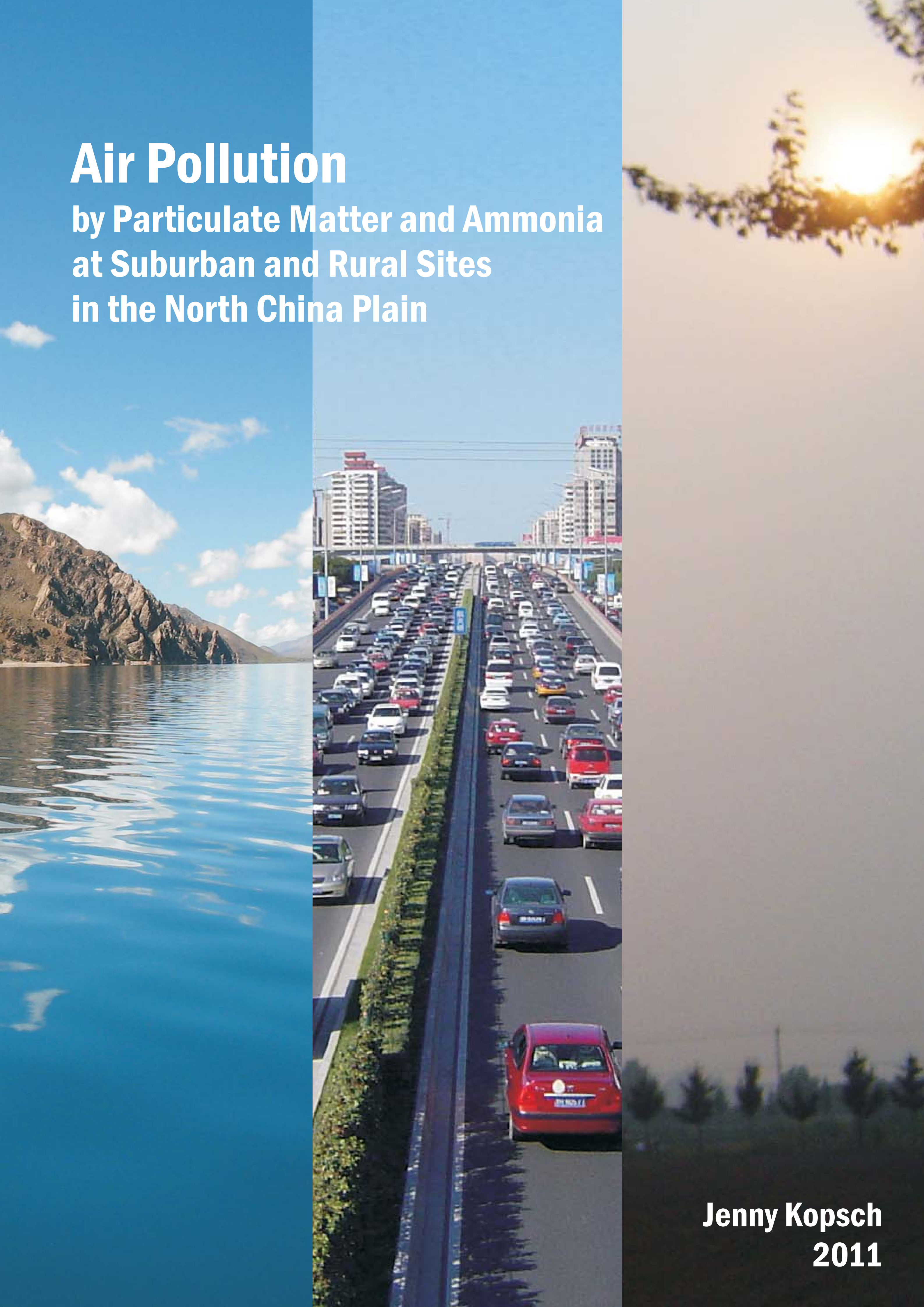
Air Pollution

by Particulate Matter and Ammonia at Suburban and Rural Sites in the North China Plain



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Air Pollution by Particulate Matter and Ammonia at Suburban and Rural Sites in the North China Plain

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1 Introduction

1.1 Preface

China is the world's most populous country and a rapidly developing nation with successful economic growth, industrialization and urbanization in recent decades. The natural conditions and limited water resources have challenged the development of agriculture in many areas of China for decades (Sternfeld, 2008). Almost two third of its territory consists of deserts and mountains 1000 m above sea level where agriculture can be practised only marginally. The last third located mostly in the east of the country harbours almost 90 % of the population. East China is characterized by intensive agriculture. This region belongs to one of the most populated and intensively used agricultural regions in the world (Taubmann, 2007) and massive pressures on natural resources have resulted from this. FAO (Food and Agriculture Organization of the United Nations) (2006) reported a large decline in cultivated land after the late 1990s due to both industrial development and urban expansion. Alarming levels of environmental pollution have been recognized in some regions, especially since the last decade, where China's economic growth has been much faster than that of most other countries (Liu & Diamond, 2008). Its environmental problems are among the most severe of any country in the world, and they are generally getting worse.

In most of China's regions, the vicious circle of poverty of the rural population and environmental problems including droughts, floods, erosion and successive loss of biodiversity can be detected (Pimentel & Dazhong, 2004). The fast growth of the economy and the intensive agricultural management in the east of China also caused air pollution, one of the most visible environmental problems in China (Wang & Mauzerall, 2006). The whole country is confronted with contamination of soil and groundwater resources and of agricultural products by e.g. industrial pollutants. Moreover, the increasing human demand for food and a shift in dietary patterns by the strongly increasing population of China has stimulated an excessive use of nitrogen (N)-containing fertilizers and the large-scale breeding of domestic livestock. It is well known that both crop and livestock production have a profound effect on the wider environment. They are the main source of water pollution by nitrates, phosphates and pesticides. They are also the major anthropogenic source of the greenhouse gases CH_4 (methane) and NO_x (oxidised nitrogen), and contribute on a massive scale to other types of air and water pollution (Sutton et al., 2009). Currently, the agricultural sector in China with its non-sustainable production also leads to land degradation, salinization, the over-extraction of water and a reduction in genetic diversity of crops and livestock - problems which jeopardize the country's future. In the middle of the 90's Smit & Yunlong (1996) stated that China's agriculture is already pushing the resource capacity to a very high degree. Ten years later, sustainability still has not sufficiently been taken into account in the development of the agricultural and industrial sectors of China (ERSEC, 2009). Economic growth, rather than environmental protection or sustainability, is still China's clear priority, as it is seen as an engine of social progress and growing wealth. China's feedback and satisfaction on non-results - no binding framework to cut emissions - after Climate Change Conference in Copenhagen in 2009 underlines its priority (China Economic Review, 2010).

In view of the dramatic degradation of China's ecological resource base and major changes of its agriculture, the Chinese government started to address environmental issues, and the importance of environmental policy and research programs has generally increased. Agricultural research in China, which is organised by government, has to face new challenges and there is a much greater appreciation now for the fact that agriculture has strong links with other sectors such as the environment. Therefore the German Research Foundation (DFG) and the Chinese Ministry of Education jointly started the first Sino-German International Research Training Group (IRTG) located at the University of Hohenheim and the China Agricultural University (CAU) Beijing in 2004. Under the title "Modeling Material Flows and Production Systems for Sustainable Resource Use in Intensified Crop Production in the North China Plain" the Research Training Group comprises 11 subprojects from various disciplines. The work presented in this study forms part of these research activities.

In the past three decades Chinese agriculture has become more and more dependent on high mineral fertilizer consumption to meet food demands. The policy-driven increased application of chemical fertilizers was a key factor in rising China's agricultural productivity, with much higher total fertilizer consumption in the economically more developed eastern coastal provinces than in the western regions. China is now both the world's leading producer and consumer of synthetic fertilizers in agriculture (Sun et al., 2008), accounting for about a quarter of the global fertilizer consumption (Gao et al., 2006). On average, nitrogen use per hectare (ha) is about three times higher than the world average. Additionally, China is the world's leading consumer of agrochemicals (FAO, 2006). The study region North China Plain (NCP) is indicative for the production and consumption of these industrial and agricultural products and representative for China's agriculture at all (Vitousek et al., 2009). Their excessive application rates and input imbalances in the NCP lead to serious environmental problems such as air, water and soil pollution and other forms of environmental damage. On the other hand, covering parts of Beijing, Hebei, Tianjin, Shandong, Henan, Anhui and Jiangsu provinces, the NCP is also indicative of the highest agricultural productivity nationwide, and therefore it is often called “China’s granary” (Böning-Zilkens, 2004). Nitrogen in its different forms plays a major role in China since it is an essential element in synthetic plant fertilizers and meets the dietary requirements of livestock and thus is of great importance in China’s struggle to maximize agricultural production. Through the intensification of the nitrogen cycle China is able to supply its population with protein-rich food, but has considerable adverse effects on the environment and human health (FAO, 2008).

The subprojects of the IRTG deal with different topics which result from unsustainable land-use patterns. The topics addressed are related to material flows, pollution analysis and cropping systems and address these at farm, regional and sectoral levels of assessment. Before the wider project aim of developing strategies to reduce N loading of agroecosystems can be achieved, it is necessary to know the amount and composition of N inputs. The thesis presented here was conducted within the subgroup “Material flows and pollution analysis”, and more specifically in subproject 1.3 entitled “The contribution of nitrogen deposition to the nitrogen budget”, and focuses on air pollution mainly by agricultural sources.

Clean air is a basic requirement for human health and well-being (WHO, 2006). Due to exceedances of critical loads the public interest and research on air pollutants such as e.g. sulphur dioxide (SO_2) has shifted to reactive nitrogen species worldwide (Gauger et al., 2008; Aneja et al., 2008; Galloway, 2005). As outlined above, agriculture is an important sector contributing to air quality problems in China. The excessive and unbalanced use of N-fertilizers in the NCP is a major environmental concern. Winter wheat – summer maize crop rotation systems with a joint nitrogen application of between 500 and 700 kg N ha^{-1} yr^{-1} for both crops are common in some parts of the NCP (Guo, 2002; Roelcke, 2005). The nitrogen use efficiency of the crop rotations in this region is often below 30 %, and considerable amounts of nitrogen are lost both by leaching into the groundwater and by emission of gaseous nitrogen species. Urea and ammonium bicarbonate are the main N fertilizers used in China and contribute more than 90 % of total N fertilizer in the NCP. These two fertilizers have great potential of ammonia (NH_3) volatilization. Besides NH_3 volatilization from N fertilizers, there are other significant sources of atmospheric pollution with reduced nitrogen compounds (NH_y). Both fertilised and manured fields as well as emissions from animal husbandry in the NCP, and particularly in the surroundings of Beijing, contribute to high loads of reduced nitrogen.

At the same time, the increasing car fleet causes traffic-related problems and increasing emissions of oxidised nitrogen. Apart from Beijing and its suburbs, other densely populated towns in the NCP have to face similar air pollution problems. In Beijing itself, the number of vehicles increased dramatically by a factor of 6 from 0.66 million in 1994 to 4 million in 2009 (China Daily, 2009) as can be seen in Figure 1.1, and both traffic and vehicle emissions of NO_x and particulate matter (PM) are expected to further increase. Besides the traffic, industrial facilities and co-generation power plants must be regarded as the most important sources of urban air pollution. The rapid growth of China's economy resulted in a high demand for energy, with main polluters often being old industrial complexes and coal-fired power plants. Energy use and air pollution have been synonymous in China for decades, especially in urban areas. During the 1990s, some megacities, such as Beijing, were constantly listed among the 10 most polluted cities in the world (He et al., 2002). According to the World Health Organization (WHO, 2009) Beijing, parallel to several other Chinese cities, still is one of the most polluted cities in the world and is not in compliance with international and even national air quality guidelines. In rural areas, air pollution is also severe because a significant number of industrial facilities that are highly dependent on coal as primary energy source are located in the countryside (Tang, 2004). China leads the world in the production and consumption of coal, with 25 % of the world's total (Liu & Diamond, 2005). During winter, coal heating is an additional emission source in North China due to the common domestic use of coal. The reliance on coal in China as the principle source of energy has resulted in air pollution dominated by sulphur dioxide, particulates, NO_x and acid rain (Fang et al., 2009; Yang et al., 2002a). Burning of biomass and agricultural waste is also common in the NCP. In summary, the combustion processes have inherent characteristics that lead to the release of both gaseous and particulate pollutants that impact air quality, human health, and climate (Gaffney & Marley, 2009).

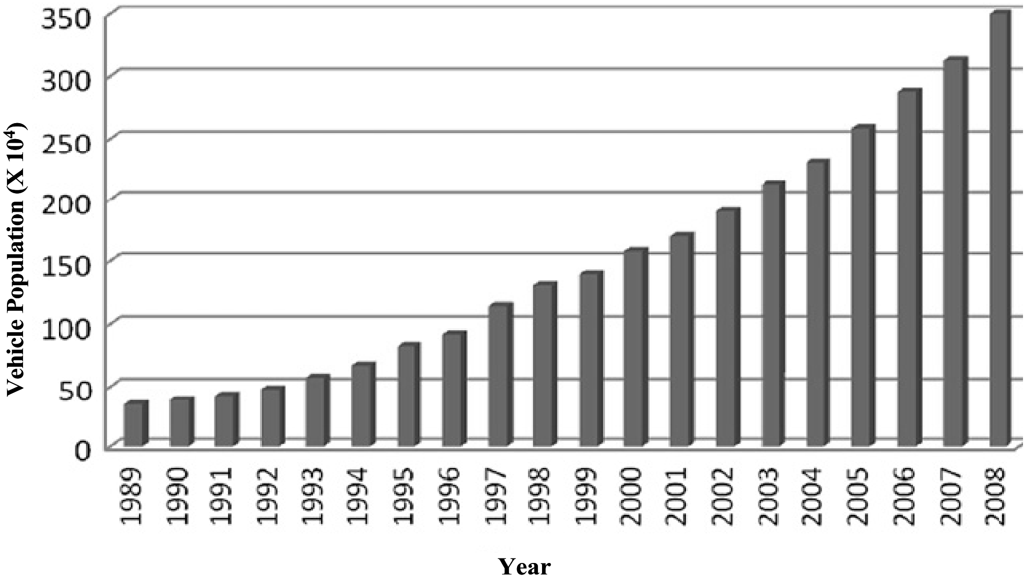

Figure 1.1: The growth of motor vehicle fleet in Beijing (Source: Guo et al., 2010).

An increasing range of adverse health effects has been linked to air pollution, especially to airborne PM (EPA, 2010a; UBA, 2009a; Hopke, 2009; WHO, 2006). Particles, the main ingredient of haze, smoke and airborne dust, also present in NCP, can lead to serious air quality problems. Concerning the impact on climate, air pollution in China cannot be regarded separately. Changes of concentrations of aerosols caused by anthropogenic emissions change the energy balance of the climate system (IPCC, 2007). NCP is one of the regions contributing much to that change. However, the Atmospheric Brown Clouds (ABC) present in Asia may have caused dimming and cooling effect at the surface in Eastern China (Ramanthan & Feng, 2009; Ramanthan et al., 2008).

All air pollution facts concerning NCP touched will be discussed in detail in the following chapters but the named factors of air pollution in general and the specific conditions in NCP with the related disturbances of the environment indicate a complex field of research. The statement from Zhang Lijun, former vice minister of China's State Environmental Protection Agency (SEPA): "In the future 15 years, the population of China will reach 1.46 billion and the Gross Domestic Product (GDP) will double, the (air) pollution load will increase by four to five times" (The New York Times, 2005), emphasises the urgent need for air pollution research. The present study aims to document air pollution in the NCP and discusses problems in air pollution control that will have to be overcome in the future.

1.2 Research objectives

Due to the variety and large number of emission sources, the NCP suffers from serious air pollution. Emissions from rural and urban areas in the NCP stem from slurry applications on fields, from animal husbandry and the growing emissions of oxidised nitrogen species from traffic exhaust and industry. All of them are expected to generate high atmospheric concentrations of reactive nitrogen species and high deposition loads (Galloway et al., 2003). The understanding of the extent and effect of the nitrogen deposition has therefore become an increasingly important subject for research.

To date very little is known about air pollution in the NCP, especially atmospheric nitrogen and its source and sink budgets. The release of NO_x from fossil fuel combustion, NH_3 from agricultural production and particulate N from a range of human activities, results in wet and dry deposition of oxidised (NO_x, NO_3^-) and reduced (NH_3, NH_4^+) nitrogen to the land surface. Excessive loads of nitrogen deposition have the potential to damage a wide range of terrestrial and aquatic ecosystems via over-fertilization, eutrophication and direct poisoning of plants and animals. Atmospheric nitrogen deposition and its variability over time and space have to be known to get a complete picture of the nitrogen balance and to close the knowledge gap for a more sustainable resource use management in the NCP. Up to now, reliable estimates of atmospheric NO_x and NH_y in the NCP are largely lacking, and a monitoring network comparable to European or U.S. standards does not yet exist. It is important to quantify their concentrations in the atmosphere in order to assess the level of exposure to pollution of both population and environment in the NCP.

The work of subproject 1.3 aims to test the following hypothesis in the context of the International Research Training Group: Atmospheric NH_y deposition in the NCP contributes substantially to the nitrogen nutrition in cropping systems.

From this two main research objectives can be defined:

i. atmospheric NH_y deposition has to be taken into account in nitrogen budgets of these systems;

ii. atmospheric NO_x deposition in the NCP is of minor importance compared to NH_y deposition, but has also to be taken into account in the overall balance.

The aim of this dissertation, which represents the initial work conducted within subproject 1.3, is to monitor air pollution and dry nitrogen deposition and its effects in the NCP. Within this work experiments were conducted to monitor dry deposition of particulates, NO_x and NH_y in the NCP. In order to study the effects of nitrogen deposition an active biomonitoring system was also examined in the NCP. We wanted to test the hypothesis if unfertilised test plants exposed in the field could use the local nitrogen deposition in order to increase biomass and nitrogen levels.

The study comprised measurements of atmospheric concentrations of fine, coarse and total suspended particulates as well as NH_3 in the NCP. These measurements have been the starting point of field observations in the NCP to understand the trends in chemically important gases and particles. Moreover, this study forms a basis for the recording of long-term trends over a wide range of temporal and spatial scales and also contributes to provide a database to test models on the composition of the current atmosphere.

Since there was no air monitoring network in the NCP at the onset of this study, one main part of the work consisted of setting up and testing of measuring devices under the special conditions in the NCP.

2 State of the Art

A wide range of air pollutants exists in the atmosphere. Particle pollution is often made up of a mixture of different components, including acids, organic chemicals, metals, and soil or dust particles. This study is focussing on reactive nitrogen species in the atmosphere with special emphasis on PM pollution. As an introduction, an overview on air pollutants in general, particulate matter and the nitrogen cycle will be provided in this chapter, followed by the description of specific nitrogen species investigated. Additionally, an introduction into the deposition process of particulates and gases will be given. Finally the specific nitrogen species and their effects on human health and plants will be described, followed by an outline of international and national air quality standards, guidelines and legally binding criteria as policy options for air quality management. Air pollution research in China will be described in further detail in a separate chapter.

2.1 Air pollutants – Principles and definitions

2.1.1 General

The atmosphere consists of a few very common gases, such as nitrogen, oxygen, and argon, and many trace gases, including carbon dioxide (CO_2), methane, and ozone (O_3). Figure 2.1 gives the approximate proportions of the main constituents in the atmosphere for dry air at earth level (Sterner, 1999). The start of fossil fuel combustion, industrial processes and intensive agriculture on a large scale in the nineteenth and twentieth century resulted in huge amounts of gases and aerosols to be emitted into the atmosphere. According to Seinfeld & Pandis (1998, p. 49) air pollution is defined “as a situation in which substances that result from anthropogenic activities are present at concentrations sufficiently high above their normal ambient levels to produce a measurable effect on humans, animals, vegetation, or [solid] materials”.

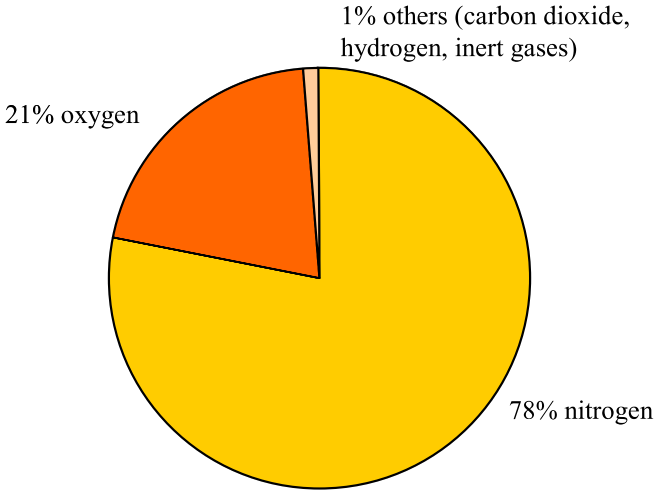

Figure 2.1: Approximate concentrations of the main air constituents in the atmosphere.

Air pollution has severe effects, which in extreme cases can act on the global scale, with increasing global warming and the depletion of the ozone layer being typical examples. On local scales, three processes can be defined in relation to air pollution:

- emission where pollutants are emitted directly at the source,
- transmission which describes the distribution and in part conversion of pollutants in the atmosphere over various distances,
- deposition, as air pollutants are depleted from the atmosphere and deposit after short or long-range transport both as solid particles and in solution. This process will be explained in detail in chapter 2.2.

Emissions can be derived from both anthropogenic and natural sources. Anthropogenic emissions chiefly include NO_x, PM, volatile organic compounds (VOC), SO_2, CO_2 and carbon monoxide (CO), dust and heavy metals (lead, cadmium), and they result from traffic exhausts, industrial processes and combustion. Natural emission sources include volcanic eruptions, windborne dust storms, sea spray, vegetation fires and the vegetation itself producing air pollutants as well.

“Air pollutants may be either emitted into the atmosphere (primary air pollutants) or formed within the atmosphere itself (secondary air pollutants)” (Harrison, 2006, p. 9). Air pollutants such as SO_2, CO, VOC, carbonaceous and non-carbonaceous particles are chiefly primary air pollutants. Their concentration is normally the highest one at the emission source. The bigger the distance to the emission source the smaller is the resulting concentration of primary air pollutants as they mix with the ambient air. Apart from changing the concentration, the emitted primary air pollutants can be converted by chemical reactions within the atmosphere into secondary air pollutants (e.g. ozone, secondary particles, or NO_x that can occur both as primary and secondary air pollutant) with new characteristics and impacts. The transport and conversion of air pollutants are affected by the height of the emission source, the overall amount of pollutant emitted, the characteristics and composition of specific air pollutants, topography and meteorological factors such as transport between atmospheric layers, solar radiation, temperature (T), relative humidity (RH) and wind. These factors are also influenced by seasonality. During winter temperature inversions are regularly forming above cities. Under these conditions, dilution and transport within the atmosphere is minimized and concentrations of primary air pollutants are sharply increasing.

In general, air pollutants in the atmosphere are depleted by various processes which result in pollutant specific exposure times in the atmosphere reaching from hours to days and weeks. Accordingly, different loads of air pollutants can be transported over only several metres up to thousands of kilometres, as will be further described in chapter 2.2 on deposition processes for the air pollutants investigated in this study.

Besides the distinction between primary and secondary air pollutants, air pollutants can be classified according to their aggregate state. Air pollutants can be gases, liquids or solids suspended in the air or in solution.

2.1.2 Particles

Particulate air pollutants comprise material in solid and liquid phase suspended in the atmosphere which is also the very same definition which is used for aerosols. According to Seinfeld & Pandis (1998, p. 97) “an aerosol particle may consist of a single continuous entity of solid and liquid matter containing many molecules held together by intermolecular forces and primarily be larger than at molecular dimensions (> 0.001 µm)”. Atmospheric particles can be either primary (emitted directly as particle such as soot particles from a chimney) or secondary aerosols (formed in the atmosphere by gas-to-particle conversion process such as nitrates) with diverse chemical compositions that are highly dependent on their source. Particles can change their size and composition by condensation or evaporation of vapour species, by coagulating with other particles, by chemical reactions, or by activation in the presence of water super saturation to become fog and cloud droplets. Particles can then be removed from the atmosphere via wet and dry deposition (see chapter 2.2), so that they often have a very short life time in the atmosphere varying from a few days to a few weeks, in comparison with the often long life times of trace gases, which can be varying from seconds to centuries. Close to the ground, dry deposition of particles is the predominant removal mechanism of particles from the atmosphere. At higher altitudes, scavenging by water droplets and subsequent wet deposition is the main removal mechanism.

