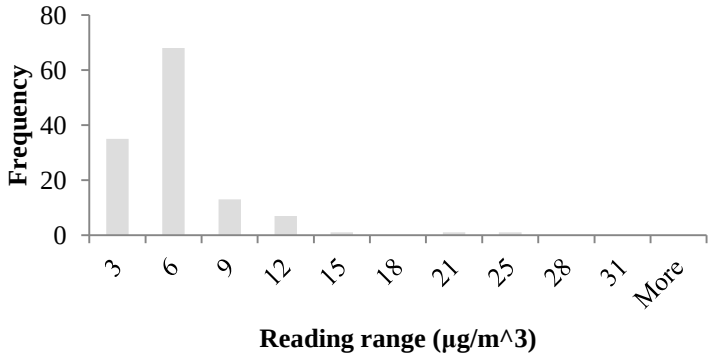

Figure A.12: 2010 diffusion tube reading distribution

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