Primary and secondary particles can have both natural and anthropogenic sources as shown in Table 2.1. Terrestrial dust (soil and rock debris), volcanoes, sea spray and biomass burning are natural sources of primary particles (Seinfeld & Pandis, 1998). Furthermore, pollen, spores, microorganisms and small plant and animal residues also form potential natural sources. Secondary particles from natural sources can originate from methane released from wetlands, N_2O through biological activities in soil and submersed sediments, a wide range of gases leaked from volcanoes (SO_2, H_2S, NH_3), hydrogen sulphides from oceans and nitrates from soils and water (UBA, 2005).

Anthropogenic emissions leading to primary particles can be caused by stationary sources such as fossil fuel combustion plants (power plants, heating power plants or waste combustion plants), domestic fuel combustion (gas, wood, fuel, and coal), industrial processes (e.g. metal and steel production) and landfills. Primary particles can also be caused by mobile sources such as traffic (mainly by diesel trucks and cars). Besides vehicle exhaust fumes, there is also vehicle-related material as e.g. tire abrasion and other residues on the road surface as an important source. Air, shipping and rail traffic, construction sites and agricultural operations are further mobile sources.

Anthropogenic emissions sources leading to secondary particles release reactive gases such as sulphur oxides (SO_2, SO_3), nitrogen oxides (NO, NO_2), NH_3 and NMVOCs by either release directly as reactive particle or after undergoing chemical transformation to a species that condenses as a particle into e.g. ammonium sulphate, ammonium nitrate (NH_4NO_3), an aldehyde and ketone. Secondary particles can be transported over long distances and thus lead to air pollution in regions far way from its original source. The most important anthropogenic sources for secondary particles are again stationary combustion plants (power plants, industrial plants, domestic fuel combustion as sources of SO_2, SO_3, NO, NO_2), agriculture (NH_3), petrochemistry and chemical industry in general (NMVOC) (UBA, 2005; EPA, 2010a; Harrison, 2006).

Table 2.1: Natural and anthropogenic sources of particles with regard to their size

sources		**particle size in µm**
natural sources	soil erosion (incl. dust storms as a direct result)	1 - 150
	volcanism	0.005 - 150
	sea spray	1 - 20
	natural fires	0.005 - 30
	biogenic dust (pollen, spores)	2 - 50
	biogenic dust (bacteria, virus)	0.005 - 10
anthropogenic sources	stationary combustion (heating, energy production)	0.005 – 2.5
	mobile combustion (traffic)	0.005 – 2.5
	smelting	0.1 - 30
	industrial processes (metallurgical processing)	0.005 – 100
	insecticides	2.5 - 10
	fertilizer, lime	10 - 150
	mixed debris from construction and building sites	10 - 150
	cigarette smoke	0.02 - 10

(adapted from UBA 2005; MPG, 2004)

The appearance of particles such as form, dimension and volume differs a lot and the determination of these parameters is only possible with sophisticated measurement techniques. Therefore, the measurement of the “equivalent diameter” has been used to describe the particle size. Particles with the same equivalent diameter have the same physical behaviour. Often the term aerodynamic diameter has been used, too, equivalent with the diameter of a ball with the density of about 1 g cm^{-3} having the same deposition velocity during calm or laminar air stream like the observed particle. In this study the term aerodynamic diameter is used in this context, too.

Figure 2.2 shows the typical distribution of particle surface area of an atmospheric aerosol with principal modes and particle formation. Three modes can be determined: the nuclei mode (A), the accumulation mode (B) and the third mode (C) which does not have an equivalent standardized term in the literature, but is often named “coarse mode”. After Seinfeld & Pandis (1998), the nuclei mode, extending from 0.005 to 0.1 µm diameter, is formed from condensation of hot vapours during combustion processes and from nucleation of atmospheric species to form fresh particles. Particles of this mode have a very short lifetime in atmosphere and are normally lost by coagulation with larger particles. Particles of the nuclei mode account only for a few percent of the total mass of airborne particles.

The range of the accumulation mode extends from 0.1 to about 2.5 µm diameter (Seinfeld & Pandis, 1998). As the name of this mode already suggests, particles of this size tend to accumulate further following condensation and coagulation. They have the longest atmospheric lifetime in comparison to particles of the two other modes. These particles share the biggest part of the total mass of airborne particles and usually account for most of the aerosol surface area (Seinfeld & Pandis, 1998). These particles can be emitted directly, such as in smoke from a fire, or they can form from chemical reactions of gases such as sulphur dioxide, nitrogen dioxide and some organic gases. Their sources include power plants, gasoline and diesel engines, wood combustion, high-temperature industrial processes such as smelters and steel mills, and forest fires.

The third mode, the coarse mode, begins from 2.5 µm diameter (Seinfeld & Pandis, 1998). The range of the coarse class is unclear in literature. Most authors use a scheme similar to the one shown in this study where the coarse mode reaches almost to a diameter of 100 µm (e.g. BUWAL, 2006). Particles of this mode are formed by mechanical processes such as re-suspension of terrestrial material, see spray and plant material in the atmosphere. Due to their sources, formation processes and relatively short atmospheric lifetime, particles of the coarse mode are strongly dependent on place and time. “Coarse particles can be generally divided into rural, natural crustal material such as dust and into urban particles such as road dust re-suspended by traffic (also called re-suspended dust), construction and demolition, industries; and biological sources” (EPA, 2010a).

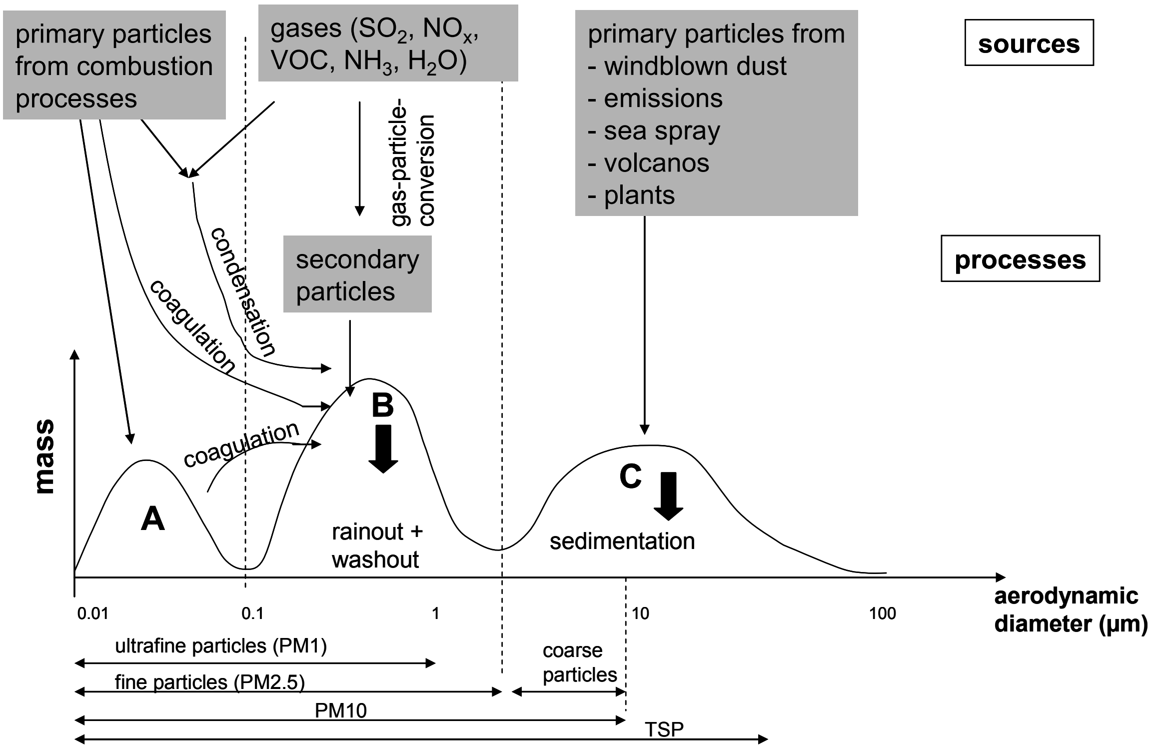

Figure 2.2: Schematic illustration of distribution of particles in relation to their sources and process (A = nucleation mode, B = accumulation mode, C = coarse mode) (adapted from BUWAL, 2006).

Due to these modes the particles have different names, respectively. Sometimes the names are not properly used in literature and do not correspond with the modes and therefore will be explained in detail. The official international name is “particulate matter”. In Germany, Austria and Switzerland the terms ‘Staub’ (Kuhlbusch et al., 2004), ‘Schwebestaub’ (Spangl et al., 2006) or ‘Schwebstaub’ (UBA, 2009b; BUWAL, 2005) are often used instead to describe particulate matter. There is no uniform use of those terms in all German-speaking countries at all. The abbreviation for particulate matter used in these European countries is nonetheless conforming to the international one: PM.

In general, there is a distinction between ultra fine, fine, coarse and total suspended particulate matter. Ultra fine particles have an aerodynamic diameter less than 0.1 µm (PM1). A subset of ultra fine particles with diameters between about 0.01 and 0.1 µm are named Aitken-mode particles; freshly formed particles with diameters below about 0.01 µm are named nucleation-mode particles (EPA, 2005).

Particles with a diameter less than 2.5 µm (PM2.5) are defined as fine particles and those greater than 2.5 µm and less than 10 µm are defined as coarse particles (EPA, 2010b; WHO, 2006; EC, 2008). The definition for coarse particles does not correspond with the definition of the coarse mode described before. Total suspended particulate matter (TSP) comprises all particles which are suspended in the atmosphere. The upper limit of the aerodynamic diameter for TSP is not clearly defined as described further.

The names and definitions for particles used in German language are sometimes misleading in comparison with English ones. The international definition for ultra fine particles is the same in German-speaking countries (ultrafeine Partikel). But the usage of ‘Feinstaub’ or ‘Feinschwebstaub’ (fine particles) in German-speaking countries comprises not only particles less than 2.5 µm but also particles up to a diameter of 10 µm (PM10) diameter (UBA, 2009b; BUWAL, 2005; Spangl et al., 2006). TSP (in Germany: Gesamtschwebstaub; in Austria: Gesamtschwebestaub) has no clear defined upper limit in English-speaking countries, but often refers to particles with a diameter of less than 50 µm, while at times this boundary is extended to 100 µm (Harrison, 2006). In Europe there are also differences. Switzerland has a clear limit and defines all particles with a diameter less than 57 µm as TSP (BUWAL, 2006), similar to Germany where the diameter boundary is set to 60 µm (UBA, 2009b). The term “suspended particulate matter (SPM)” (Schwebstaub) used in ambient air measuring technology in Germany comprises only those particles which are largely homogeneously suspended in the ambient air up to an aerodynamic diameter of around 30 µm (VDI, 1999). German engineers argue that particles having an aerodynamic diameter > 30 µm are generally, in the statistical sense, no longer homogeneously distributed in the ambient air. Nonetheless, the German term TSP comprises both homogeneously and non-homogeneously particles suspended in the ambient air. EPA (2005) defines TSP as those particles measured by high volume samplers used within its monitoring network which have cut points of aerodynamic diameters that vary between 25 and 40 µm depending on wind speed (WS) and direction.

The study presented here forms part of an international project with English as project language. Therefore, English names for particles will be used. Due to the fact that German measuring devices have been used in this study detailed information on cut points of impactors and thus the size of collected particles will nonetheless be given in chapter 3 of the Material and Methods chapter.

2.1.3 Reactive Nitrogen

Nitrogen is required by all organisms and essential for life. The primary source of this nitrogen is the atmosphere. The atmosphere contains 78 % nitrogen which therefore has the greatest total abundance of all atmospheric gases (see chapter 2.1.1). Nonetheless, almost 99 % of the nitrogen in the atmosphere (di-nitrogen=N_2) is chemically very stable and non-reactive (Galloway et al., 2003). “Before gaseous di-nitrogen molecules can be used by organisms, the triple bonds of non-reactive N_2 molecules must be broken down" (Cowling et al., 2002, p. 2). Single atoms are an example of reactive forms of nitrogen (Nr), and can bond with other elements – chiefly oxygen, carbon, or hydrogen (Cowling et al., 2002). In summary, Nr includes all biologically active, photo-chemically reactive and other N compounds in the atmosphere and biosphere of the Earth, including: i) inorganic reduced forms of N (e.g., NH_3, NH_4^+), ii) inorganic oxidized forms of N (e.g., NO_x, HNO_3, N_2O, NO_3^-, NO_2^-), and iii) organic compounds (e.g., urea, amino acids, amines, proteins, nucleic acids, etc.) (Galloway et al., 2003; Cowling et al., 1998).

Breaking the triple bonds between gaseous di-nitrogen atoms requires a substantial energy input. "Natural oxidation of di-nitrogen occurs in such high-temperature natural processes as lightning, volcanic eruptions, and wild fires" (Cowling et al., 2002, p. 2). The resulting nitrogen oxides are ultimately deposited on the Earth's surface as biologically available nitrates. The other natural process of Nr creation occurs through biological nitrogen fixation which was the dominant reactive nitrogen source for the terrestrial biosphere before introduction of synthetic fertilizer production and "green revolution" of agriculture in the 1960's (Figure 2.3). Up to that time, "the rate of Nr creation was less than the demand in many terrestrial and aquatic ecosystems. The remarkable diversity among plants, animals, and microorganisms found in nature is believed to be partly the result of intense competition among life forms – many of which evolved under N-limited conditions" (Cowling et al., 2002, p. 2). Both processes the natural oxidation and the biological N fixation were in equilibrium and the natural N-cycle was closed.

Recent global changes in the N-cycle

Reactive nitrogen in the environmental reservoirs has increased dramatically since the beginning of industrialization in 1860 (Figure 2.3) (Galloway, 2004). Since that time the increase of fossil fuel combustion processes have resulted in the increasing conversion of atmospheric N_2 into NO_x. Additionally the introduction of the Haber-Bosch process after 1945 as a commercially available method for converting N_2 into NH_3 was the starting point for the global anthropogenic fertilizer production. "Without the availability of [anthropogenic] N fertilizer…the enormous increase in food production over the past century, which in turn has sustained the increase in the human population, would not have been possible" (Gruber & Galloway, 2008, p. 293). Actually, around 100 million tons of N_2 is being converted into NH_3 for agricultural fertilizers every year (Max Planck Forschung, 2004). Both Nr sources together with widespread planting of nitrogen-fixing legumes are the largest Nr creation sources globally (UBA, 2009a). Worldwide Nr creation increased from ~15 Tg N in 1860 to 187 Tg yr^{-1} in 2005 (Galloway et al., 2008). That means Nr is accumulating in the environment because its creation rates are greater than the rates of removal through de-nitrification and biological N fixation to non-reactive N_2. Figure 2.4 illustrates the whole Nr cascade including atmospheric, terrestrial and aquatic components of the biosphere that affect the environment. However, the dominant Nr distribution process globally is the atmospheric transport and subsequent deposition (Galloway et al., 2008).

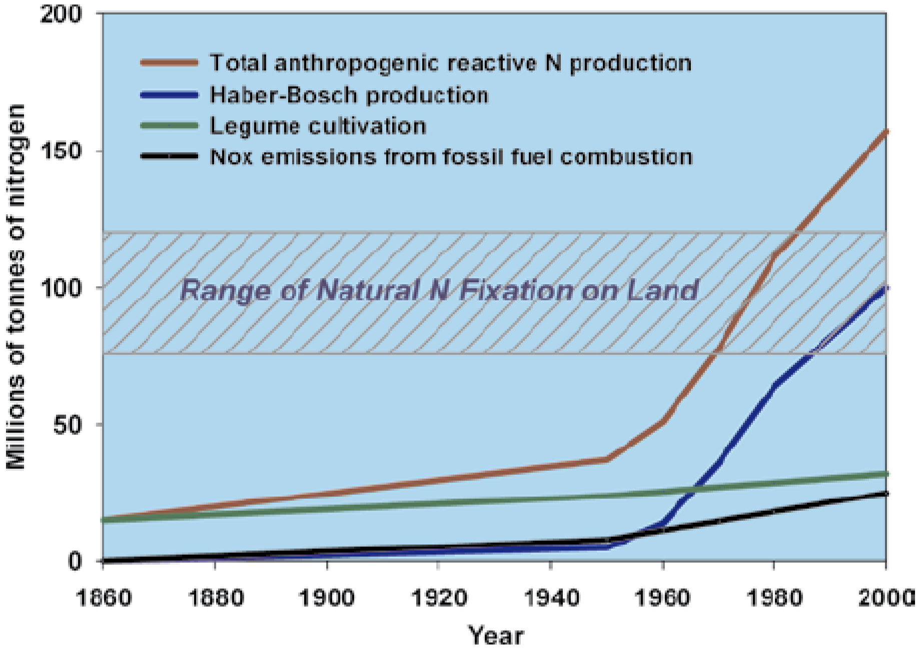

Figure 2.3: Historical trends of Nr formed annually by human activity, including cultivation of N-fixing legume crops, the Haber-Bosch process of synthetic production (primarily to manufacture N fertilizers), and emissions of NO_x from combustion of fossil fuels. For comparison, also shown is the “natural range” of N fixation (about 100 million tonnes of N per year) that occurs in native terrestrial ecosystems, primarily by bacteria in symbiotic associations with plants (Source: UNEP, 2007; based on data in Galloway et al., 2004 and Smil, 2001).

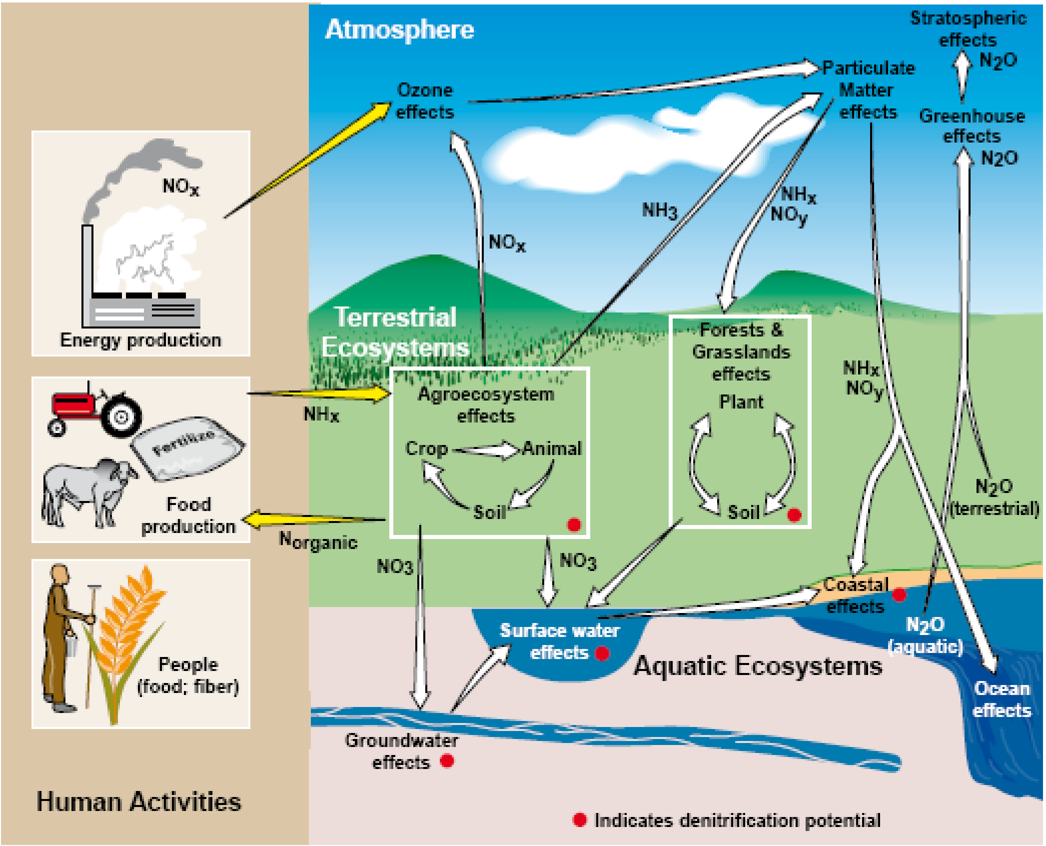

Figure 2.4: Illustration of how Nr emanating from energy and food production cycles among atmospheric, terrestrial and aquatic components of the biosphere affects environmental quality in each location. Red dots indicate locations where denitrifying bacteria may convert nitrogen back to unreactive NO_2 (Source: Van der Hoek et al., 1998).

Referring to the deposition studies in other projects in the study area both Nr-forms in the atmosphere, gases and particles, were of interest. In general, gaseous Nr species are NH_3, NH_2R, NO, NO_2, N_2O_5, HNO_2, HNO_3 and $C_2H_3NO_5$. Particulate Nr species occurring in the atmosphere are NO_3^- and NH_4^+ (salts) as well as NO_2^-, NO_3^- and NH_4^+ (liquid) (Fangmeier, 2007; Dämmgen, 2005a).

In this study measurements of particulate Nr species as well as NO_x and NH_3 were conducted in the NCP, and therefore these specific nitrogen compounds will be explained further in the following chapters.

NO_x

The sum of NO and NO_2 is known as NO_x ($NO_x = NO + NO_2$). Although NO and NO_2 have quite different physical properties, chemical affinities and environmental impacts, they are often lumped together (Colls, 2002). NO_x contributes towards Nr in the atmosphere mainly through air emissions and combustion of fossil fuels or biomass (Galloway et al., 2003).

NO is formed in two ways: The thermally formed NO is a result from the reaction between nitrogen and oxygen in the air at high temperature (> 2000 °C). Fuel NO is formed when nitrogen in the fuel is oxidised in fuel burning. Typically, fuel nitrogen contents are 0.5 – 1.5 % in oil and coal (Colls, 2002). Combustion processes always emit a mixture of NO_2 and NO, but between 90 and over 99 % of combustion NO_x release is in the form of NO. In power stations, the temperature is too low to produce thermal NO and most of the NO_x originates from the coal itself (Widory, 2007).

In the atmosphere, NO is quickly converted into the more toxic NO_2; "the pollutant of far greater concern in relation to human health" (Harrison, 2006, p. 25). This oxidation through O_2 is less important and not significant during the combustion process. Although most of the direct emissions will be as NO, the source strengths are given in the literature as NO_2 equivalent, since the entire NO is potentially available for oxidation to NO_2.

The conversion of NO into NO_2 is strongly facilitated through available ozone which is present in the atmosphere originating from a range of sources, including atmospheric transport from the stratosphere. "There is also a pathway by which the chemical processes involving ozone and NO_x can be reversed, with nitrogen dioxide breaking down as a result of absorption of sunlight to form nitric oxide (NO) and an oxygen radical (O), which reacts with an oxygen molecule (O_2) to re-form ozone (O_3). The three reactions are as follows:

1. $NO + O_3 \rightarrow NO_2 + O_2$
2. $NO_2 + h\upsilon$ (sunlight) $\rightarrow NO + O$
3. $O + O_2 \rightarrow O_3$" (Harrison, 2006, p. 25)

Reaction 2 depends on sunshine and becomes ineffective at night. Since each of these reactions is relatively fast, an equilibrium (the photostationary state), containing amounts of all three components, is rapidly established (Harrison, 2006). Nonetheless, after Colls (2002) this equilibrium can be disturbed in urban areas, near to NO sources, where O_3 becomes depleted and the NO concentration is higher. In rural areas, away from NO sources, the NO_2 concentration is often higher than that of NO if there is sufficient ozone present which converts all NO to NO_2 (reaction 1). The equilibrium can also be disturbed by special atmospheric conditions. The extent of mixture of NO and O_3 is important in this respect. Moreover, in case of inversion which usually occurs during winter and at night there is often not sufficient ozone to complete the conversion (Harrison, 2006).

In general, NO_x has a short residence time in the lower atmosphere of only about a day (Colls, 2002). The principal sink for NO_x is oxidation to nitric acid HNO_3 which is the major oxidation product of NO_x in the atmosphere. HNO_3 "is predominantly formed during the daytime via the homogeneous gasphase reaction of NO_2+OH or via heterogeneous chemistry that involves the hydrolysis of dinitrogen-pentaoxide (N_2O_5) on the aerosol surface at nighttime" (Pathak et al., 2009, p. 1711). Nitric acid is highly soluble in water and can therefore be easily removed from the atmosphere with precipitation. The conversion from NO_x to HNO_3 taking place in the gas phase is not significantly influenced by NH_3 levels (Fangmeier et al., 1994). In the presence of NH_3, HNO_3 can be converted into an ammonium nitrate aerosol (NH_4NO_3), a secondary particulate matter. This formation process is also reversible:

4. HNO_3 (nitric acid) + NH_3 (ammonia) ↔ NH_4NO_3 (ammonium nitrate)

Ammonium nitrate can dissociate back to nitric acid and ammonia, a process favoured by high temperature and low relative humidity as described by Harrison (2006, p. 28). After Pathak et al. (2009, p. 1711) generally, ammonium nitrate is formed in areas with high NH_3 and HNO_3 concentrations and low temperatures. Due to both formation pathways important diurnal and seasonal fluctuations in the amounts of ammonium nitrate in the air occur. Nonetheless "the neutralization of acidic sulphate by ammonia is favoured over the formation of ammonium nitrate via a homogeneous gas phase reaction between ammonia and nitric acid. Therefore, ammonium nitrate in PM is typically associated with significantly neutralized or ammonium-rich sulphate" (Pathak et al., 2009, p. 1711).

Overall, the newly generated pollutants are an important source of organic, nitrate and sulphate particles currently measured as PM10 or PM2.5. The contributions of various pathways of nitrate formation to mainly secondary PM mass are less well known compared to the formation of sulphate, which is strongly influenced by cloud/fog processes. "The production of sulphate and nitrate and their resulting contributions to PM2.5 mass depend on such factors as the emission mix of the precursors (SO_2, NH_3, NO_x), the levels of oxidants in both the gas and aqueous phases, the characteristics of pre-existing aerosols,… and meteorological conditions" (Pathak et al., 2009, p. 1712).

While NO_x is emitted from a wide variety of sources, the top three source categories of NO_x emissions are on-road mobile sources, electricity generating units, and non-road mobile sources. "On a global scale, emissions of nitrogen oxides from natural sources far outweigh those generated by human activity" (Forastiere et al., 2006, p. 331). After Sivertsen (2006, p. 47) high nitrogen dioxide levels, combined with ultra fine particles and other oxidants, have become one of the major air pollution problems in urban areas all over the world. Together with VOC, increased concentrations of NO_x can lead to increased concentrations of ozone and thus enhance the greenhouse potential of the atmosphere. Furthermore NO_x are one of the main components of the mixture of pollutants classically referred to as “photochemical smog” as described by Sivertsen (2006, p. 47). NO_2 absorbs visible solar radiation and contributes to impaired atmospheric visibility as well as absorbing visible radiation and thus potentially playing a direct role in global climate change.

Furthermore NO_x is also an agricultural air pollutant since agricultural operations such as tillage, burning, application of manure and fertilizers, and animal feeding operations are all potential sources of NO_x and PM (Aneja et al., 2008).

Ammonia (NH_3)

“The least known part of the nitrogen cycle is the reduced nitrogen form” (Erisman et al., 2007, p. 141). The largest uncertainties in emissions rates, from all sources, on all scales exist for the reduced nitrogen form gaseous ammonia (Galloway et al., 2008). “NH_3 is the most important alkaline component in the atmosphere” (Schjørring, 1997, p. 3). It reacts readily with acidic substances such as sulphuric acid (H_2SO_4), nitric acid (HNO_3), nitrous acid (HNO_2), or hydrochloric acid (HCl) to form ammonium salts that occur predominantly in the fine particles with a diameter less than 2.5 µm (Finlayson-Pitts & Pitts, 1999; Krupa, 2004). A small amount of NH_3 (approximately 1 %) reacts with hydroxyl (OH) radicals to form $NH_2 + H_2O$ which can subsequently be oxidized to NO by HNO_3 (Galbally & Roy, 1983; Krupa, 2004). Both the particulate ammonium and the gaseous ammonia are the major forms of reduced nitrogen in the atmosphere.

The transport of NH_3 in the atmosphere is influenced by the neutralization reactions with sulphuric and nitric acid, and the fine particulate NH_4^+ salts formed have a longer atmospheric residence time than the precursor species (Schjørring, 1997). Fangmeier et al. (1994) summarizes that this conversion is the most effective mechanism in removing gaseous NH_3 from the atmosphere with estimated conversion rates from gaseous NH_3 to particulate NH_4^+ of 10^{-3} s^{-1} to 5×10^{-5} s^{-1}. “The rate of conversion between gas to particle… primarily controls the spatial distribution of a specific NH_3 source’s contribution to atmospheric deposition” (Phillips et al., 2004, p. 3470).

NH_3 is quantitatively the largest emission from agricultural operations (Aneja et al., 2008). Table 2.2 summarizes examples of estimates for global NH_3 emissions during the 90’s. On a global basis, current estimates underline that agriculture dominates NH_3 emission to the atmosphere (Sutton et al., 2008). Studies in Europe name NH_3 as the most important component, with more than 90 % being determined by agricultural emissions (Erisman et al., 2007). NH_3 primary sources to the atmosphere are "waste products of domesticated livestock (including hogs, cattle, poultry, and sheep) and fertilizer applications to croplands and pastures… with smaller contributions from industrial and vehicular sources…" (Edgerton et al., 2007, p. 3340). Especially intensive livestock farming leads to large point sources of NH_3 emissions (Cape et al., 2008). "Biomass burning is also known to be a source of NH_3 and NH_4^+... although the overall contribution of this source to NH_3 emission budgets is poorly understood" (Edgerton et al., 2007, p. 3340).

As described by Loubet et al. (2009, p. 206) NH_3 can also be emitted directly by plants which can act as both sinks and sources for NH_3 depending on their nitrogen nutrition status and the atmospheric NH_3 concentration. That bi-directional transport shown by ammonia can be expressed in terms of an internal leaf concentration of ammonia (intercellular NH_3) which is in a dynamic equilibrium with the ambient air concentration, often referred to as compensation point. Most important for the NH_3 exchange between atmosphere and plant is the concentration gradient between atmosphere and intercellular NH_3: if ambient air concentrations are greater than the compensation point, then deposition occurs, but if the compensation point is greater than the ambient air concentration, then the surface acts as a source rather than a sink and NH_3 is emitted by plants (Fangmeier & Jäger, 2001). Agro-ecosystems intensively fertilized with N may in this regard act as a source for NH_3 rather than as a sink (Krupa, 2003). Moreover, fertilized fields can first act as an emission source, but again, when the ambient concentration increases because of nearby sources, this might be reversed (Erisman et al., 2008). The atmosphere–biosphere exchange rate in source areas is therefore largely driven by the compensation point. In general, the biosphere-atmosphere exchange of ammonia is a topic of its own because it is a spatially and temporally very variable process which has not been fully understood yet. Therefore, current research activities are addressing this topic especially via the modelling of emission and deposition fluxes taking place at the same time. Experiments are set up within e.g. the Integrated EU project NitroEurope that focuses on this topic (Erisman et al., 2008).

Table 2.2: Global atmospheric sources of ammonia

Source	Ammonia Emissions (10^6 ton N year^{-1})	%
Dairy cattle	4.3	8
Non-dairy cattle	8.6	16
Buffaloes	1.2	2
Pigs	3.4	6
Poultry	1.9	4
Sheep/goats	1.5	3
Other animals	0.7	1
Subtotal domestic animals	*21.6*	*40*
Fertilizers	9.0	17
Agricultural crops	3.6	7
Biomass burning	4.1	8
Seas	8.2	15
Other sources	7.2	13
Total	**53.7**	**100**

(adapted from Erisman et al., 2007; data from Asman et al., 1998; Bouwman et al., 1997)

2.2 Dry Deposition

Deposition comprises all processes by which particles and gases are transported from the atmosphere onto surfaces of soil, water, plants, animals and humans. Dry and wet deposition is defined “as the ultimate paths by which trace gases and particles are removed from the atmosphere” (Seinfeld & Pandis, 1998, p. 958). According to Gravenhorst et al. (2000) dry deposition is defined as the transport to the Earth’s surface without water as a transport medium. Wet deposition is the transport to the Earth’s surface in aqueous form such as rain, snow, hail, and fog. Both processes occur naturally and are combined as total deposition (Schmitt et al., 2005). The process of wet deposition will not be explained in more detail here, as this study focussed on the measurement of dry deposition. The underlying processes will be described further now.

Some authors divide the transport process of dry deposition into (adjusted after e.g. Hainsch, 2004; Krupa, 2003; Seinfeld & Pandis, 1998):

- transport onto Earths’ surface by Brownian motion (for particles; analogous to the molecular diffusion of gases)
- inertial separation (impaction)

- transport onto Earth's surface by gravitational settling (sedimentation)

Most authors simply define dry deposition as "the transport of [any] gaseous and particulate species from the atmosphere onto surfaces in the absence of precipitation" (Seinfeld & Pandis, 1998, p. 959), including sedimentation and impaction. This definition has been used in the following study, too.

The most important factors that govern the dry deposition are (according to Gravenhorst et al., 2000; Seinfeld & Pandis, 1998):

- characteristics of the depositing species (for gases: solubility and chemical reactivity; for particles: size, density and shape).
- physical and chemical characteristics of the boundary layer in the atmosphere (e.g. level of turbulence in the atmosphere, especially in the layer nearest the ground).
- physical, chemical and biological characteristics of the receptor surface itself (non-reactive surfaces such as e.g. street pavement; natural surfaces such as vegetation, soil, water, and humans).

After Jacobsen (2005, p. 665) a deposited pollutant may be re-suspended into the air when wind or an eddy blows over a surface and lifts the pollutant. According to Seinfeld & Pandis (1998, p. 959), the final step of the dry deposition process is actual uptake of the vapour molecules or particles by the surface. Gaseous species may be absorbed into the surface; particles simply adhere. The rate at which a molecule is deposited to the earth's surface, including oceans, is called deposition flux. After Heard (2006, p. 45) the vertical flux is the average over time and area of the product of the vertical velocity and the mixing ratio of the species. It can be determined e.g. via the rate of which plants release a gas into the atmosphere or take up a gas through stomatal or surface uptake. Fluxes of reactive nitrogen species are usually determined by a combination of concentration measurements and micrometeorological modelling (Dämmgen, 2005b).

"While the wet deposition of nitrogen is relatively straightforward to measure, it is much more difficult to determine the dry deposition of nitrogen aerosols and gases, because this measurement greatly depends on the properties and the structure of the receptor surface" (Schmitt et al., 2005, p. 1079). Moreover, the degree of difficulty is mainly due to the dry deposition velocity (V_d) which is "…highly variable depending, among others factors, on daytime-nighttimes micrometeorological conditions such as wind characteristics, radiation, temperature, humidity, pH of the receptor and roughness of the surface…" (Krupa, 2003, p. 183). Dry deposition velocities are generally parameterized as the inverse sum of a series of resistances such as aerodynamic resistance, resistance to molecular diffusion or to surface interactions, canopy resistance or stomata, mesophyll, and cuticle resistance (Jacobsen, 2005). Deposition models derived from these resistances have been developed to simulate and estimate dry deposition. Most insights into the spatial distribution of nitrogen deposition result from modelling studies (Verhagen & Diggelen, 2006).

For particles, the factor most strongly influencing the deposition velocity is the particle size. The difference from the V_d of gases is that particles are heavier than gases and because of their weight they tend to stay on a surface once they deposit, especially in the absence of strong winds or turbulences causing re-suspension (Jacobsen, 2005). Fine particles have low deposition velocities and thus prolonged atmospheric residence times due to their transport onto surfaces by Brownian motion (Krupa, 2003). Figure 2.5 illustrates residence times of particles in relation to their size. In general, fine particles such as ammonium sulphate or ammonium nitrate tend to have long atmospheric residence lifetimes ranging from ~ 1 to 15 days due to the decrease in dry deposition velocity (Aneja et al., 2001) and therefore may be transported and deposited at great distances downwind from the source. In case of an atmospheric residence time of 6 days and a wind velocity of 5 m s^{-1} these ammonium salts can even be transported over distances of about 2500 km (Irwin & Williams, 1988). "…Very large particles have a short atmospheric existence, tending to fall out rapidly through gravity and wind-driven impaction processes. …[Therefore, only] few particles in the atmosphere [are] exceeding 20 µm in diameter, except in areas very close to sources of emission" (Harrison, 2006, p. 11). In general, the size-dependence of deposition rates and the atmospheric life time of particles are still critical subjects requiring further investigation as Balestrini et al. (2007, p. 746) stated.

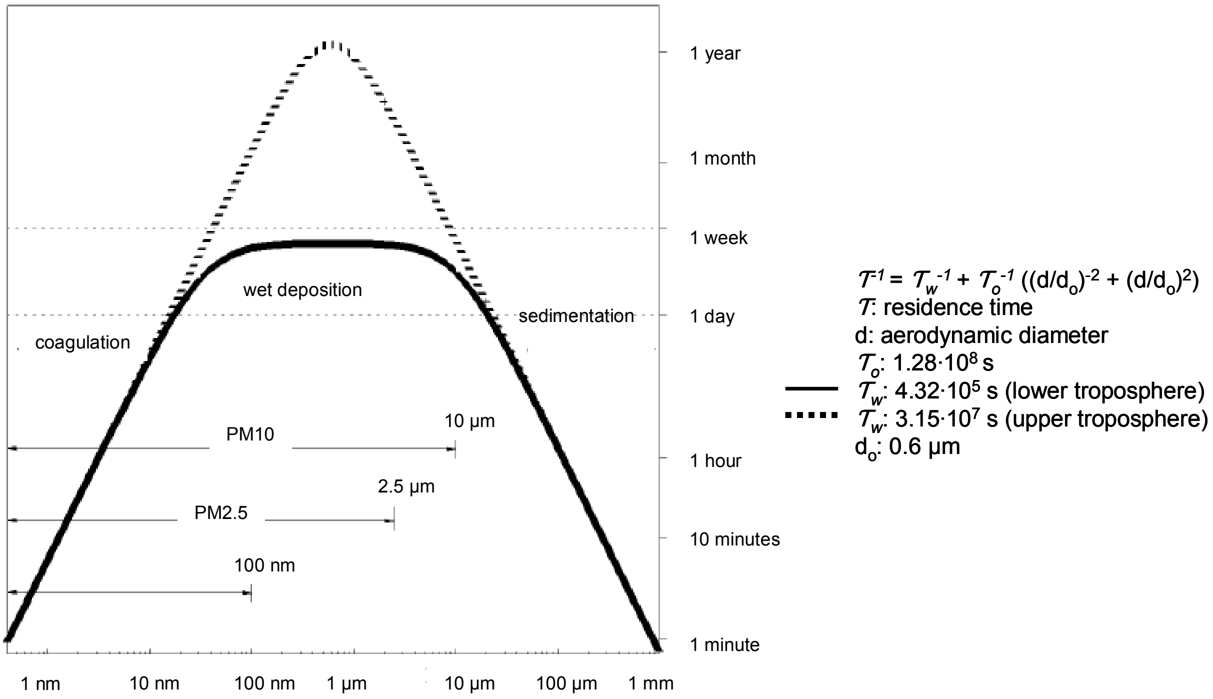

Figure 2.5: Residence time of particles in the troposphere (adapted from UBA, 2002).

For ammonia the dry deposition is the most important removal process from the atmosphere (Van Pul et al., 2006). Since NH_3 is able to stick to almost any surface, its dry deposition is only limited by the transportation rate to the surface (Asman, 1998; Van Pul et al., 2006). After Krupa (2003) values of V_d for NH_3 are ranging from 0.3 to 3.0 cm s^{-1}. There are several pathways for dry deposition of NH_3. The NH_3 is either deposited by stomatal absorption and non-stomatal adsorption to canopy surfaces (e.g. Schjørring, 1997), deposited as particulate ammonium essentially by Brownian diffusion or transformed by chemical reactions with other gases or aerosols (e.g. Nemitz et al., 2004). Loubet et al. (2006, p. 2) summarizes that the large variability of NH_3 deposition near sources is known to depend critically on the canopy structure surrounding the source (roughness, side fluxes), the NH_3 emissions from the canopy, the litter, or from the soil as well as the non-stomatal NH_3 fluxes. The uptake of ammonia by plants occurs mainly through the stomata. Other pathways are the absorption of NH_3 to dew on plants (Moumen et al., 2004) or the absorption of NH_3 to the thin water film on a leaf's epidermis (Nemitz et al., 2004). Similar to NH_3, the uptake of NO_2 by plants also occurs mainly through the stomata. The low reactivity and water solubility imply a low V_d and thus low levels of deposition in general (Dämmgen et al., 2005c).

Normally, high concentrations of NH_3 are found close to surface and near to emission sources whereas a strong decrease in concentrations with increasing distance from the sources has been reported in several studies (e.g. Fowler et al., 1998; Pitcairn et al., 1998; Aneja et al., 2001).

Phillips et al. (2004) reported that a considerable fraction of NH_3 (20–40 %) can deposit near its source resulting in a short lifetime (less than 1 to 5 days), low source height, and relatively high dry deposition velocity (e.g. Asman et al., 1998; Aneja et al., 2001). "Consequently, NH_3 concentrations depend on near surface winds…, turbulences, atmospheric stability, surface roughness and other properties, as well as on the spatial distribution of sources" (Phillips et al., 2004, p. 3470).

As described in chapter 2.1.3 "the exchange of ammonia is basically induced by differences in concentration between the atmosphere and the surface. The actual exchange flux depends on the sign and magnitude of the concentration difference, as well as on the efficiency of all mechanisms involved in the transport and transfer.[…] Quantifying the ammonia deposition has been the subject of many studies over the last two decades" (Wichink Kruit et al., 2007, p. 1276). Especially the quantification of the exchange of ammonia above fertilized (e.g. Dämmgen et al., 2005d) and unfertilized (e.g. Wichink Kruit et al., 2007) agricultural areas is important in terms of obtaining a correct mass balance of ammonia over a regional scale.

2.3 Effects on human health and plants

Atmospheric reactive nitrogen returned to the surface by deposition processes can cause adverse effects on human health and the environment. As Gruber & Galloway (2008, p. 293) stated the negative consequences of nitrogen additions are substantial and manifold, ranging from eutrophication of terrestrial and aquatic ecosystems to global acidification and stratospheric ozone loss. Galloway et al. (2003) comprehensively described the particular fact that anthropogenic nitrogen can cause a cascade of environmental and human health problems. "For example, an emitted molecule of nitrogen oxide can first cause photochemical smog and then, after it has been oxidized in the atmosphere to nitric acid and deposited on the ground, can lead to ecosystem acidification and eutrophication" (Gruber & Galloway, 2008, p. 293).

Besides the concentration and exposure time of PM, the size of particles is a very important toxicological factor. Particle size is directly linked to their potential for causing human health problems (EPA, 2010a). Since the 1980's it is well known that there is a correlation between the aerodynamic diameter of particles and their depths of infiltration into human lungs (Kuhlbusch & John, 2000). "The lung is constructed for the exchange of oxygen and carbon dioxide between the air and the blood.[…] The exchange takes place in the functional unit called alveolus, but before reaching this region the inspired air passes pharynx, larynx, trachea, and the […] bronchi which end in the alveoli" (Sterner, 1999, p. 117). Figure 2.6 illustrates the particle transport into the human pulmonary system with regard to particle size distribution.

Particles with a diameter more than 10 µm are already separated in nose and throat and cannot pass the larynx. Particles with a diameter of less than around 4 µm can pass through larynx and bronchi to the lung lobe. The ultra fine particles can even pass the alveoli. In the alveoli, the distance between air and blood is very small - approximately 1µm, and this ensures that the diffusion of the compounds that reach the alveoli is rapid and efficient (Sterner, 1999). In the alveoli, the ultra fine particle will come in contact with and be adsorbed on the moist inner walls through Brownian diffusion. Generally, the smaller particles can pass deeper into the human respiratory system and even reach the blood. It seems that PM1 can enter each organ by blood circulation. Ultra fine particles have been detected in liver, heart and even brain during animal experiments (Koller, 2005).

According to Sterner (1999, p. 119) the dissolvable constituents of ultra fine particles will be absorbed quickly, but macroscopic particles that do not dissolve can be staying in the alveoli for prolonged times because there is no ciliary escalator there. “Eventually, special cleaner cells of the immune system called macrophages enter the [alveola] from the blood, engulf the particle by endocytosis and degrade it both chemically and enzymatically with the contents of their lysosomes.” However, particles of some materials, e.g. quartz, cannot be degraded. “This leads to the stimulation of cell (fibroblast) division in the area, and new layers of connective cells are formed on the inside of [alveola]. As a result the distance between air and blood increases, and the diffusion rate for oxygen decreases.” Human beings exposed chronically e.g. to quartz dust may develop irreversible and disabling fibrosis.

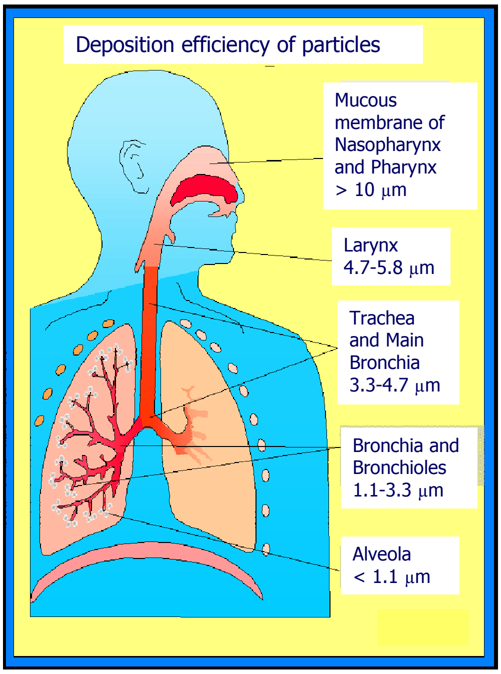

Figure 2.6: Particle transport into the human pulmonary system with regard to particle size (adapted from Kuhlbusch, 2000; DIN ISO 7708, VDI 2463 Bl. 1).

With regard to health effect studies PM10 are also named “inhalable particles” (EPA, 2010a) or “thoracic particles” (Brunekreef & Holgate, 2002) whereas PM2.5 are the “respirable particles” (uniform use in literature). Both particle fractions are typically measured within the atmosphere for the purposes of health effects studies which have been subject to intense investigations in recent years.

Brunekreef & Holgate (2002, p. 1233) reported that exposure to PM in general has been associated with increases in mortality and hospital admissions due to respiratory and cardiovascular diseases. The authors showed that “these effects have been found in short-term studies, which relate day-to-day variations in air pollution and health, and long-term studies, which have followed cohorts of exposed individuals over time”. The effect on shortening life expectancy due to PM pollution has been estimated at 1–2 years (Brunekreef, 1997). Pope et al. (2009) directly assessed associations between life expectancy and fine-particulate air pollution in 51 U.S. metropolitan areas with their results suggesting that multiple factors affect life expectancy. To current knowledge, both observational and experimental PM health studies imply that particle characteristics are determinants of toxicity although direct causality is still discussed (Querol et al., 2008; WHO, 2007). Definite links between specific characteristics and the risk of various adverse health effects have yet to be identified (Samet et al., 2006). It has proven very difficult to disentangle the PM effects differentiating by their size, chemistry and source in relation with daily mortality by statistical methods (Anderson, 2009). More research and PM monitoring data are needed to increase the ability to evaluate spatial and temporal associations with greater accuracy.

After Sterner (1999, p. 119) air contaminants in the form of gases and vapours such as NO_x and NH_3 should in principle have no problem to reach the alveoli as airborne molecules. Nonetheless, on their way to the alveoli, they also come into contact with mucous membranes which absorb them. “In that sense, the upper human respiratory tract can be compared with a scrubber that purifies the air from water-soluble and reactive contamination.” This means that hydrophilic molecules generally do not reach the alveoli as efficiently as solid particles in the air. Highly reactive gases such as NH_3 are also strongly irritating to the mucous membranes in the nose. Thus their respiration becomes blocked and NH_3 cannot be inhaled in larger quantities.

NO and NO_2 will be irritating in high concentrations but can be inhaled if occurring in low concentrations. “When they reach the alveoli, their reactivity may harm the cell walls so that the epithelial cells start to leak. The additional liquid [entering the alveoli] will increase the distance between air and blood and block the diffusion of oxygen” (Sterner, 1999, p. 120). The worst case for humans exposed to these gases is that pulmonary oedema form which has to be treated immediately. Numerous epidemiological studies have used NO_2 as a marker for the air pollution mixture of combustion-related pollutants, in particular traffic exhaust pollution. After Forastiere et al. (2006, p. 375) nitrogen dioxide concentrations closely follow vehicle emissions in many situations. The author argues that health risks from nitrogen oxides may potentially result from nitrogen dioxide itself, correlated exhaust components such as ultra fine particles and hydrocarbons, or products of chemical reactions involving nitrogen dioxide as well as e.g. ozone and secondary particles. For the author the issue is complicated by the fact that PM10 or PM2.5 are indicators for both regionally transported, more homogeneously distributed particles as well as for locally produced, rather non-homogeneously distributed combustion particles. NO_2 is often recognized as an indicator of locally produced particles and thus used to establish spatial variability in air pollution concentrations, mainly from mobile sources. But NO_2 remains inseparable from the often unknown particle emissions from combustion sources, and in particular from mobile sources. After Forastiere et al. (2006, p. 375) it is therefore difficult to determine whether the effects observed for nitrogen dioxide and PM are independent effects of the gaseous pollutant nitrogen dioxide and of PM or independent effects of locally produced fine and ultra fine carbonaceous particles and of regionally transported accumulation-mode particles.

Besides the impacts on human health, PM, NO_x and NH_3 are also leading to a wide range of different environmental problems. As described by Cowling et al. (2002, p. iii) most forms of life are adapted to use Nr efficiently, and addition of Nr to most ecosystems leads to increased uptake, storage, and use and hence to increased productivity within ecosystems. Species in general vary in their growth requirements for N. While annual crops require large amounts of added N to maximise production, many native plant species require much lower levels of N as reported by Pitcairn et al. (2006, p. 942). High exposure to atmospheric NH_3 will eventually lead to toxic effects in plants (Erisman et al., 2007). Long-term exposures with low to moderate NH_3 concentrations on the one hand do not appear to indicate toxicity (Castro et al., 2008).

Pitcairn et al. (2006, p. 942) describes that increased inputs of atmospheric N can lead to a loss in biodiversity when slow-growing species with low N requirements are out-competed by more vigorous species able to respond positively to increased N levels. The author argues that lower plants species such as e.g. lichens, which obtain N largely from rainfall and other atmospheric inputs, are most at risk from enhanced N deposition. In general, “changes in species composition associated with increased N deposition and particularly with NH_3 emissions from intensive agriculture have occurred over much of Europe” (Pitcairn et al, 1998, p. 41). It has been shown that reduced N inputs are more effective in decreasing biodiversity than oxidised N since reduced N is more readily available to stimulate plant growth (Pitcairn et al., 2003).

Recent studies underline the role of cuticle resistances (see also compensation point in chapter 2.1.3) in NH_3 fluxes in semi-arid natural vegetation to be the most important factor in regulating the deposition flux (Sutton et al., 2007). Scientists agree that more work is necessary to investigate the role of this resistance, which determines the NH_3 concentration and therefore has implications. Another research field has been acknowledged by Erisman et al. (2007) who reported on increases in ambient NH_3 and NH_4 in remote areas of Europe which requires quantitative explanation and more detailed measurements. Other studies on semi-natural vegetation show that increased levels of reduced N are much more harmful to plants than oxidised N which does not imply that oxidized N is less important (Erisman et al., 2007). These examples only demonstrate some of the newly observed effects and uncertainties associated with NH_3. Scientists are aware of the urgent need for a more complete scientific understanding of these issues and try to update data on NH_3 fluxes and reservoirs regionally and globally.

2.4 Legislation

Several guidelines and standards exist for nitrogen dioxide and particulate matter in ambient air. Table 2.3 lists the most recent air quality guidelines and standards recommended by the WHO, the United States (EPA), EU, and China.

Table 2.3: Air quality guidelines and standards for NO_2, PM10 and PM2.5 according to WHO, EPA, EU and China

	Actual maximum concentration allowed when averaged over time		
	1 h	24 h	1 year
Nitrogen dioxide ($\mu g\ m^{-3}$)			
WHO	200		40
EPA	~200[a]		100
EU	200[b]		40
CNAAQS		80-120[c]	40-80[c]
PM10 ($\mu g\ m^{-3}$)			
WHO		50[d]	20
EPA		150[e]	[f]
EU		50[g]	40
CNAAQS		50-250[c]	40-150[c]
PM2.5 ($\mu g\ m^{-3}$)			
WHO		25[d]	10
EPA		35[h]	15[i]
EU		[j]	25[k]
CNAAQS			

[a] Exact number according to EPA: 0.100 ppm (=189 $\mu g\ m^{-3}$). To attain this standard, the 3 year average of the 98th percentile of the daily maximum 1-h average at each monitor within an area must not exceed 0.100 ppm.

[b] To be exceeded on no more than 18 days per year.

[c] Range of Chinese National Ambient Air Quality Standards (class I - III).

[d] 99th percentile or 3 days per year.

[e] To be exceeded on no more than once per year on average over 3 years.

[f] EPA is revoking the annual PM10 standard because there is insufficient evidence linking health problems to long-term exposure to inhalable coarse particle pollution (December, 2010).

[g] To be exceeded on no more than 35 days per year.

[h] 3 year average of the 98th percentile of 24-h concentrations.

[i] 3 year average of the annual mean concentrations.

[j] Not yet defined (as of December, 2010).

[k] Target value beginning from 11.07.2010; binding limit value for all EU member states from 2015 – mean concentration of the years 2013, 2014, 2015; limit value from 2020: 20$\mu g\ m^{-3}$).

Source: WHO, 2006; EPA, 2010a; EPA, 2010c; EC, 2008; SEPA, 2010; SEPA, 1996

The WHO air quality guidelines have been developed in response to global threats of air pollution to public health (WHO, 2006). The guidelines for e.g. PM are based on both sensitive indicators such as physiological measures (e.g. changes in lung function, inflammation markers) and the most critical and traditional population health indicators, such as mortality and unscheduled hospital admissions. “Although these guidelines are neither standards nor legally binding criteria, they are designed to offer guidance in reducing the health impacts of air pollution based on expert evaluation of current scientific evidence” (WHO, 2006, p. IX). Of particular importance for WHO (2006, p. 1) in deciding that the guidelines should apply worldwide was the substantial and growing evidence of the health effects of air pollution in the low- and middle-income countries of Asia, where air pollution levels are the highest. In general, the guidelines are intended to support a broad range of policy options for air quality management as well as for the decision making processes in countries all over the world to revise or retain the national guideline values.

The U.S. Clean Air Act directs EPA to set National Ambient Air Quality Standards (NAAQS) for pollutants that the Agency has listed as ‘criteria pollutants’, based on their likelihood of harming public health and welfare (EPA, 2010a). PM and NO_2 are those pollutants besides four others. The Clean Air Act requires EPA to review standards once every five years to determine whether revisions to the standards are appropriate (EPA, 2010a). Regarding NO_2, recently EPA has made revision of NAAQS in order to provide requisite protection of public health. Specifically, EPA is establishing a new 1-hour standard at a level of 100 ppb, based on the 3-year average of the 98th percentile of the yearly distribution of 1-hour daily maximum concentrations, to supplement the existing annual standard. After EPA (2010d) the agency is also establishing requirements for an NO_2 monitoring network that will include monitors at locations where maximum NO_2 concentrations are expected to occur, including within 50 meters of major roadways, as well as monitors sited to measure the area-wide NO_2 concentrations that occur more broadly across communities. Regarding PM standards EPA was strengthening the 24-hour fine particle standard from the 1997 level of 65 $\mu g\ m^{-3}$ to 35 $\mu g\ m^{-3}$, and retains the current annual fine particle standard at 15 $\mu g\ m^{-3}$. The Agency also is retaining the existing national 24-hour PM10 standard of 150 $\mu g\ m^{-3}$. But with respect to the annual PM10 standard the Agency is revoking the limit giving reason that there is no scientific proved link between long-term exposure to current levels of coarse particles and health problems (EPA, 2010a). EPA (2010a) says that it is protecting all Americans from effects of short-term exposure to inhalable coarse particles by retaining the existing daily PM10 standard.

In comparison with U.S. and Asian countries the European Union insist on much tougher standards. The new directive on ambient air quality and cleaner air of the European Union (EC, 2008) entered into force in June 2008. It merges four earlier directives and one Council decision into one single directive on air quality (EC, 2008). Daily PM10 levels should not exceed 50 µg m^{-3} more than 35 times in a year. The mean annual limit value for PM10 is 40 µg m^{-3}. While the latest WHO air quality guidelines identified fine particles (PM2.5) as one of the most dangerous pollutants for human health, the new EU directive sets objectives and target dates for reducing population exposure to PM2.5 (WHO, 2010). The PM2.5 limit value of 25 µg m^{3} is an annual target value which will be legally binding criteria in 2015. The daily PM2.5 limit value has not been defined yet (as of December, 2010). In Europe air quality standards for PM10 and PM2.5 limit values apply to the whole European territory and have to be converted into national laws according to the EU Directive 2008/50/EC (EC, 2008). The air quality standards mean that hotspots as well pristine areas have to meet the same air quality target values concerning the ambient air levels of pollutants. That can be a problem in the sense that allowable pollution limits are likely to be so high as to be irrelevant to rural sites and can even lead to increasing air pollution there, in a worst case scenario (Querol et al., 2008). In some rural areas of Europe PM10 and PM2.5 exceedances can be observed as well as they were also predicted by modelling within EMEP (European Monitoring and Evaluation Programme) network (EMEP, 2009). Regarding values obtained for these rural areas it is unclear if they are regional or rural or even mixed with urban background levels. EU countries have different rural sites with specific regional characteristics and the density of sites is very irregular across territory. In the scientific community is therefore actually a discussion on the necessity of a new legally binding definition for ‘hotspots’, ‘urban background’ or ‘rural background’ in a way that the definition is applicable for air quality standardization in all EU member states (Querol et al., 2008).

One speciality in Germany is that citizens have the right for clean air. By law German administrative bodies are obliged to install air quality plans as well as to set out measures in order to attain the thresholds. Citizen can take institutions to court in case of their inactivity.

In Europe, the EU Directive (2008/50/EC) sets two limits on ambient concentration of NO_2, which must be achieved by 2010: an annual mean limit of 40 µg m^{-3} and an hourly limit of 200 µg m^{-3} that must not be exceeded on more than 18 occasions each year. Besides the limit values for NO_2 EC has even determined one alert threshold. In case of measurement about 400 µg m^{-3} over three consecutive hours at locations representative of air quality over at least 100 km^{2} or an entire zone or agglomeration, whichever is the smaller, alarming level is reached. This level means there is a risk to human health from brief exposure for the population as a whole and at which immediate steps are to be taken by the Member States (EC, 2008).

Besides of the protection for human health the EU Directive contains also critical levels for the protection of vegetation with e.g. 30 µg m^3 for NO_x. This level was fixed on the basis of scientific knowledge, above which direct adverse effects may occur on some receptors, such as trees, other plants or natural ecosystems but not on humans (EC, 2008).

The Chinese National Air Quality Standards (CNAAQS) specify TSP, PM10, NO_x and NO_2 besides other pollutants. PM2.5 is not covered. According to these standards Chinese territory is divided into three classes: class I is protected areas and nature reserves, class II is residential areas, commercial, transportation and residential mixed areas, cultural areas and general industrial areas specified in urban planning as well as rural areas, and class III is for industrial areas (SEPA, 2010). Cities should meet class II concerning the CNAAQS which is considered to be safe and acceptable (SEPA, 1996; He et al., 2002). Since the year 2000, a daily air pollution index (API) describes air quality levels (or often named grades) for many Chinese cities. The API includes concentration values of SO_2, NO_2, PM10, CO and O_3 which are single indexes respectively (see Table 2.4). These single indexes determine the API in that sense the API of a week or day is the maximum of the single indexes of pollutants reported and the pollutant with the highest single index is cited as the major pollutant and thus forms the API index (Oberheitmann, 2007; He et al., 2002).

Table 2.4: Air pollution index in China

Air pollution index	daily mean (µ g m^3)	
API	**NO_2**	**PM10**
50	80	50
100	120	150
200	280	350
300	565	420
400	750	500
500	940	600

Source: SEPA 2010; Oberheitmann, 2007

The Chinese Ministry of Environmental Protection has described the levels of air pollution in relation to API connected with recommendations for the population (see Table 2.5).

Apart from that the Law on Air Pollution Prevention and Control of the People's Republic of China exists since 1987. The law requires that all industrial plants that discharge pollutants into the air must comply with the rules for pollution control (He et al., 2002). Several policies, regulations and the CNAAQS followed after that law but e.g. these standards are not comparable with EU standards since they are no threshold or limit values. Exceedances of the

CNAAQS have no consequences. Furthermore there is neither effective implementation of air quality control including target or limit values nor sustainable air quality management countrywide. The Olympic Games in 2008 pushed the Chinese government in that way to launch air pollution control measures such as e.g. vehicle emission control. Especially Beijing has launched a series of local emission standards connected with ten stages of so called emergency control measures (Hao & Wang, 2005). Since June 2009 Beijing labels its cars in green or yellow according to their emissions; non-local cars have to apply for the label before entering Beijing. Furthermore SEPA publishes on its website that it is planned to develop a regional plan for air pollution prevention and control including sustainable management policies for the areas Beijing, Tianjin, Hebei, Shanxi, Inner Mongolia and Shandong (SEPA, 2010).

Table 2.5: Definition of air quality levels within API

API	Description	Air quality level	Impact on human health	Recommendations by SEPA
0-50	excellent	I	Daily activities will not be influenced	none
51-100	good	II		
101-150	slightly polluted	IIIA	Symptoms intensify heart and lung diseases of sensitive persons.	Heart and lung patients shall reduce physical activities outdoors.
151-200	lightly polluted	IIIB		
201-250	moderate polluted	IVA	Symptoms of heart and lung patients aggravate massively. Symptoms can occur at healthy persons.	Old persons, heart and lung patients shall reduce physical exercise and avoid being outdoors.
251-300	polluted	IVB		
301-500	heavily polluted	V	Physical activities of all persons are limited to low level, heavy lung and heart problems can occur.	Old persons, heart and lung patients shall avoid physical exercise and avoid being outdoors. Whole population shall avoid activities outdoors.

Source: SEPA, 2010; Oberheitmann, 2007; He et al., 2002

2.5 Air pollution in North East China

Viewed from the skyscrapers in the centre of Beijing, the mountains surrounding the city in the North and West often only shine through the hazy horizon or even fully disappear in thick dust. Figure 2.7 is synonymous for the air pollution in North East China where the ‘blue-sky’ days are in the clear minority and low visibility days dominate especially in cities and their suburbs. Air pollution has become the most visible environmental problem in China as stated by Wang & Mauzerall (2006, p. 1706).

Figure 2.7: View from study site Dongbeiwang to Taihang and Funiu mountains located at the West of Beijing (northern part of NCP) during a 'blue-sky' day on 21st of September 2005 (left) and during a 'normal' hazy day on 9th of September 2005 (right).

TSP, PM10 and PM2.5 are the major air pollutants in China (Fang et al., 2009). Moreover, PM10 is the primary air pollutant today, having replaced SO_2 and NO_x (Yao et al., 2009). North East China represents one of two large air pollution areas in China suffering profoundly from PM air pollution (Yi et al., 2007). Due to the rapid growth in vehicle numbers and the fast industrial development experienced by these areas, high concentrations of PM10 and NO_x have increased the levels of atmospheric air pollution. With an increasing number of air pollution episodes and reported low visibility days, a series of publications on atmospheric particles in North East China and especially Beijing has been published.

Intensive field measurements on PM were carried out in Beijing, focussing on structure and composition of PM (e.g. Wang et al., 2008a; Wu et al., 2008; Duan et al., 2006; Sun et al., 2004), ageing processes of particles (Meier et al., 2009), and their sources (e.g. Westerdahl et al., 2009; Han et al., 2007a; Zheng et al., 2005; Chan et al., 2005; Cao et al., 2002). Publications often put a special focus on dust events (e.g. Dillner, et al., 2006; Wang et al., 2006a; Xia et al., 2005; Xie et al., 2005a; Cheng et al., 2005). Some campaigns of the PM sampling in Beijing included the investigation of Nr species (Pathak et al., 2009; Han et al., 2007b; Duan et al., 2006; Lun et al., 2003; He et al., 2001). Most of the PM campaigns carried out in Beijing cover only a short-term period lasting from days to no more than one month. Only few authors report on seasonal (e.g. Han et al., 2007b; Zheng et al., 2005; Sun et al., 2004), weekly (e.g. Guinot et al., 2007; Duan et al., 2006) or even annual measurements (Zhao et al., 2009; Wu et al., 2008). The only PM long-term monitoring nationwide study lasting more than five years was carried out by Wang et al. (2008b) in which PM2.5 and PM10 were collected during summertime and wintertime in Beijing between 2001 and 2006. A first regional air quality simulation for Beijing area was carried out by Streets et al. (2007) in relation to the Olympic Games in 2008. PM flux measurements using Eddy-covariance have been carried out in desert areas of northern China for the first time by Fratini et al. (2007). Moving from the city of Beijing into its suburbs or into the North China Plain, publications on air pollution and especially on PM are still scarce.

Overall, recent PM air pollution studies in China concentrated mainly on investigations of PM2.5, rather than on PM10 and TSP. Tables 2.6 to 2.8 summarize average concentrations of PM2.5, PM10 and TSP measured in China respectively (with emphasis on Beijing), covering the time period from the beginning of 2000, and articles published in international journals. Many studies collected PM data at urban sites, especially in Beijing, with measurements often occurring on roofs of universities. Only few studies include measurements at more rural areas. Zhao et al. (2009) are an exception, as they conducted measurements in the northern part of the NCP. That rural site was located on a slope of a hill surrounded by mountains in every direction except the southwest, and results are highly influenced by valley topography rather than the rural setting. Other PM Beijing studies often include the Ming Tombs or the mountains as rural site. No published PM measurements conducted directly on agricultural sites in China were found.

Zhao et al. (2009) did the most recent publication on PM in Beijing. This is the only study reporting on continuous PM2.5 measurements carried out from 2005 to 2007. This time period refers almost to the same measuring period as the present study. Other published PM data in general refers to earlier time periods or estimations. Choi et al. (2008) for example only estimated daily PM10 averages nationwide for the year 2005 by using API values of 31 ground stations, where Beijing with more than 85 $\mu g\ m^{-3}$ tops the list of the major polluted cities including also Taiyuan, Jinan and Chongqing as major pollutant areas.

Recent NO_x measurements in China were reported by Chan & Yao (2008), Xie et al. (2005a), Ta et al. (2004), and He at al. (2002). The annual average NO_2 concentration has stayed at a level of about 70 $\mu g\ m^{-3}$ in Beijing (Chan & Yao, 2008) often meeting the air quality grade III (SEPA, 2010). Several studies only used API values for further predictions such as Lin & Cheng (2007) who investigate the formation rates and factors affecting gaseous and particulate nitrate based on theoretical evaluations regarding potential NO_2 oxidant reactions. NO_x measurements on agricultural sites were conducted by Pang et al. (2009). They measured NO_x and N_2O emissions from the croplands cultivated with three typical vegetables in the Yangtze River Delta of China in 2006. The NO fluxes showed mean averages of 33.8, 360 and

76 ng N m^{-2} s^{-1} for cabbage, garlic, and radish fields. Furthermore, Cao et al. (2008) investigated NO_x and NO_2 emission factors from crop residue burning in China.

International publications on real-time measurements as well as long-term studies on NH_3 for agricultural sites in China are very rare. Ammonia measurements in Beijing were carried out by Yao et al. (2003) showing that NH_3 concentrations vary between 4.6 and 42.4 µg m^{-3}. Most studies report on NH_3 estimations, only. Recent studies developed NH_3 emission inventories (e.g. Wang et al., 2005a; Streets et al., 2003; Klimont et al., 2001), estimating that approximately 20 % of global NH_3 emissions derive from China.

Total N deposition in China only has been investigated by Lue & Tian (2007) up to now. By using the kriging technique they interpolated different sampling data (precipitation data from the 80ies and 90ies from CAWAS, Centre for Atmosphere Watch and Services, and CMA, China Meteorological Administration, data from EANET, East Asian NET, from 2000 until 2004 and estimated deposition fluxes) to estimate wet and dry N deposition nationwide.

In general, quantitative information on dry deposition levels in China, especially in relation to reactive nitrogen, are insufficient. There is a big knowledge gap for the North China Plain in relation to this topic and continuous air pollutant monitoring data are lacking (Yang et al., 2002a). N_2O emissions from a maize–wheat rotation field were monitored in the Fengqiu County, Henan province, from June 2004 to June 2005, with results published by Ding et al. (2007). Furthermore Yang et al. (2008) measured PM10 and NO_x emitted from crop residue burning during harvests only, on the agricultural fields of Suqian region, Jiangsu province, from 2001 to 2005.

Continuous Nr dry deposition measurements in the NCP including PM, NH_3 and NO_x have only started with begin of research by the Sino-German IRTG. Long-term PM measurements were carried out in the North China Plain for the first time within this study in 2005 and 2006 (Kopsch et al., 2006), followed by 5-days-per-month PM measurements afterwards (Shen et al., 2009; Shen et al., 2011). The first measurements of gaseous NH_3 in the NCP within this study (Kopsch et al., 2006) have been completing this pioneer work on dry deposition. Formerly there were only estimates on dry nitrogen deposition in the NCP available from Liu et al. (2006), He et al. (2007) and Zhang et al. (2008) who conducted parallel studies on wet and total nitrogen deposition in the same study region. Data derived from these measurements have been used to estimate NH_3 emissions in the NCP (Zhang et al., 2010a).

Table 2.6: PM2.5 measurements in Beijing and China since year 2000 (according to international publications)

Place	Site	Time period	Average concentration µg m^3 daily	weekly	monthly	annual	measuring device	References
Beijing	urban	2005			71, 85, 122, 63[a]		TEOM 1400a ambient particulate monitor (Rupprecht & Patashnick, USA)	Zhao et al., 2009
		2006			100, 81, 81, 112			
		2007			74, 92, 74, 98			
	rural (northern part of NCP)	2005			40, 65, 48, 31[a]			
		2006			101, 61, 52, 45			
		2007			60, 59, 45, 44			
Beijing	rural	July 2005			68		RAAS2.5-400 sampler (Anderson, USA)	Pathak et al., 2009
Beijing	urban	Oct. 2004 (16 days)	53				TEOM 1400, (Rupprecht and Patashnik, USA)	Zhang et al., 2007a
Beijing	urban	Aug. 2004 (3 weeks) collected PM< 2µm	57 (12 h)					Gros et al., 2007
Beijing	urban	March-Apr. 2004	103 (non-dust days) 213-303*				Medium Volume Sampler	Wang et al., 2007
Beijing	urban	2001-2004					Minivol	Oanh et al., 2006
		May-Oct. (wet season)	104 (wet)					
		Nov.-Apr. (dry season)	168 (dry)					
Beijing	urban	2001-2004 (spring)	107 (non-dust days) 409*				Medium Volume Sampler	Wang et al., 2006b
Beijing	urban	2001-2003			107 (summer) 182 (winter) 145 (spring; 402*)		Medium Volume Sampler (Beijing Geol. Instr.-Dickel Co.)	Zhang et al., 2010b
Beijing	urban	2001 - 2003			198 (winter '01) 213 (spring '02) 536 (only Mar.'02) 80 (summer '02) 112 (spring '03) 107 (autumn '03)		Medium Volume Sampler (Beijing Geol. Instr.-Dickel Co.)	Han et al., 2007b
Beijing	urban	Aug. 2003	93 (179 max.)[b]				DustTrak, TSI Model 8520	Chan et al., 2005
Beijing	urban	winter + summer 2002/2003			75-82 [c] (summer) 135-182 [c] (winter)		Medium Volume Sampler (Beijing Geol. Instr.-Dickel Co.)	Sun et al., 2004
Beijing	urban	Jul./Aug. 2002		66			Hi-Volume (Anderson) + Harvard Honeycomb (Rupprecht & Patashnik, USA)	He et al., 2006
		Oct. 2002		78				
		Jan. 2003 (one week respectively)		77				
Beijing	urban	Aug. 2001-Jul. 2002				163 (n=50)	Harvard Honeycomb (Rupprecht & Patashnik, USA)	Huang et al., 2006
Beijing	urban	Aug. 2001-Sept. 2002		23-199	80 (autumn) 122 (winter) 76 (spring) 89 (summer)	102	Low-flow rate sampler (Aerosol Dynamics Inc., Berkeley, CA)	Duan et al., 2006
Beijing	urban rural	2001 (7-days per month; 12 h per day)		36 (urb., summer) 29 (rur., summer) 177 (rur. spring)*		106	Beijing Geologic Instruments + High Volume XH-1000 sampler (Hebei Sailhero High-tech Co.)	Shi et al., 2003
Beijing	urban	Apr./May 2001	123*				Anderson impactor	Cheng et al., 2005
Beijing	urban	10 days March 2001		106* (10 days)			AIHL design cyclone separator	Dillner et al., 2006
Beijing	urban rural	each quarter 2000 (6-day intervals)			61 (Jan.) 139 (Apr.) 99 (Jul.) 106 (Oct.)			Zheng et al., 2005
Beijing	urban rural	Apr. 2000	64-262* (urban) 29-230* (rural)				RAAS2.5-400 sampler (Anderson, USA)	Xie et al., 2005a

[a] order of numbers = spring, summer, autumn, winter

[b] measurement at different heights

[c] range of 3 sites

* including dust storm events

Continuation of Table 2.6

Place	**Site**	**Time period**		**Average concentration µg m^3**			**measuring device**	**References**
			daily	**weekly**	**monthly**	**annual**		
other Chinese sites								
Shanghai	urban	May/June 2005			67		RAAS2.5-400 sampler (Anderson, USA)	Pathak et al., 2009
Taicang (50 km NW of Shanghai)	urban	May 2005	67				TEOM 1400a ambient particulate monitor (Rupprecht & Patashnick, USA)	Gao et al., 2009
Shanghai	urban	Sept./Oct. 2003 Mar/Apr. 2004 Aug. 2004 Nov. 2004 - Jan. 2005	96 (12h) 135 (12h) 72 (12h) 83 (24h)			95	Medium Volume Sampler	Wang et al., 2006c
Lanzhou	urban	June/Jul. 2006			65		RAAS2.5-400 sampler (Anderson, USA)	Pathak et al., 2009
Guang-zhou	sub-urban	May 2004			55		RAAS2.5-400 sampler (Anderson, USA)	Pathak et al., 2009
Hong Kong	road	Nov.'00 - Oct.2001 (every 6th day)	58			58	Partisol Sampler (Rupprecht & Patashnick, USA)	Louie et al., 2005
	urban		34			31		
	rural		24			27		
Hong Kong	urban	Nov.-Dec. 2002			41		RAAS2.5-400 sampler (Anderson, USA)	Cheung et al., 2005

Table 2.7: PM10 measurements in Beijing and China since year 2000 (according to international publications)

Place	Site	Time period	Average concentration µg m^3				measuring device	References
			daily	weekly	monthly	annual		
Beijing	urban	Aug.-Sept. 2007	190				Thermo Fisher Model FH62C14	Wang et al., 2008a
Beijing	urban	Oct. 2004 (16 days)	100 96 (min) 356 (max)				TEOM 1400, (Rupprecht and Patashnik, USA)	Zhang et al., 2007a
Beijing	urban	Aug. 2004 (3 weeks) collected PM > 2µm	72 (12 h)					Gros et al., 2007
Beijing	urban	Jan. 2004 (15 days)	173				TEOM 1400, (Rupprecht and Patashnik, USA)	Zhang et al., 2007b
Beijing	urban	2001-2004 May-Oct. (wet season) Nov. Apr. (dry season)	180 (wet season) 262 (dry season)				Minivol	Oanh et al., 2006
Beijing	urban	Aug. 2003	111[a] (368 max)				DustTrak, TSI Model 8520	Chan et al., 2005
Beijing	urban	2001-2003			180 (summer)[b] 263 (winter) 244 (spring) 430 (spring*)		Medium Volume Sampler (Beijing Geol. Instr.-Dickel Co.)	Zhang et al., 2010b
Beijing	urban	winter + summer 2002/2003			150-172 [c] (summer) 184-293 [c] (winter)		Medium Volume Sampler (Beijing Geol. Instr.-Dickel Co.)	Sun et al., 2004
Beijing	urban	Sept.-Nov. 2002			154 (Sept.) 139 (Oct.) 171 (Nov.)		TEOM1400a + ACPM Series 5400 (Rupprecht & Patashnik, USA)	Duan et al., 2005
Beijing	urban	2001-2003 (only spring)	194					Wang et al., 2004a
Beijing	urban	Aug. 2001 - Sept. 2002			157 (autumn) 154 (winter) 188 (spring) 119 (summer)	155	Low-flow rate sampler (Aerosol Dynamics Inc., Berkeley, CA)	Duan et al., 2006
Beijing	urban	Apr./May 2001	254*				Anderson impactor	Cheng et al., 2005
Beijing	urban rural	2001 (7-days per month; 12 h per day)		365 (urb., spring)* 227 (rur., spring)* 68 (urb., summer) 47 (rur., summer)	365 (march)*	230	Beijing Geologic Instruments + High Volume XH-1000 sampler (Hebei Sailhero High-tech Co.)	Shi et al., 2003
Beijing	urban rural	Apr. 2000	120-898* (urban) 66-849* (rural)				RAAS2.5-400 sampler (Anderson, USA)	Xie et al., 2005a

[a] median; measurement at different heights

[b] mean of each season for 3 years

[c] range of 3 sites

* including dust storm events

Continuation of Table 2.7

Place	Site	Time period	Average concentration $\mu g\ m^3$				measuring device	References
			daily	weekly	monthly	annual		
other Chinese sites								
Wuhan	urban rural	Sept. 2003-Sept. 2004	156 (urban) 118 (rural)				Wuhan Tianhong High Volume Sampler (Th-1000CII)	Querol et al., 2006
Guiyang	urban	Jul. 2003	59				Medium Volume Sampler (Wuhan Tianhong Intelligence Instr.)	Xie et al., 2005b
Xian	urban	2001-2003 (only spring)	179 ('01) 173 ('02) 125 ('03)				API	Wang et al., 2006d
Anyang	urban	Apr. 2001-Dec. 2001			180 (winter) 140 (spring) 123 (summer/ autumn)	145	Medium Volume Sampler (Wuhan Tianhong Intelligence Instrumentation Facility, TH-150)	Bi et al., 2007
Tianjin	urban	Dec. 2000-Oct. 2001			144 (winter) 153 (spring) 99(summer)	123		Bi et al., 2007
Jinan	urban	Dec. 1999-Sept. 2000			182 (winter) 139 (spring) 63 (summer)	115		Bi et al., 2007
Urumqui	urban	Jan. 2002-Jul. 2002			197 (winter) 134 (spring) 60 (summer)	141		Bi et al., 2007
Yinchuan	urban	Jan. 2002-Oct. 2002			144 (winter) 161 (spring) 75 (summer)	133		Bi et al., 2007
Taiyuan	urban	Apr. 2001-Jan. 2002			226 (winter) 170 (spring) 164 (summer/ autumn)	186		Bi et al., 2007

Table 2.8: TSP measurements in Beijing and China since year 2000 (according to international publications)

Place	Site	Time period	Average concentration µg m^{-3} daily	monthly	annual	measuring device	References
Beijing	urban	March-Apr. 2004	240 (non-dust days) 493-613*			Medium Volume Sampler	Wang et al., 2007
Beijing	urban	2001-2004 May-Oct. (wet season) Nov. Apr. (dry season)	305 (wet season) 440 (dry season)			Minivol	Oanh et al., 2006
Beijing	urban	2001-2004 (spring)	339 (non-dust days) 1949*			Medium Volume Sampler	Wang et al., 2006b
Beijing	urban	2001-2003		290 (summer) [a)] 435 (winter) 495 (spring) 2170 (spring*)		Medium Volume Sampler (Beijing Geol. Instr.-Dickel Co.)	Zhang et al., 2010b
Beijing	urban	2001 (winter) 2002 (spring, summer, winter) 2003 (spring, autumn)		475 (winter '01) 1410 (spring '02; 2272 (only Mar.'02) 225 (summer '02) 362 (spring '03) 238 (autumn '03)		Medium Volume Sampler (Beijing Geol. Instr.-Dickel Co.)	Han et al., 2007b
Beijing	urban	Apr.-May 2001	212 (non-dust days) 305-648*	360* [b)]		Anderson Impactor	Cheng et al., 2005
Beijing	urban	10 days Mar. 2001	246-930*			AIHL design cyclone separator	Dillner et al., 2006
other Chinese sites							
Yulin (W of Beijing)	sub-urban	Mar.-Apr. 2004	269 (non-dust days) 1105-1458*			Medium Volume Sampler	Wang et al., 2007
Duolun (N of Beijing)	sub-urban	Mar.-Apr. 2004	153 (non-dust days) 353-1632*			Medium Volume Sampler	Wang et al., 2007
Shanghai	urban	Sept./Oct. 2003 Mar/Apr. 2004 2 days Aug. 2004 Nov. 2004 - Jan. 2005	146 (12h) 293 (12h) 167 (12h) 268 (24h)		230	Medium Volume Sampler	Wang et al., 2006c

[a)] mean of each season for 3 years
[b)] mean of 16 days
* including dust storm events

3 Material and Methods

3.1 Area under investigation

The NCP is located at the east of Taihang and Funiu mountains, covering parts of the provinces of Beijing, Hebei, Tianjin, Shandong, Henan, Anhui and Jiangsu. Mongolia is to the north, the Gobi desert is approximately 400 km to the northwest of Beijing, the Yanshan Mountain range is to the north, and the Bohai Gulf and Yellow Sea is to the east and southeast, respectively (Figure 3.1).

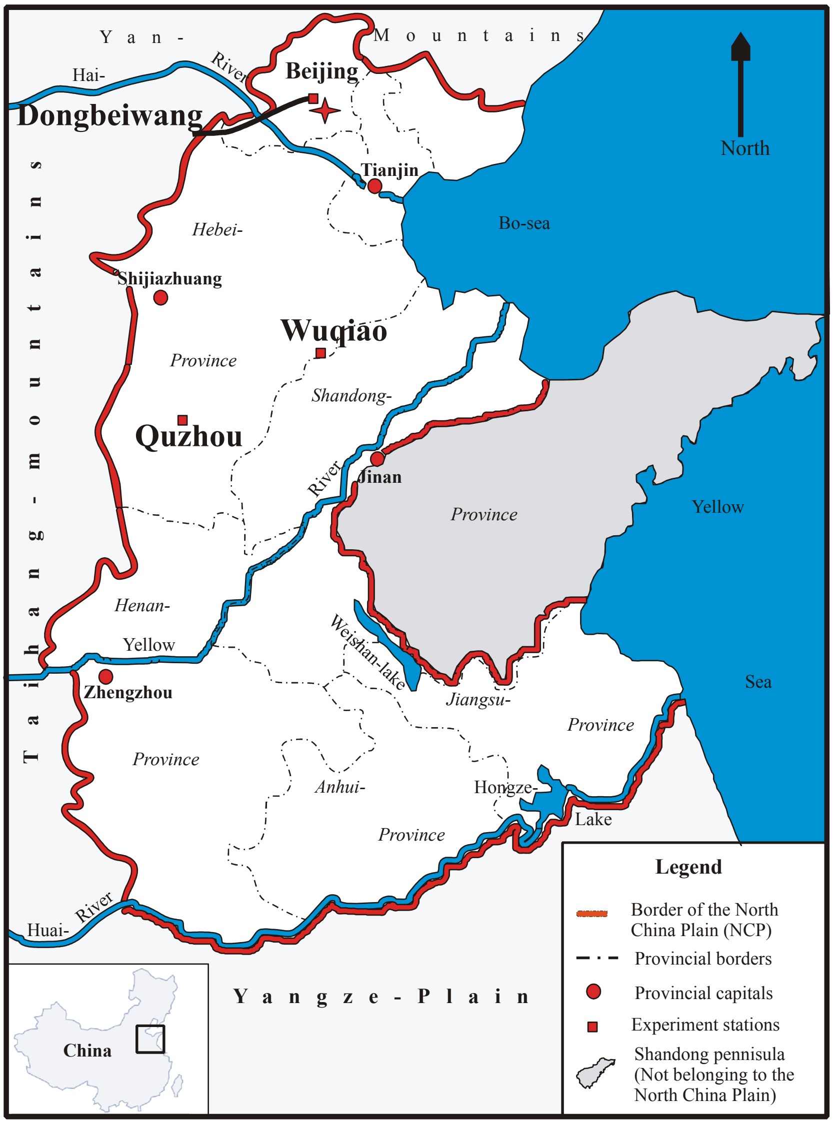

Figure 3.1: Detailed map of NCP with experimental sites Dongbeiwang (DBW), Wuqiao (WU) and Quzhou (QZ) (Source: Rumbaur, 2009).

The NCP is the largest East Asian alluvial plain covering an area of about 328.000 km^2 in total (Bareth, 2004). The area lies between 32° to 41° northern latitude and 113° to 120° eastern longitude, with an elevation up to 100 m above sea level. The maximum north to south extension of NCP is about 900 km; from west to east maximum extension is about 600 km. The climate in the north western third of the NCP is characterized as cold semi-arid, the intermediate strip as warm sub-humid and the south eastern third as warm humid. Overall, the climate is dominated by the East Asian monsoon with a north to south gradient in mean temperature ranging from 12 to 14.5 °C annually. In general, distinct shifts in weather between seasons occur from hot and humid in the summer to cold and dry in the winter. There is also a north to south gradient in total annual precipitation whereas the east is stronger influenced by precipitation than the west. Annual precipitation ranges between 500 – 600 mm in the northern part (Beijing with 632 mm) and 600 – 900 mm in the southern part. Precipitation clearly shows seasonality. Rainy season is from May to September with maximum rainfall in July and August (about 60 % of annual precipitation in the northern part, 50 % in the southern part respectively). In the northern part of the NCP, the maximum wind speeds occur in the spring, with slightly weaker winds in the winter and significantly lower wind speeds in the summer and autumn (Zhao et al., 2009). Dominant soils are Fluvisols; Cambisols and and Luvisols are also present there. Vegetation period is 180 – 200 days (Böning-Zilkens, 2004). The NCP is the most important agricultural region of China with wheat (34 %), maize (20 %) and soybean (8 %) as dominating crops (Taubmann, 2007). Winter wheat and summer maize double cropping system with three harvests in two years are most common in the NCP. It provides approximately 41 % of wheat and 25 % of maize yield of China’s total grain yield (Böning-Zilkens, 2004). Due to the high variability and often lack of precipitation in spring, crops have to be irrigated on large scale.

Experiments of this study were conducted at three experimental sites located in the NCP (see also Figure 3.1). The experimental sites Quzhou (QZ) (36°52’N, 115°00’E) and Wuqiao (WU) (37°41’N, 116°37’E) are located in the province Hebei. The experimental site Dongbeiwang (DBW) (40°03’N, 116°16’ E) is located in the northern part of the NCP, in the north west of Beijing. All experimental sites are agricultural field stations of the CAU where the surrounding area is generally open with agricultural fields. Even if DBW is located in the NCP the experimental site has to be named suburban due to its nearness to Beijing. The station may be influenced by a normal street, not a busy highway, at a distance of around 0.5 to 1 km. WU and QZ are rural sites, located nearby small villages. Performing parallel measurements at all three sites was a logistical challenge due to the distances from one site to the other (WU is around 350 km away from Beijing; QZ is around 450 km away from Beijing; there is no direct connection between WU and QZ), the street conditions (there is no highway), and the lack of public transportation (there is only a railway system from Beijing to Handan, located near QZ). The accomplishment of all experiments meant as a minimum one arrival and one departure day for each site. Therefore it was very time consuming and intensive in travelling to run all measuring devices foreseen within this study at all three sites at the same time. Since all measuring devices had to be tested if they are appropriate for the conditions in the NCP we decided to concentrate on the following:

The PM study was done at DBW due to safety conditions. In general, safety of measuring devices at all experimental sites was a problem. In comparison to other studies all measuring devices were not installed on a roof of an institute building but directly on the agricultural fields located around the experimental station building. To avoid damage or robbery a cage was built for the PM sampler. Another reason for the PM study at DBW was the lack of energy on agricultural fields at QZ and WU. Only at DBW mains supply for the measuring device could be provided. The NH_3 measurements as well as the bioindication experiment were carried out at all three sites. The regularly check of these experiments in WU and QZ was organized twice a month, supported by the staff of the experimental sites who checked experiments daily. The NO_x measuring device was tested at the lab of CAU in Beijing. In general, the vegetation periods (at all sites: winter wheat-maize double cropping system) in 2005 and 2006 were covered by measurements as well as the wintertime 2005/2006. On-site measurements started in March 2005 and terminated in November 2006, yielding 21 months in total.

3.2 High Volume Sampler and gravimetric measurements

A complete High Volume Sampler consisting of PM2.5, PM10 and TSP impactors was transported from Germany to China. A classical particle mass concentration sampler was chosen to start with PM concentration measurements in the NCP. The most common means to obtain the sampled mass and/or chemical characterisation over an integrated period is PM sampling on filter in high- or low-volume gravimetric samplers (Wieprecht et al., 2004).The reason for choosing the High Volume Sampler DIGITEL DHA 80 (Walter Riemer Messtechnik, Germany) was its long-term application in practice in national, federal and research monitoring sites of Germany as well as in neighbouring countries (Spindler et al., 2010; Franzaring et al., 2009; Bruckmann et al., 2008; Viana et al., 2008; Gnauk et al., 2005; Hueglin et al., 2005). Experiences from monitoring sites of e.g. the German Federal State Baden-Württemberg (Zentrum für Umweltmessungen, Umwelterhebungen und Gerätesicherheit Baden-Württemberg (UMEG) could be used for own work. The measurement of PM mass concentration by DIGITEL DHA 80 has been described in VDI guideline 2463, part 11 (VDI, 1996). Accordingly, the instrument has been tested strictly according to high standards and criteria and has been recommended for outdoor measurements. Another important fact is that DIGITEL DHA 80 can easily be calibrated by user after some time of operation by checking the volumetric flow regulating device (rotameter). Other PM samplers can only be calibrated by the company itself before selling (e.g. frmOMNI, BGI Inc., USA, used by Shen et al., 2009). Other advantages of DIGITEL DHA 80 are the automatic filter changer and the large effective filter diameter of 140 mm. Moreover, the robustness of the measuring device ensured a long lifetime under the specific conditions in the NCP. Figure 3.2 shows the High Volume Sampler in operation during different vegetation periods at DBW site.

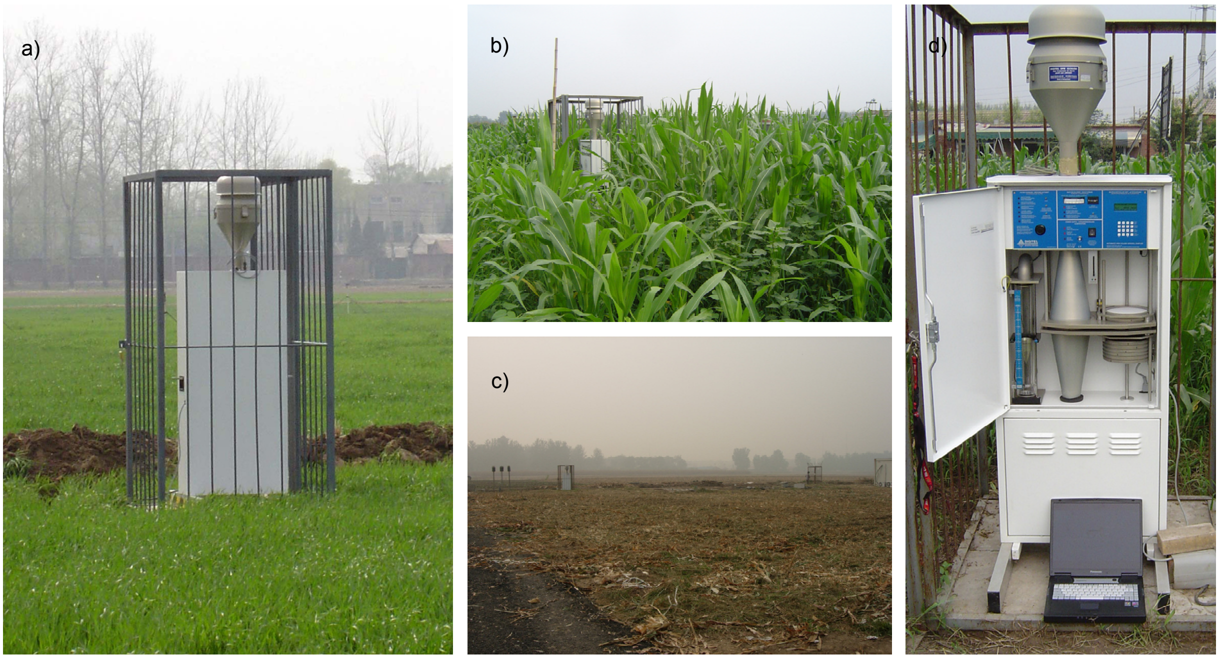

Figure 3.2: High Volume sampler with PM2.5/PM10 impactor in operation at DBW site: a) winter wheat in April 2005; b) maize in August 2005; c) after harvest in October 2006; d) view inside of the instrument while data logging.

The High Volume Sampler was installed in the field after DIGITEL (2004) instructions. On the DBW site the air flow of the High Volume sampler ($30\ m^3\ h^{-1}$ or $720\ m^3\ d^{-1}$ flow rates) has been under electronic control during the whole operation. Each sampler operation, like start and finish time and filter change was recorded automatically on PCMCIA card. At midnight (24:00 Hrs.) the filters were changed automatically to the flow position at the pre-set time. The power supply and voltage stability were ensured by the field container to guarantee a stable sampling. The tightness of the instrument was tested regularly. A rotameter controlled the selected air flow rate. This value has been calibrated first at the beginning of a measurement session. Furthermore sealing rings of filter holders were checked regularly. The High Volume Sampler in operation was checked daily at the beginning of measurements at DBW site.

PM10 and PM2.5 impactors with 10 jets each and cutpoints of 10 µm and 2.5 µm respectively were used. These impactors could optionally be connected with heating to prevent freezing during winter. Furthermore a TSP inlet with an open circular slot being part of the VDI guideline 2363, part 11 (VDI, 1996), was used. The focus of PM measurements was on PM10 and PM2.5 samples. Therefore, TSP sampling was carried out for short measuring periods only. The different particle sizes could not be sampled simultaneously and impactors were changed according to work plan.

The airflow in all impactors was unrestrained. It is recommended to carry out regularly maintenance of impactors by cleaning them each second month and by lubricating them each month (PM10) or every second week (PM2.5) (LUA NRW et al., 2005). Due to high PM pollution at DBW the intervals for maintenance were shortened and all impactors were cleaned and lubricated every fifth day. Figure 3.3 illustrates the difference of a cleaned versus a polluted PM impactor. For lubricating the inlets of impactors Basilone® (Bayer, middle viscous) has been used.

Figure 3.3: Top view on opened PM impactor before (right) and after (left) cleaning of impactor plate. Picture of dirty impactor was made after 5 days in operation. (all photos taken in 2006).

Glass fibre filters (GF10, Schleicher & Schuell) with a diameter of 150 mm were used for high volume sampling, with collection efficiency of 99.8 % as described in VDI guideline 2463, part 1 (VDI, 1999). These filters are very robust; they have low moisture retention, and high collection efficiencies at relatively low drop in pressure (Wieprecht et al., 2004). Due to the relatively high cost of quartz fibre and membrane filters, GF filters were used for routine particle sampling at DBW. Only during last quarter of the monitoring campaign quartz microfibre filters with diameter 150 mm (QMA, Whatman®/Schleicher & Schuell) and a collection efficiency of 99.99 % (VDI, 1999) were used for measurements. QMA filters have superior resistance to artefact effects and moisture absorption, but they are very fragile and were handled with as much care as possible. They are also recommended for routine particle sampling and more suitable for chemical analyses, but much more expensive. In general, all filters used in the High Volume Sampler were loaded homogeneously on an area with a diameter of 140 mm.

For gravimetric determination of PM mass concentration according to DIN EN 12341 (1998), PM samples were taken during 24 hours (from midnight to midnight of the following day) on pre-conditioned and pre-weighted filters. Before weighting, the filters were equilibrated in the balance room at a constant relative humidity of about 50 % and a constant temperature of about 21 °C for minimum of 48 hours. The filters used in the field were removed from instrument into the clean transporting magazine. Two transporting magazines with a capacity for 15 filters each ensured flexible measurements (hourly to daily) and avoided contamination. Unloaded and loaded filters were transported with these magazines from field to the weighting room and back. The above described conditioning was carried out for every filter under constant conditions, also after sampling and before weighting. In order to ensure constant data quality, the conditioning operation and weighting has been performed not only in China but also in Germany. Since it was impossible to store all filters in an air-conditioned balance room in China during whole monitoring campaign, filters were weighted after conditioning and stored in a non-air conditioned and clean place in paper bags with small silica gel bags until return flight to Germany. In Germany, all filters were immediately stored in the air-conditioned balance room of the Department of Ecotoxicology, University of Hohenheim, and equilibrated over a period of about a week as recommended in VDI (1999) before weighting again due to control or further analysing steps. The gravimetric weighting was made on electronical micro-balances (ISO 9001, BS 2000 S, Sartorius, in China and AE163, Mettler, in Germany). Blank filters were handled like normal sample filters, also inserted into High Volume Sampler and removed again and further treated like normal samples. In order to account for the changing weight of the filter material, a set of blank filters was additionally stored in the air-conditioned balance room in Germany and weighted once a month during whole monitoring campaign.

The particle mass concentration was calculated according to VDI (1999) taking into account the sampling period, the particle mass and the volumetric sample flow resulting in the mean concentration:

$$c = \frac{m_2 - m_1}{\int_t \dot{V} \cdot dt} = \frac{m_2 - m_1}{V}$$

here:

c	particle mass concentration in mg m^3
m_1	mass of blank filter in mg
m_2	mass of laden filter in mg
$\dot{V}$	air sample flow rate in m^3 h^{-1}
t	sampling time in h
V	air sample volume in m^3

The contributions of the three PM fractions (TSP, PM10 and PM2.5) to dust loads and the PM2.5 to PM10 ratio (PM2.5/PM10) were calculated for DBW based on hourly respectively daily samples. The ratios were calculated for those times when the impactors for each fraction were changed one after the other, based on hourly respectively daily intervals, which occurred in 2006 only. Due to this one by one impactor change the ratios of the three PM fractions might be not as accurate as in a parallel measurement. Thus it might occur that e.g. a higher daily PM10 than TSP concentration is shown in the ratio diagrams. This is caused by the fact that PM10 was measured during one day, followed by TSP measurement the day after with e.g. more preferable meteorological conditions leading to decrease of PM pollution compared with the day before. TSP always includes PM10 and it is technically of course impossible to obtain higher PM10 loads than TSP during the same time. The hourly change of the impactors was carried out for 24 hours once per month during study period in 2006. Thus, contributions of the three PM fractions were determined for 24 hours in August, in September and in October 2006. Daily changes of the three impactors occurred for 3 weeks in October 2006. The seasonal variations of the PM size distributions in 2006 were calculated based on the normal daily TSP, PM10 and PM2.5 samples.

Due to unforeseen occasions during monitoring campaign some particularities influencing the measurements will be described further.

During dust storm periods in spring, automatic filter change was carried out after 12 hours or even after 8 hours to avoid overloading of filters. Since Zentrum für Umweltmessungen, Umwelterhebungen und Gerätesicherheit Baden-Württemberg (UMEG) or Hessisches Landesamt für Umwelt und Geologie (HLUG) had no experience with overloading of GF filters, an appropriate filter change during dust storms had to be tested. During the first days of dust storm the overloading of filters was visible after 24 hours and particles did not retain on filter surface anymore (see Figure 3.4). By daily checking the weather forecast and the filters in the operating High Volume Sampler, the filter change could be adapted and correct loading of filters could be ensured.

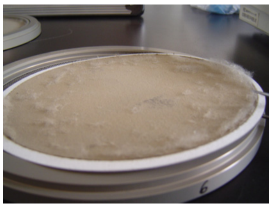

Figure 3.4: Overloaded filter with PM during dust storm event on 30th April 2005.

The entire sampling system has to be cleaned as required by the extent of contamination, but in any case at least after every six months. The conditions in the NCP required regularly cleaning of the machine at least three to four times per month. According to the manufacturer the feed turbine is maintenance free. Nonetheless, heavy pollution and energy breakdowns caused a turbine damage of the High Volume Sampler in winter 2006. In general, energy breakdowns and overload of the power supply at DBW site occurred several times but could be recorded and did not influence the PM concentration data. A new turbine was installed and the damaged one sent back to manufacturer who confirmed that the turbine damage was caused by pollution and thus overload of turbine over long time (which was unique in the history of the manufacturer) and not by energy breakdowns which nevertheless underlines the robustness of the sampler.

Concerning PM measurements with QMA filters, UMEG detected that DIGITEL DHA 80 is going to be overloaded with PM mass concentration of about 80 to 100 µg m^{-3} by using these filters. The reason is the lower air resistance of QMA filters in comparison to GF filters. Therefore QMA filters become ‘tight’ very fast and even in Germany QMA filters are changed after 12 hours routinely. Furthermore conditioning of QMA filters is much more difficult in comparison to GF filters. GF filters react only slightly on changes of relative humidity in comparison to QMA filters (Dr. Ralf Lumpp, 2005a). Hueglin et al. (2005) also noted that the use of QMA filters is delicate in sense of gravimetric determination of PM mass. Based on that information, continuous use of QMA filters was no longer considered for measurements in NCP. Due to high PM concentration in NCP much more QMA filters than GF filters would have been required for gravimetric measurements and costs would have been exploded. Additionally, quality assurance for conditioning of QMA filters under lab conditions in China became questionable. Since focus was on gravimetric measurements first, GF filters were used; later some measurements with QMA filters were carried out.

PM measurements by High Volume Sampler were interrupted in 2006 due to force majeur. Due to regulations of Chinese customs the instrument had to be exported from China to Germany in spring 2006. The instrument was then re-imported to China and installed again at DBW in August 2006.

3.3 Passive sampler

Concentrations of atmospheric NH_3 were measured using Radiello® passive samplers. Passive samplers can only integrate exposure to give a cumulative value. Hourly fluctuations in pollutant gas concentrations that are important to exposure–plant response relationships cannot be determined directly. Passive samplers operate by diffusing the sampled gas from the atmosphere across the sampler volume, usually an inverted tube, to a sink or chemical absorbent according to Fick's law (Cox, 2003).

Since the method represented the first gaseous NH_3 measurements in the NCP and because of the low cost and flexibility of placement, passive sampling systems made them attractive for usage in NCP. After visiting field sites of Forschungsstelle für Umweltbeobachtung (FUB) in Switzerland and sharing their long-term experiences with passive samplers, Radiello® passive samplers were selected for the measurements in China. They have been recommended for observing ammonia concentrations due to the simple sampling method and its reliable application in different monitoring sites (Thöni, 2004; Thöni & Seitler, 2009). Moreover, the absorption rates of Radiello® passive samplers do not change between 10 to 90 % humidity and 0.2 to 10 $m\ s^{-1}$ wind speed. This characteristic fits very well for usage in NCP with respect to variable climate conditions in NCP. Another advantage of Radiello® passive samplers is the fact that they are part of an interlaboratory comparison and publications are available. Furthermore passive samplers do not need energy supply which has been a very important reason for choosing them for NH_3 concentration measurements in NCP.

Radiello® passive samplers consist of the adsorbing cartridge and the diffusive body (made of microporous polyethylene having an average porosity of about 25±5 µm, a diffusive path length of 18 mm and thickness of 1.7 mm). A mountable polypropylene shelter was used to protect tubes from rain, wind, sun, and contamination. Three NH_3 diffusion tubes per site and period were placed at 2 m height above ground (see Figure 3.5) after Radiello® instructions (2003). A minimum of two replicates per site are recommended (Thöni, 2004; Dr. Ralf Lumpp, 2005b). Due to first test phase in NCP three replicates per site have been installed. Cartridge and diffusive body changes have been carried out after 12 to 15 days for passive samplers, different due to travelling between stations. At DBW, QZ and WZ two sites were equipped respectively, one close to the meteorological station and the other on an experimental field. At DBW a second experimental field was equipped with passive samplers at three different heights. Furthermore, Radiellos® were installed at Changping another site in the NCP, by Chinese colleagues and analysis results were provided by CAU for comparison. Some contamination of the shelters of the passive samplers occurred at the meteorological station at DBW due to bird faeces (see Figure 3.5). First NH_3 measurements at the three locations in the NCP with passive samplers started in May 2005. Continuous NH_3 measurements during both study years were done at DBW only due to the logistical conditions.

Figure 3.5: Passive sampler in operation: a) interior view of shelter with three replicates; b) at WU, winter wheat, arrow marks energy mast located in agricultural field where samplers were installed; c) at DBW, winter wheat, close to the High Volume Sampler; d) at QZ, winter wheat; e) at DWB, bamboo stick with samplers located in summer maize field; f) at DBW, contamination of shelter by birds (all photos taken in 2005).

Correct handling of passive samplers is essential for reliable NH_3 measurements. Basics of handling with passive samplers are described in DIN EN 13528 (2004), part 3. Additional handling instructions provided by FUB ensured data quality. Main risks exist during change of cartridges of passive samplers as well as during analyses and can lead to contamination. Therefore one-time hand gloves (PE) were always used during handling with Radiellos®. Cartridge change took place in the field. Exposed cartridges were placed into their original tubes which were packed into tight plastic bags. They were stored in a cooling box during travelling between sites; back in Beijing samples were stored in a refrigerator. The cartridges were sent to FUB and analysed by ion chromatography according to VDI (2010). Detailed information on analysis and quality assurance can be found in Seitler & Thöni (2009).

Diffusive bodies have been re-used after FUB (2005) instructions. They were washed with a dish detergent, put into ultra-sonic bath for 20 min, washed with plenty of deionised water and finally dried before re-usage. According to Radiello® manufacturer PM10 may be harmful to diffusive bodies since they can obstruct the pores. Due to high PM pollution in NCP and permanent visible pollution of diffusive bodies by airborne dust, diffusive bodies have been re-used only three times and then have been replaced by new ones.

3.4 NO_x Analyser

In the framework of subproject 1.3 one NO_x analyser (AC31M type) and a NH_3 converter were transported to China in 2006 to perform NO_x and NH_3 measurements. The NO_x analyser operates on the principle of chemiluminescence: The chemiluminescence emitted during the oxidation of nitrogen oxide molecules with ozone can be used to determine the NO concentrations: $NO + O_3 \rightarrow NO_2 + O_2 + h\nu$. Chemiluminescence measurements take place in a reaction chamber. The air passes trough an ozone generator first and flows into the chamber then. The oxygen in the air is partially converted into ozone by means of UV irradiation. A constant flow of sample gas enters the reaction chamber via another entrance noozle and is mixed in it. In order to determine the concentrations of NO_2, the sample gas first passes trough a thermocatalytic converter which reduces NO_2 to NO prior to the analysis: i) operation without converter = NO measurements, ii) operation with converter = NO_x measurements, iii) difference between NO_x and NO measurement = NO_2 concentration (Environnement S.A., 1997). In addition to the NO_x analyser, the NH_3 converter rack enables the NH_3 continuous measurement. The air sampled by the pump of the analyser flows on the one hand, through the NH_3 rack where the NH_3 is oxidized into NO, and then, on the other hand through the molybdenum converter oven where the NO_2 is reduced into NO. The sample goes then into the reaction chambers where the NO_x ($NO + NO_2$) and NO_y ($NO + NO_2 + NH_3$) quantities are measured. The value $NO_y - NO_x$ is the NH_3 quantity in the sample (Environnement S.A., 2002). The instrument can measure either NO_x or NH_3, not both together.

The measuring device was checked and basically calibrated in cooperation with HLUG before transporting to China. Furthermore instructions for reliable NO_x measurements in China were given by HLUG. Control calibration of the NO_x analyser in China was foreseen with portable permeation. Due to logistical reasons the NO_x analyser was tested in China for only almost half a year in 2006. The instrument was installed in the laboratory of CAU first. It was known that the instrument will need some time to run smoothly after the transport from Germany. Such sensitive measuring devices need at least half a year minimum test phase before they can be adopted within monitoring sites (Kettenbach, 2005). It was impossible to stabilize the NO_x analyser in China within given time. Steps which had been trained in Germany did not reach level of continuous running of instrument with valid data. So called mux signals of instrument were not in normal range showing problems with the molybdenum converter. External circumstances made adjusting of the instrument more difficult. On the one hand installation of the instrument was done during beginning of the rainy season. The measuring device is known to be very sensitive to humidity and the laboratory room was not air-conditioned. Especially continuous NH_3 measurements in ppb range are very ambitious in relation to conditions in China as shown also by Hillebrand (2008). On the other hand several energy breakdowns at the university in the summer months hindered continuous working within test phase. Furthermore it can not be excluded that pollution of tubes, filters or other parts of the instrument inside happened during transport although the instrument was fully maintained in China after transport.

3.5 Bioindication experiments

In order to study the effects of nitrogen deposition an active biomonitoring system was tested in 2005 at three sites in NCP and at various locations in SW-Germany as described in Franzaring et al. (2005). Clones of a European grass species (*Molinia caerulea* Moench), which is known to have spread in past decennia in regions with high nitrogen deposition loads, were used for these experiments (using the system of VDI, 2003). *Molinia caerulea* is not native in East Asia but the species *Molinia* is spread with M*olina japonia* in North East China and Korea (Clayton et al., 2008). NH_3 passive sampling with Radiellos$^{®}$ (see chapter 3.3) was run in parallel to the biomonitoring study to test whether growth and nutrient parameters of the test plants were related to gaseous dry deposition.

Clones of the bioindicator test plant species Purple Moor Grass, *Molinia caerulea*, were propagated from one single specimen originating from an oak forest edge at 8°28′E, 51°44′N from 83 m asl. In order to supply enough plant material the ramets were cultivated and propagated once more in the institute garden at University of Hohenheim during two years prior to the study. In February 2005, small ramets were torn off manually from the dense mother tussocks. After completely washing off soil from the plants, shoots were cut down to the basal nodes and roots were cut to a length of 10 cm. Clones of 5-8 g fresh biomass were then transplanted into sand filled pots and the start weights were noted for each of the 80 propagates. Pots were equipped with glass fibre wicks for automatic watering. The plant clones remained in the greenhouse until exposure in the field without application of fertilisers. Watering was made with deionised water when the water reservoir of the VDI-system was nearly empty. All of the propagated ramets survived the transplanting and were exposed at DBW, WU and QZ sites in China and 15 sites in SW-Germany in line with the standard method VDI 3957 Part 2 (VDI, 2003). Figure 3.6 shows different stages of the bioindication experiment in China. At WU and QZ, 6 replicate pots were exposed respectively, and at DBW 14 replicate pots, yielding 26 monitoring systems in NCP in total. These remained at the different field sites for three months in summer 2005. At the end of the exposure period, plant heights were measured and numbers and dry weights of green and senescent leaves, stems and flowers and the dry weights of roots were determined. The amount of rainfall and of water supplied during plant exposure was noted and a water sample was taken at the end of the study for the analysis of NH_4^+ and NO_3^- concentrations.

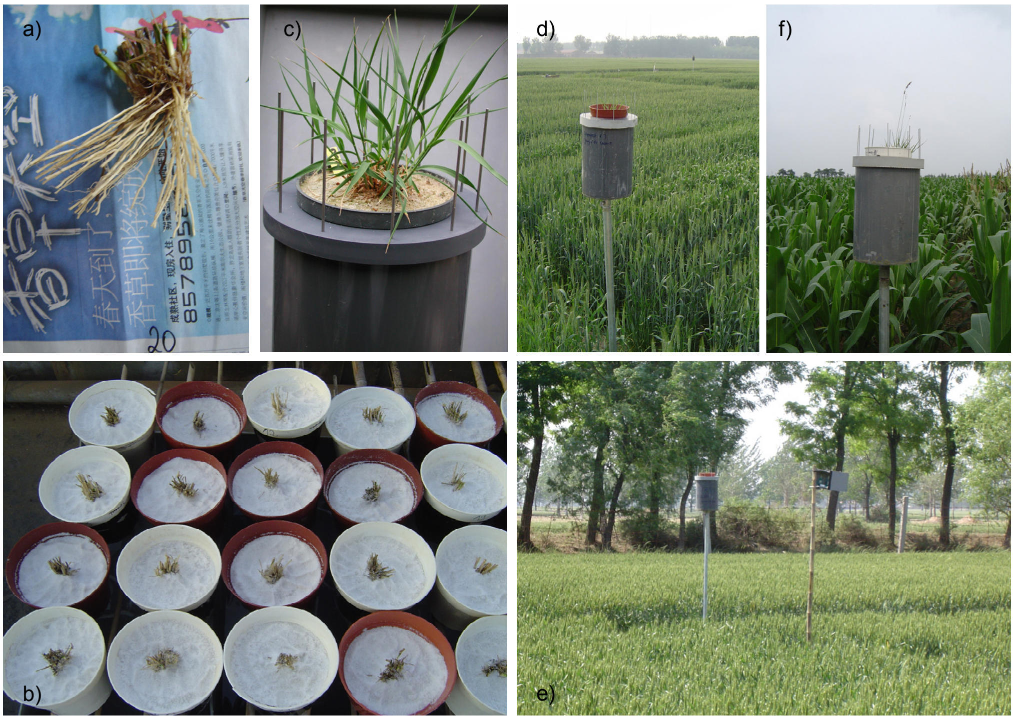

Figure 3.6: Bioindication experiment with *Molinia caerulea*: a) View on a ramet before transplanting into sand filled pot in greenhouse of CAU, b) Plant pots with clones in greenhouse of CAU, c) Ideal plant in VDI system, d) View on plant bioindicators at DBW, e) View on plant bioindicators and Radiello® system at QZ, f) View on plant bioindicators at WU (all photos taken in 2005).

3.6 Filter analyses (test phase)

In order to test the determination of particulate ammonium and nitrate on glass fibre filters a series of aliquots of these filters (5 cm diameter disc for filter sample) with PM loads of the spring season 2005 were ultrasonically extracted according to Steubing & Fangmeier (1992). Ammonium and nitrate were measured by a Continuous Flow Analyzer; total N was measured by an Elemental Analyzer (EA) at LA Chemie, University of Hohenheim.

3.7 Mass spectrometry

Nitrogen isotopic compositions were determined by combusting GF and QMA filters with PM samples using a Delta^{Plus} XP isotope ratio mass spectrometer (EA/IRMS, ThermoFinnigan). An aliquot of sample (5 mm diameter disc for filter sample) was placed in a tin cup, introduced into EA and then oxidized in a combustion column packed with CuO at 1020 °C. The derived NO_x (and CO_2) was introduced into the reduction column to reduce to N_2 at 650 °C. The resulting gasses were then isolated on a gas chromatograph installed in the EA system and their amounts were measured with a thermal conductivity detector. N_2 and CO_2 gases were transferred to EA/IRMS via an interface (ConFlo II) for isotopic ratio measurement. The isotopic composition of N was calculated using the equation

$\delta^{15}N = [(^{15}N/^{14}N)_{sample} /(^{15}N/^{14}N)_{standard} - 1] * 1000.$

Acetanilide was used as standard to calculate total nitrogen and $\delta^{15}N$ ratio. Samples were analyzed at least in duplicate with a maximal difference of 0.089 % and 0.206 ‰ in total nitrogen and its $\delta^{15}N$, respectively. All the data reported here were corrected for field blanks.

3.8 Climate data

Meteorological data, including temperature, relative humidity, wind speed, wind direction, and rainfall, were collected simultaneously at DBW. Meteorological data for WU and QZ do not include wind data. Climate data stemmed from the CAU and were provided by Dr. Ciu in 2007. Measurements of bulk deposition at all three sites were performed and provided by Y. Zhang (2006).

3.9 Statistics

Data input was done using Excel 2003 for Windows. Descriptive analysis of data was done with SSC STAT. For statistical calculations of wind data the program WRPLOT VIEW (Lakes Environmental Software Version 6.5.1) was used. Isodat NT (Version 1.5) was used for instrument control of IRMS and data evaluation of isotopic values.

4 Results and Discussion

4.1 Meteorological conditions

Meteorological parameters such as T, RH and WS measured at DBW were calculated from the hourly values provided by CAU and were used to obtain daily, monthly and seasonal averages. Wind direction data were calculated from the 10-min values provided by CAU. Rainfall was collected at daily intervals as described in chapter 3.7. The data was examined for seasonal trends, with the seasons defined as follows: autumn – September and October; winter – November until February; spring – March until May; summer – June until August.

DBW climatology is characterized by cyclic and contrasted seasonal conditions. The site is a Dwa or Dwb climate according to the KÖPPEN classification (Heyer, 1993). Monthly averages of temperature, air humidity and wind speed are shown in the Figures 4.1 and 4.2 for both study years. The mean annual temperature was 10.4 °C and 11.8 °C for the years 2005 and 2006, respectively. The mean annual relative air humidity was 56 % and 61 % in the years 2005 and 2006. During August the relative humidity reached a maximum with averaged 83 % in both years. The wind flow during both years was mainly from south east to south west (around 50 %) and from west to north (around 30 %) (Figure 4.3). Wind speeds were generally low and showed an inverse annual course in comparison with air humidity. The highest wind speeds were recorded during spring with averaged 3 m s^{-1} and maximum peaks up to 6 m s^{-1} comparable with reported meteorological conditions during the same season by Duan et al. (2006). Spring in DBW was generally of low RH and stronger wind speeds resulted in frequently dust events as often reported for the whole of the north China (Chan & Yao, 2008; Han et al., 2007b). During summer time the wind speeds decreased and reached minimum values in August in both years. In summary, light winds with wind speeds less 2 m s^{-1} were predominating during both years as also reported for Beijing by Wu et al. (2008).

Climate conditions at DBW were characterized by significant day-to-day and night-day variability which will be shown in the following chapters on PM results. Although meteorological conditions appeared comparable in 2005 and 2006, the temperature and RH weekly variability was significant, which called for careful examination of these two parameters in the interpretation of detailed data. The precipitation pattern showed a clear seasonality between a dry winter season and a rainy summer season.

During the study period of PM levels in 2005 at DBW, the sum of precipitation was about 406 mm whereas 87 % of the sum was recorded during the rainy monsoon season (also called wet season), namely during June, July and August. The mean annual precipitation ranges between 500 and 650 mm for the Beijing region (Rumbaur, 2009). Zhao et al. (2009) recorded the total sum of 470 and 566 mm in Beijing in the year 2005 and 2006, respectively. The total annual sum of precipitation at DBW in 2005 and 2006 is unclear due to some data gaps which does not relate to the study period of PM. The rainfall data used in the present data for analysis of PM data is reliable since the precipitation events at DBW were recorded correctly during PM study periods.

In general, Wuqiao and Quzhou are characterized by warmer mean annual temperatures (14.5 °C) than DBW. Precipitation normally increases from north to south in the NCP leading to higher mean annual rainfalls in the south of the NCP, ranging from 637 to 828 mm (Rumbaur, 2009).

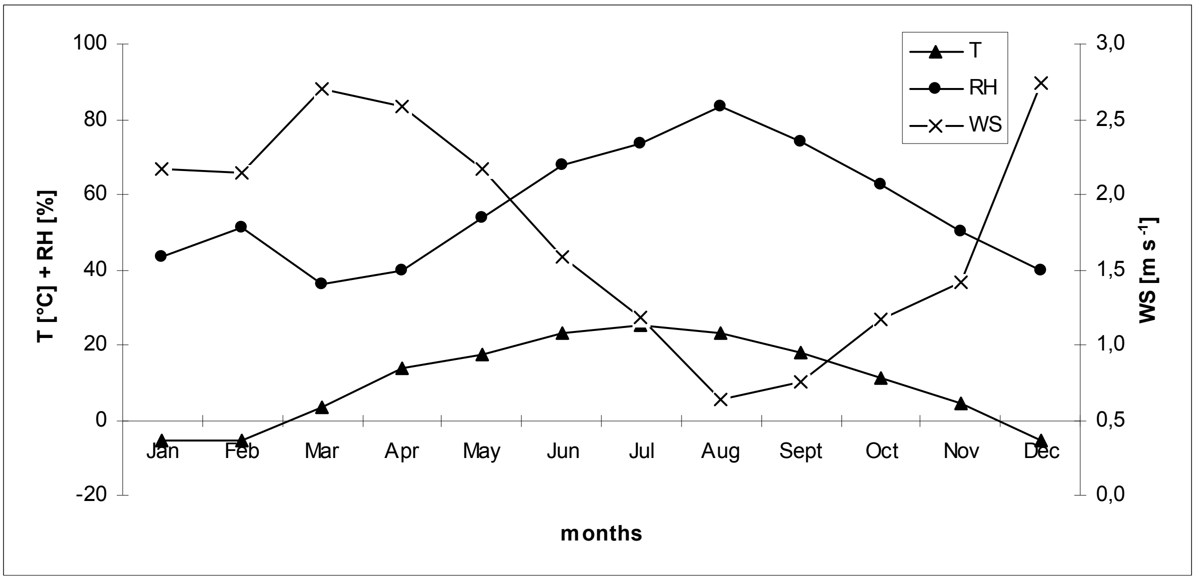

Figure 4.1: Monthly averaged temperature (T), relative humidity (RH) and wind speed (WS) recorded at 1-h intervals at DBW in 2005. Data were provided by Dr. Cui, CAU, in 2007.

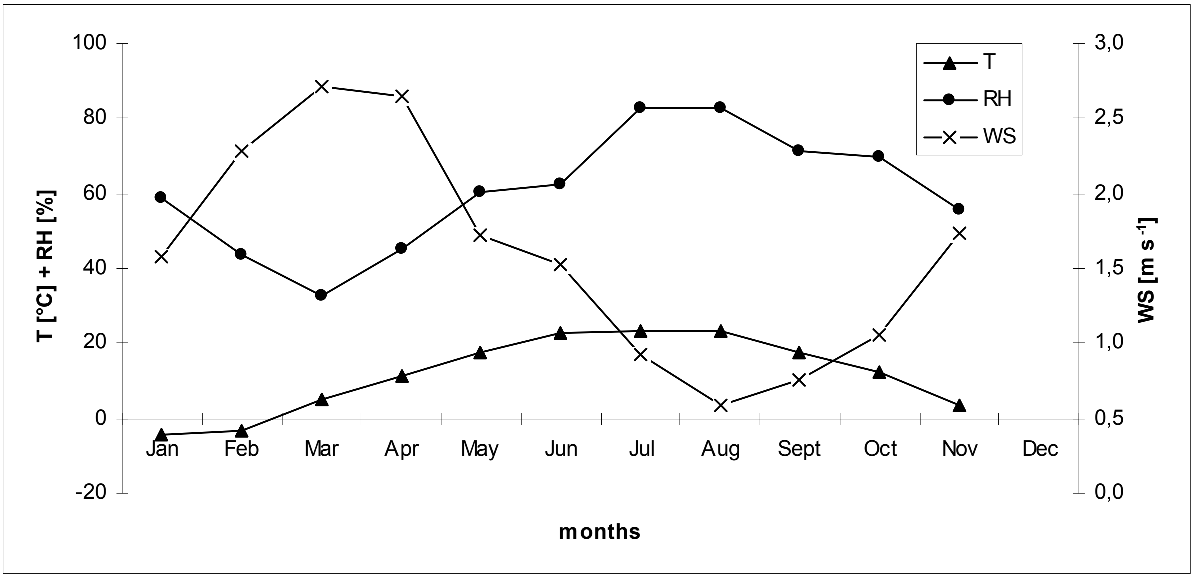

Figure 4.2: Monthly averaged temperature (T), relative humidity (RH) and wind speed (WS) recorded at 1-h intervals at DBW in 2006. Data were provided by Dr. Cui, CAU, in 2007, data from December is not available.

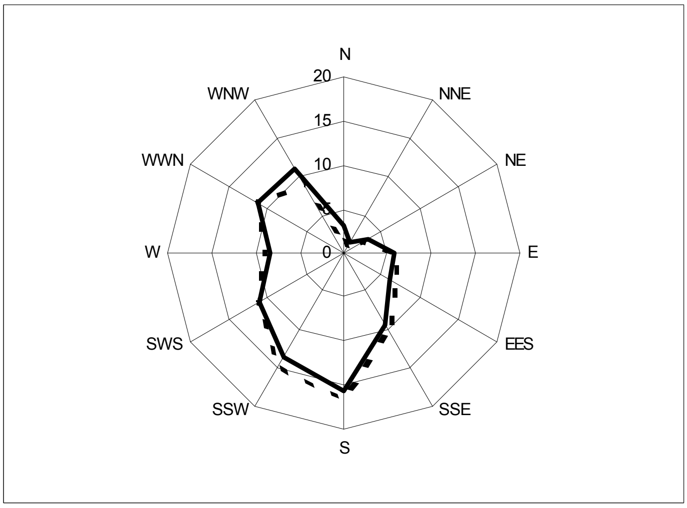

Figure 4.3: Annual wind roses indicating the frequency of wind directions obtained in 2005 (black line) and in 2006 (broken line) at DBW. Wind data are based on 10-min values and were provided by Dr. Cui, CAU, in 2007.

For latter analysis of seasonal variations of pollutant concentrations at DBW and in the NCP in general, it appears critical to also consider the influence of the atmospheric boundary layer height. "Indeed, the boundary layer height displays a significant seasonal variability with weekly average values ranging from 300 m to 900 m" as shown for the Beijing region by Guinot et al. (2007, p. 7). "This variation has a direct influence on atmospheric pollutant concentrations, from enhancement in winter (when boundary layer height is at minimum) to dilution in summer (when boundary layer height is at maximum), and needs to be considered to account for ventilation effects, too" (Guinot et al., 2007, p. 7).

Overall, diurnal, seasonal and even year-to-year variability of meteorological conditions for the Beijing region was often reported (Zhao et al., 2009; Guinot et al., 2007) and can cause differences in the diurnal and seasonal variations in PM concentrations from one year to the next. In the following chapters measured PM concentrations were compared with published values from various references, mainly measured before 2005. Only few published PM data exist from 2005 and 2006 or later. Moreover, differences in locations and sampling intervals of other PM campaigns might also contribute to discrepancies in comparison with own PM data.

4.2 Particulate Matter

From April 2005 to November 2006, totals of about 700 gravimetric measurements of PM concentrations were obtained at DBW. The daily and the hourly PM concentrations were calculated from gravimetric measurements and were used to obtain monthly and seasonal averages.

In 2005, the determination of PM at DBW lasted from 26th of April to 27th of December. One year later, particulates were collected between 5th of August and 26th of October 2006.

4.2.1 Filter conditions

Due to the fact that two filter types (QMA and GF10) were used during the study period, their gravimetric measurement results were compared with at the same time. During a short PM10 measuring period at the University of Hohenheim, both filter types were set up one day after another while using the High Volume Sampler, in total 18 days. Figure 4.4 demonstrates that the difference of the gravimetric measurements between these two filter types is not significant. Furthermore, investigations on repeated gravimetric measurements of one filter type with same PM loads were done. These control measurements of loaded GF10 and QMA filters showed averaged differences of 0.013 µg m^{-3} (n=21) and 0.002 µg m^{-3} (n=22), respectively. These results indicate that possible gravimetric weighting differences caused by different filter material might be negligible in relation to the high PM loads in China which will be reported later.

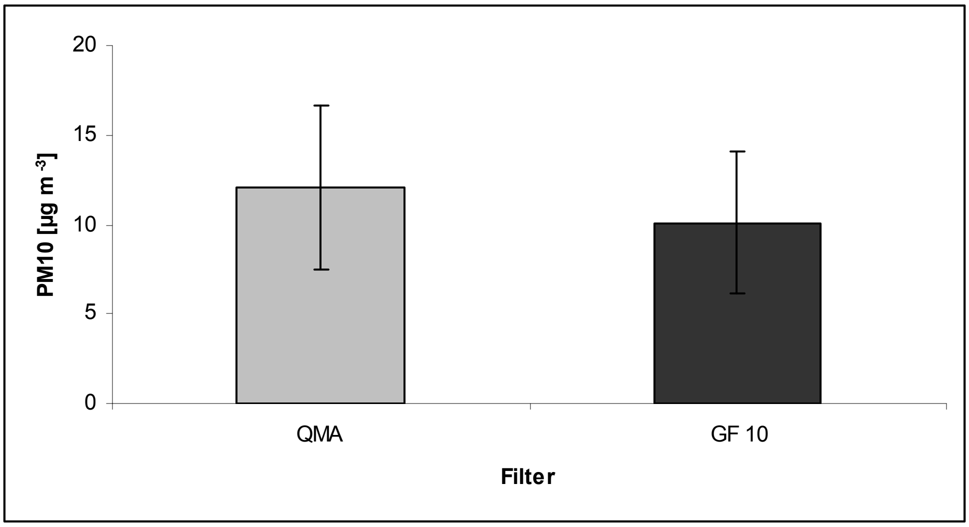

Figure 4.4: Comparison of PM10 concentrations sampled with quartz microfibre (QMA) and glass fibre (GF 10) filters (n=18) at the University of Hohenheim, Germany, in May and June 2006. Error bars represent the standard deviation.

Regarding the ^{15}N measurements some preparatory work was done before since there were no experiences available regarding the isotopic measurements of PM loaded GF or QMA filters. Due to the PM sampling the majority of ^{15}N measurements were conducted with glass fibre filters. First isotopic measurements showed low N values but high C values due to the filter material. Under these circumstances several isotopic measurements with different standards were carried out. Furthermore, different sizes of tin cups or a CO_2 trap within the mass spectrometer were tested due to the filter material.

In order to ensure the quality of data, several mass spectrometric test series of filter blanks were conducted before starting with ^{15}N measurements of the samples. Firstly, the homogeneity of one filter was investigated by using different pieces of one filter for the isotopic measurements. Secondly, filter blanks from different filter packages were tested. Thirdly, ^{15}N results of filter blanks of both filter types (GF10 and QMA) were compared with by using the same method in the mass spectrometer. An overview on obtained results is given in Table 4.1. Obviously, there were differences in filter blanks due to different filter packages as shown for the QMA filters. Therefore, five filter blanks were measured like samples during each run of the mass spectrometer in order to obtain a reliable mean blank concentration which was subtracted from each sample by hand and not by the instrument.

Table 4.1: Standard deviation of total nitrogen (N) and its isotope ratios ($\delta\ ^{15}N/^{14}N$) of glass fibre (GF10) and quartz microfibre (QMA) filter blanks (each subsample was analyzed in duplicate)

Tests	**Filtertype** **GF10**	 **QMA**
5 subsamples out of 1 filter		
N [%]	0.0402	0.0010
$\delta^{15}N/^{14}N$ [‰]	0.3256	0.5982
5 subsamples out of 5 filter		
N [%]	0.0031	0.0033
$\delta^{15}N/^{14}N$ [‰]	0.1878	2.3872

Regarding the N measurements it should be noted that aerosol samples collected on quartz fibre filters may have two types of sampling artefacts as described by Kundu et al. (2010, p. 5): (i) adsorption of gaseous HNO_3 and NH_3 onto aerosols already collected within the sampler or onto the collection substrate and (ii) dissociation of NH_4^+ salts such as NH_4NO_3 on the filter.

4.2.2 TSP – Atmospheric concentrations

Atmospheric concentrations in 2005

Daily averaged TSP concentrations were determined from 26th of April to 9th of May 2005 at DBW. Figure 4.5 shows the values covering one dust storm event followed by days with wash out and thus removal of particulates from the atmosphere caused by rain. The TSP concentrations ranged from 113 to 905 µg m^{-3}. The date give an average TSP of 403 µg m^{-3} (n= 14), which compares well with measurements performed by Oanh et al. (2006) and Wang et al. (2007) during spring in Beijing, including also dust storm days. The average TSP concentration of 174 µg m^{-3} (n=4) during the days after the rainfall at DBW is similar to published average TSP of 240 µg m^{-3} or 153 µg m^{-3} for two sites in the Beijing region during spring, excluding dust storm events (Wang et al., 2007). As can be seen in the Figure 4.5, the increasing wind speed values with averaged 3 m s^{-1} are followed by increasing TSP levels until the beginning of the precipitation which led to lower TSP levels. Obviously, the increasing dust load deposited on filter samples caused the elevation of TSP concentration and may be also associated with a considerable coarse fraction of dust particles and mineral aerosols leading to heavier weight than the same amount of fine particles.

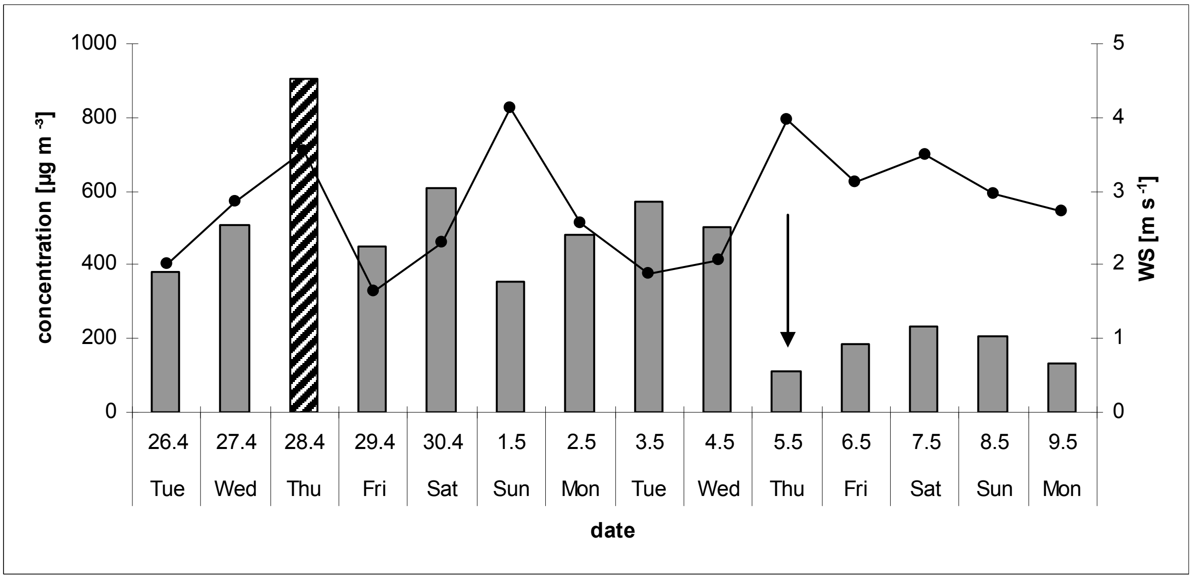

Figure 4.5: Daily TSP concentration and wind speed (WS) at DBW from 26th of April to 9th of May 2005. Patterned column marks the peak of a dust storm event on 28th of April. Arrow marks the wash out of particulates in the air caused by a rain event starting at the very early morning on 5th of May (13.6 mm precipitation on the day). Precipitation and WS data were provided by Dr. Cui, CAU, in 2007.

TSP observations at DBW reflecting the dust storm event can also be confirmed by own observations of the colours of exposed filters. Figure 4.6 shows one yellow coloured filter on the 19th of April 2005 instead of black or grey coloured filters as sampled at the days before indicating the beginning of the dust storm event. It can be seen that the yellow coloured filter is strongly related to north western winds which probably carried desert dust to DBW in contrast to the days before with south and south east winds leading to the black and grey coloured filters. It is known that mineral aerosols, mobilized during sand and dust storms in arid and semi-arid continental regions, are the dominant component of the atmospheric aerosol over large areas of the world. The Asian deserts are the second largest contributor emitting about 10-25 % of these aerosols worldwide (WMO, 2009). The Chinese desert regions such as the central Gobi Desert and the influence of the East Asian monsoon are considered to be one of the major sources for Asian dust (Wang et al., 2004b). It is also known that ABCs and dust extended from East Asia into the North Pacific during spring (Ramanathan & Feng, 2009). The fact that Beijing has been identified as one of the ABC hotspots among 13 other Asian mega cities (Ramanathan et al., 2008) shows the influence of the regional plume to PM air pollution in the NCP. Due to China's topography, strong north, west and northwest winds have an almost unhindered path east and southeast across the deserts before reaching the NCP and Beijing. Very high TSP daily mass concentrations and low visibility in Beijing are normally reported due to dust storm events in spring (Zhang et al., 2010b; Chan & Yao, 2008; Wang et al., 2007). Not only Beijing but also the study region of the NCP belongs to those regions in

China in which dust storm events occur (Wang et al., 2005b). Dillner et al. (2006) reports TSP maxima of 930 µg m^{-3} on a dust storm day in Beijing during spring comparable with the highest measured TSP concentration of 905 µg m^{-3} on the 28th of April 2005 in the present study. Hu et al. (2008) and Wu et al. (2009a) are also reporting on one dust case for Beijing region at exactly that day.

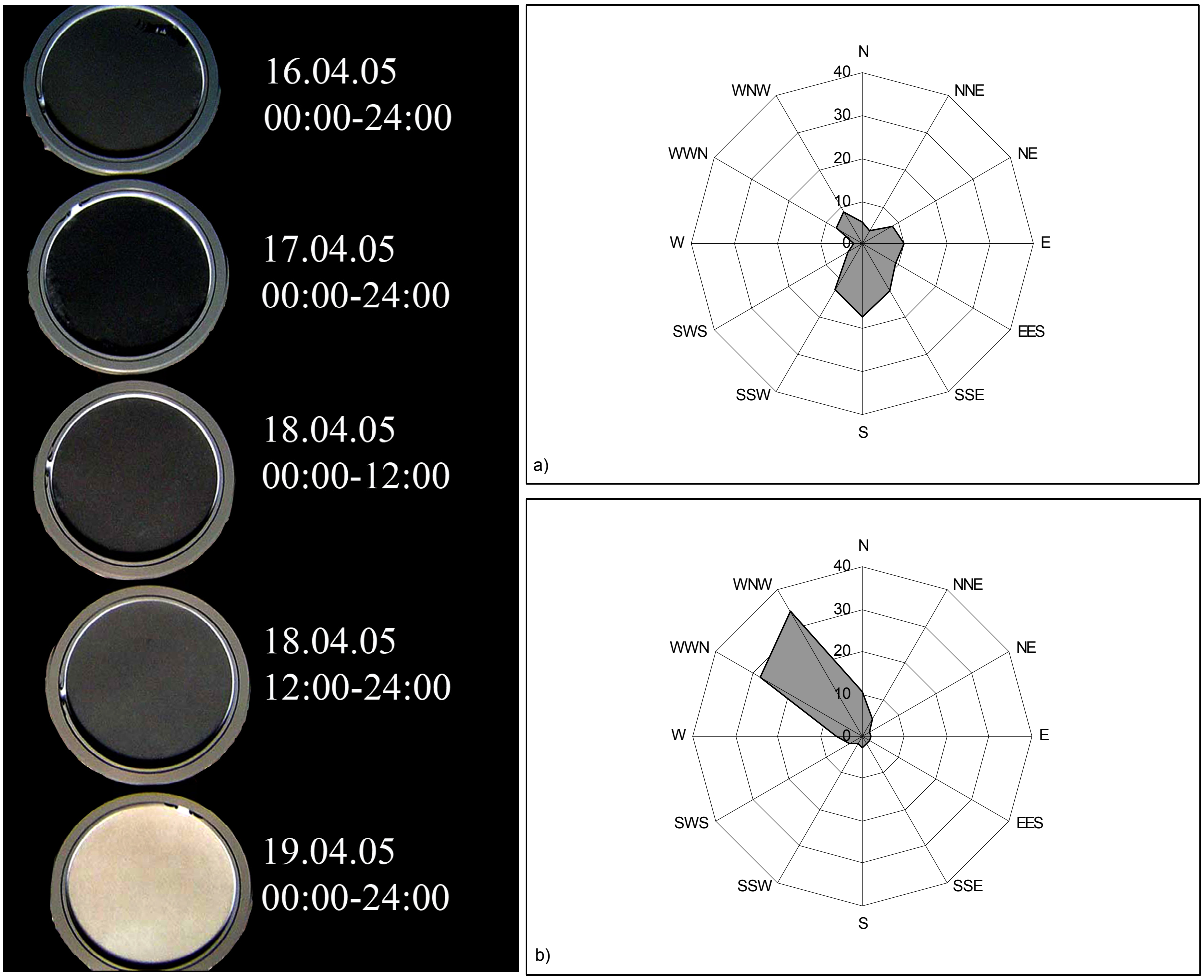

Figure 4.6: Loaded filters covering the period from 16th to 19th of April 2005 clearly showing the beginning of dust storm event on the 19th of April. Wind roses indicating the frequency of wind directions obtained a) from 16th to 18th of April 2005 and b) on 19th of April at DBW. On 19th of April wind direction changed and wind flows came mainly from north west leading air masses from desert regions to DBW as shown by yellow coloured filter. Due to the first test phase of the High Volume Sampler at DBW these filters were not weighted. Wind data are based on 10-min values and were provided by Dr. Cui, CAU, in 2007.

Wind roses were used to investigate the relationship between wind speed, wind directions and the TSP concentration. Analysis of wind data reveals that the wind flow during TSP study period at DBW came mainly from the south which corresponds with measurements in Beijing during spring done by Zhao et al. (2009). Nevertheless, Figure 4.7 shows that the highest wind speeds and the highest TSP concentrations came from the north-westerly as well as from the southerly directions. The north-westerly wind flows led to the assumption that air masses from the desert regions of China were blown to the DBW site. NASA (2005a) reported for the 28th of April, the day with the highest PM loads that the dust storm originated in the Gobi Desert near the border with Mongolia (Figure 4.8). The yellow coloured filters during the sampling period confirmed the assumption of PM transport over large distances. However, high PM concentrations in Beijing during dusty days do not necessarily mean that particles from the desert were the only source (Dillner et al., 2006). Tang & Peng (2002) found that regional dusts affect Beijing region due to land degradation in Hebei province. Those long-range transported dust particles could enter DBW site from southerly directions since the main part of Hebei province is located in the south of DBW (see also Figure 3.1) and might explain the TSP concentrations stemming from the south. Analysis of wind data underlines these assumptions showing remarkable differences in wind directions between days (Figure 4.9) leading to different colours of collected dust on filters (Figure 4.10). As can be seen e.g. on the 26th and 30th of April (also shown in Figure 4.10 as yellow filter) wind flow came mainly from north west whereas one day later the wind direction changed completely to the south westerly direction. The wind flow during the TSP peak concentration (28th of April) came from both north and south directions leading to the assumption that the collected dust may be a mixture of different natural and anthropogenic sources from different regions.

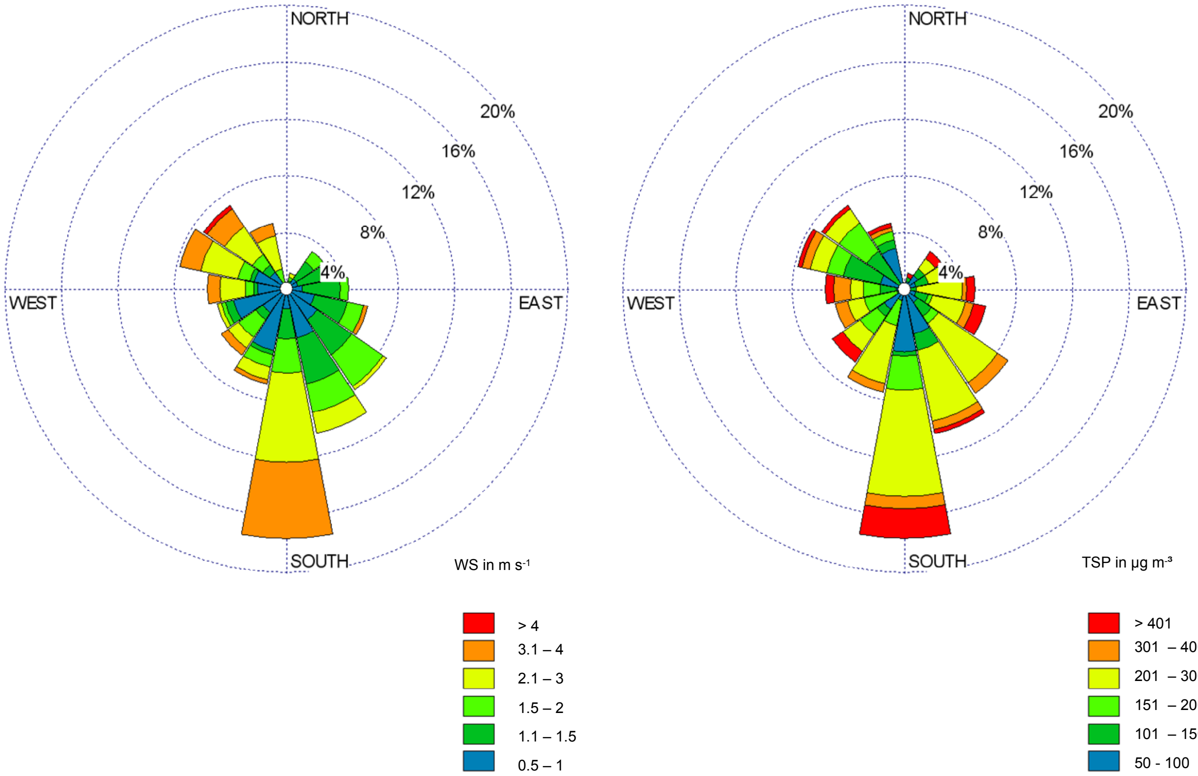

Figure 4.7: Wind roses indicating the frequency of directions along wind speed (WS) classes (left) and classes of TSP (right). Data are based on 12-h values between 26th of April and 9th of May 2005. Wind data were provided by Dr. Cui, CAU, in 2007.

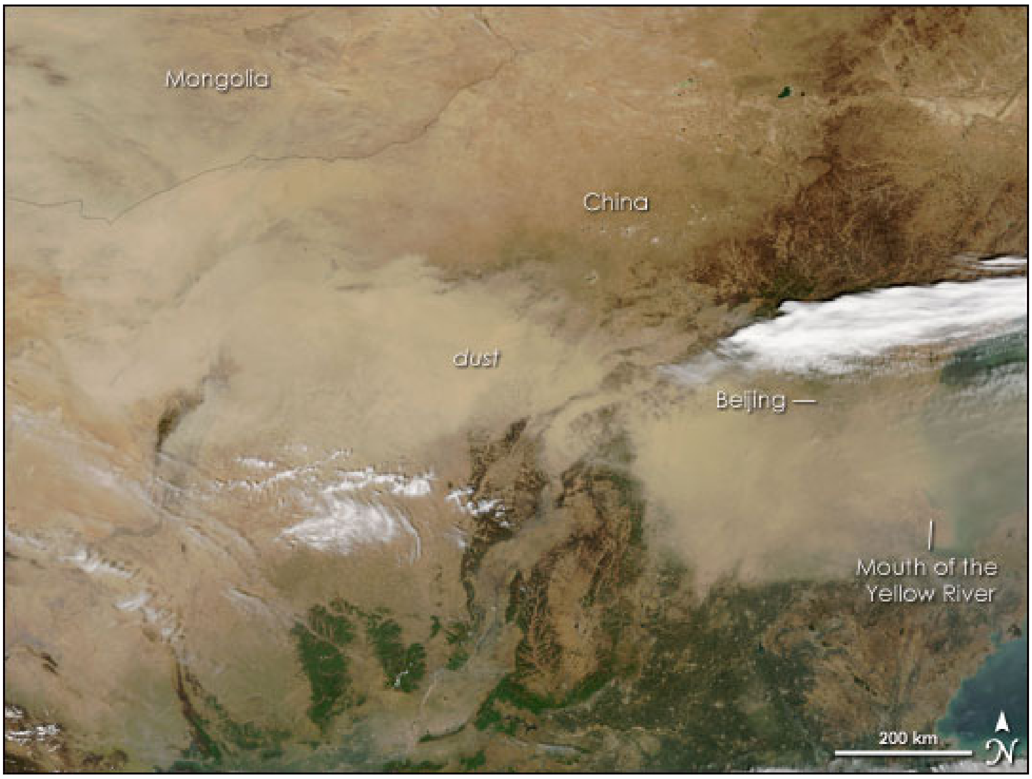

Figure 4.8: A river of dust stretched hundreds of kilometres over China, including the NCP, on April 28, 2005 (Source: NASA, 2005a).

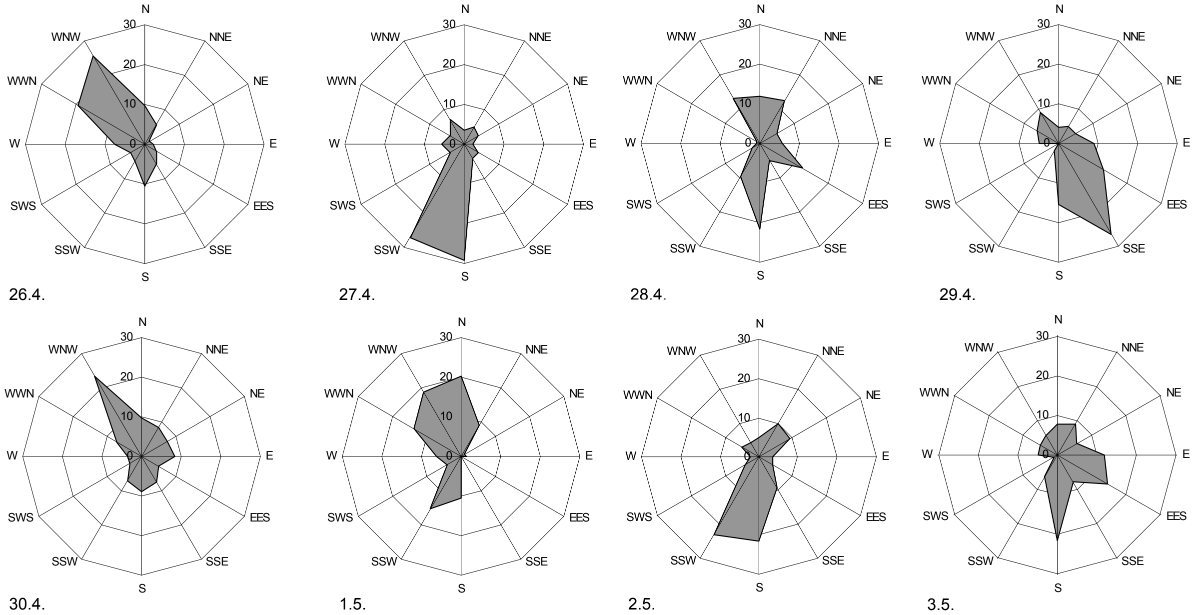

Figure 4.9: Daily wind roses indicating the frequency of wind directions obtained from 26th of April to 3rd of May 2005 at DBW. Data are based on 10-min values and were provided by Dr. Cui, CAU, in 2007.

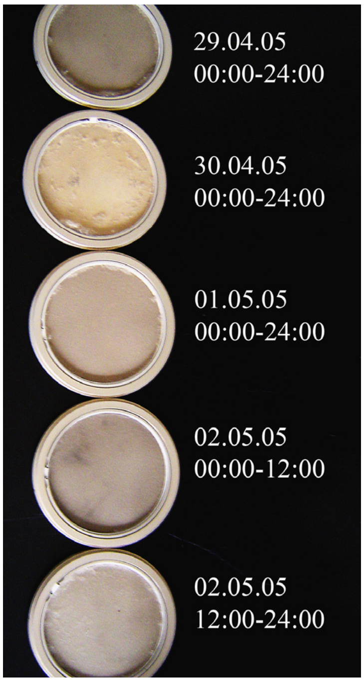

Figure 4.10: Loaded filters covering the period from 29th of April to 2nd of May 2005. Wind flows from south east leading air masses from south of Beijing city to DBW as shown by dark grey coloured filter on 29th of April. Wind flows from north west leading air masses from desert regions to DBW as shown by yellow coloured filter on 30th of April.

Atmospheric concentrations in 2006

In 2006, daily averaged TSP concentrations were observed in the period from 10th of August to 24th of October at DBW. Daily TSP values ranged from 91 to 659 µg m^{-3}. Rain events during August and in the beginning of September led to wash out of particulates and thus TSP levels were lower (Figure 4.11). Agricultural activities including harvest of summer maize, ploughing and tillage during October were the main reason for high TSP levels at DBW with the maximum daily TSP concentration of about 659 µg m-3 measured on 6th of October 2006.

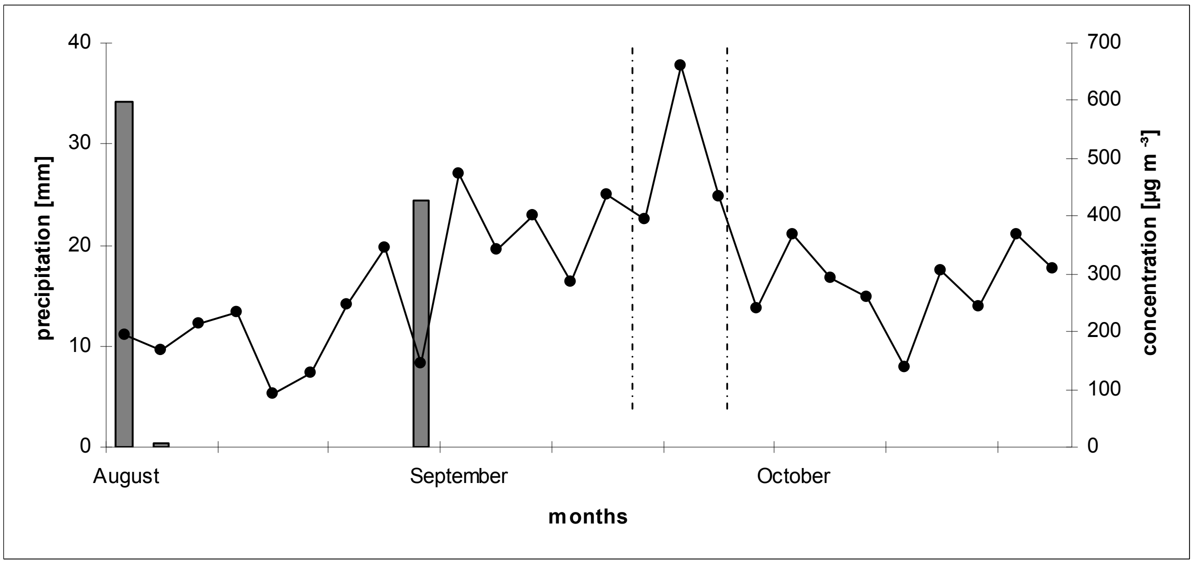

Figure 4.11: Daily TSP concentration and precipitation at DBW from 10th of August to 24th of October 2006 with averaged mass concentration of 297 ±127 µg m-3 (n=26). Marked time period from 4th to 7th of October 2006 includes harvest of summer maize, ploughing and tillage at DBW. Precipitation data were provided by Dr. Cui, CAU, in 2007.

4.2.3 TSP – Temporal variations

Temporal variations in 2006

In 2006, the mean TSP concentration in October of 342 µg m-3 was much higher than for September (250 µg m-3) and August (192 µg m-3). A negative relationship between TSP levels to wind speed ($R^2 = 0.6$) was observed in September (Figure 4.12) indicating that higher wind speeds removed particulates from the atmosphere and prevented their accumulation which led to lower PM levels. TSP levels of October were only slightly negative related to wind speed ($R^2 = 0.4$). This finding indicates that TSP levels were more influenced by other factors. The peaks of TSP concentrations were clearly related to the harvesting time. The harvest of summer maize lasted from 4th to 7th of October and included different steps of field cultivation for winter wheat as well. Furthermore biomass burning has often a remarkable contribution to atmospheric pollution in the NCP and could be detected by own observations during first weeks of October in whole Hebei province leading to higher PM levels generally. Own impressions were heavy burnt smells in the air over NCP, especially during and after the harvest week. It is widely known that domestic burning of crop residues takes place in rural areas of China. The pollutant emissions from biomass burning, such as PM, are estimated to contribute substantially to the aerosol pollution in Beijing region (Duan et al., 2004). There is still a general lack of understanding concerning emissions from rural China but the residue burning of wheat straw and corn residues, the main crop residues in the NCP, is considered to have the highest emission factors from all crops in China (Cao et al., 2008). The averaged TSP concentration in September and October at DBW was determined with 296 ±65 µg m^{-3}. Han et al. (2007b) reported on similar data with monthly averaged TSP values during autumn in Beijing (238 ±90 µg m^{-3} from September to October). The slightly higher TSP levels at DBW than in Beijing city may be explained by the position of the measuring device. Since the particle sampler in Beijing was located on a roof of a university, the High Volume Sampler used in this study was located directly on the agricultural field at DBW. Agricultural activities and field cultivation nearby the sampler during a vegetation period may have much more affected the particle sampling at DBW than the particle sampling on a roof in Beijing city. Contributions of primary (mechanical activity) and secondary (biomass burning) sources to PM levels during autumn 2006 will be also discussed in chapter 4.2.8.

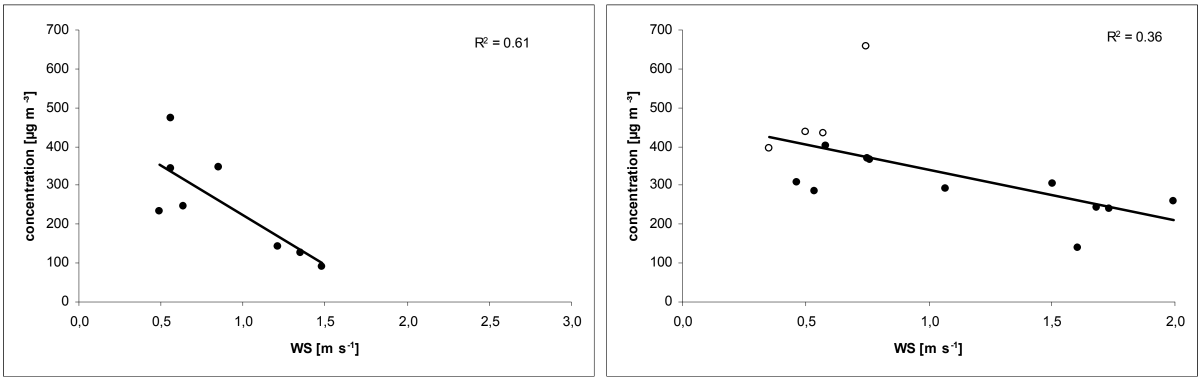

Figure 4.12: Relationship between TSP concentrations and wind speed (WS) determined at DBW during September (left) and October (right) 2006. Circles mark the harvesting time. TSP data are based on 24-h values. WS data were provided by Dr. Cui, CAU, in 2007.

It is notable that TSP concentrations showed more different seasonal variations than diurnal ones. The highest TSP concentrations appeared in spring as shown by other authors (Zhang et al., 2010b; Han et al., 2007b) due to the fact that the NCP, including Beijing, are subjected to dust storms in the spring that produce high PM concentrations. In general, the TSP levels during both years followed no weekly cycles and showed a large variability over the weekdays.

Most publications on TSP levels in China report on daily (12-h or 24-h) measurements but not on hourly ones. Due to the lack of publications on diurnal variations of TSP levels in China, the hourly concentrations measured at DBW are unique.

Hourly measurements of TSP were done on 1st of September 2006 only. The measuring day was a day without extreme weather events or agricultural influences at DBW. The referring concentration data is shown in Figure 4.13. Three peaks were recorded during the day whereas the TSP concentrations at evening were remarkable higher than those after midnight and in the early morning. Beginning from midnight the TSP concentration decreased from 260 µg m^{-3} to a minimum of 131 µg m^{-3} at 4:00 Hrs. in the morning. After that decline the TSP concentration rose up again to around 260 µg m^{-3} from 6:00 to 8:00 Hrs. on Friday morning. Between 13:00 and 15:00 Hrs. was a slight decline of the TSP concentration up to 200 µg m^{-3}. Afterwards the TSP level arose again until the maximum peak of 319 µg m^{-3} between 19:00 and 20:00 Hrs. followed by TSP concentrations up to 250 and 260 µg m^{-3} until midnight. Due to the suburban location of the DBW site the hourly TSP concentrations followed "the clock of a city". In the course of the day urban influences from Beijing city such as the increase of traffic in the early morning and in the evening as well as the decrease of traffic during lunch break are visible in the Figure. A normal working day in China starts at 8:00 Hrs, includes a lunch break (often with midday rest) from 13:00 to 15:00 Hrs. and ends between 18:00 and 20:00 Hrs. These times are relatively strict and most employees do not have flexible working times. Therefore the urban traffic can be related easily to those times and can be confirmed by own observations during the study period. The high TSP levels during late evening can be related also to the traffic. Especially the slight increase between 19:00 and 20:00 Hrs. causing the maximum peak may be related to the truck traffic. Heavy diesel trucks were forbidden to enter into the urban area of Beijing from 8:00 to 19:00 Hrs. (Wu et al., 2008). After 19:00 Hrs. many trucks carry material to and from construction sites in Beijing region. Especially near DBW site, new construction sites have been established and the surroundings developed very fast from a rural and partly suburban area to an urban one with paved streets and more traffic. Therefore, truck traffic strongly influences the increase of particle concentration in the night at DBW which will be also shown for PM10 and PM2.5 measurements later. Wind speed was low on 1st of September so that most of TSP may have originated from nearby sources.

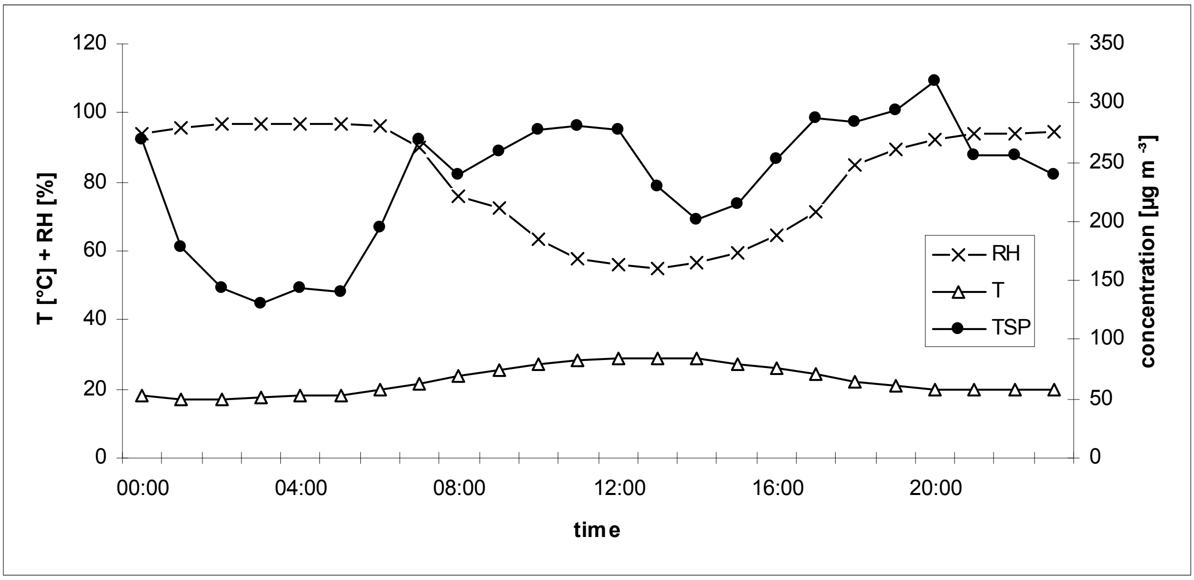

Figure 4.13: Diurnal variation of TSP concentrations recorded at 1-h intervals at DBW on 1st of September 2006. Daily averaged mass concentration was 235 ±54 µg m^{-3} (n=24). T and RH data were provided by Dr. Cui, CAU, in 2007.

4.2.4 PM10 – Atmospheric concentrations

Atmospheric concentrations in 2005

Observations of PM10 were done from May to September 2005 at DBW. The results are presented in Figure 4.14. The levels of daily PM10 concentrations at DBW exceed European (50 µg m^{-3}) and even Chinese (150 µg m^{-3}) thresholds by far. The EU standard for the number of tolerated daily exceedances - no more than 35 days per year - is not met at DBW. Results of the PM10 measurements in 2005 showed 126 exceedances of the daily mean European threshold in only 128 days. The daily PM10 concentration averaged 168±73 µg m^{-3} and was three times higher than the European threshold over the complete sampling period and corresponds to published average PM10 levels during these months recorded to be 180 µg m^{-3} (n=89; Oanh et al., 2006). In comparison, the number of exceedances of the European daily mean threshold in rural European regions is less than 20 times per year (BUWAL, 2005). Moreover, the Chinese threshold is also not met at DBW. About 52 % of the measured daily PM10 values were higher than the daily Chinese threshold, also named Chinese Grade II standard.

In general, the PM10 concentrations mirrored the course of agricultural activities at DBW such as harvests and irrigation events. The maximum daily PM10 of 412 µg m^{-3} represented the harvest of winter wheat done on 18th of June 2005 at DBW. Another daily PM10 peak with 262 µg m^{-3} showed the harvest of spring maize, the second harvest during the year, on 19th and 20th of September 2005. Low daily PM10 concentrations of 128 µg m^{-3} recorded on 26th of

May and 118 µg m^{-3} on 4th of July 2005 were clearly related to those days where agricultural fields at DBW had been irrigated. Furthermore, changes of daily PM concentrations over time can be related to the occurrence of rainfall, with lower PM10 levels on days with or after precipitation events and thus wash out of particulates from the air as shown e.g. for 23rd of July 2005 with 46 µg m^{-3} PM10 and 108 mm precipitation. During the study period of PM10 levels air humidity and temperature averaged to 72±13 % and 22±3 °C, respectively (Figure 4.15). PM10 levels did neither show a relationship to air humidity nor to temperature during whole study period but for certain time periods. On the one hand high PM and high RH values were noted on the same day. High air humidity in relation with low wind speed definitely caused the swelling of particles. On the other hand there were also very low PM and high RH values on one day. The highest RH values with 96 % and 98 % were related to the lowest PM10 values with 28 µg m^{-3} respectively 46 µg m^{-3}. Heavy rainfalls occurred during these days and were the reason for the low PM levels.

As indicated in Figure 4.14 some high PM peak concentrations may be related to wet sample filters. Gravimetric measurements made in China could not exclude such measuring errors because no air conditioned weighing room was available.

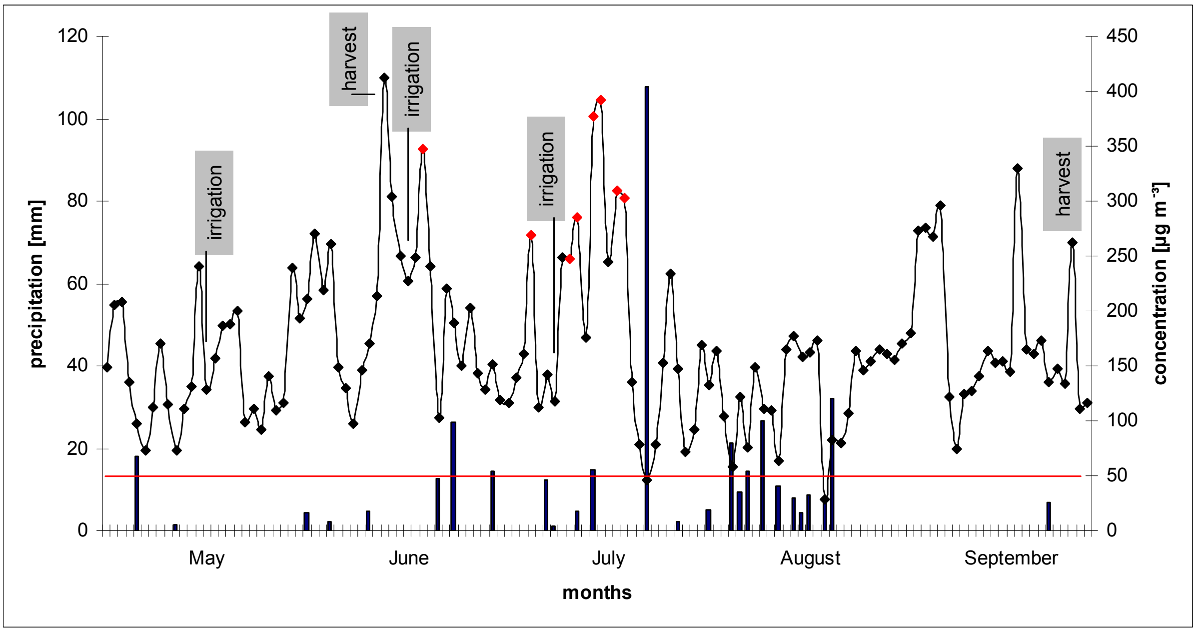

Figure 4.14: Daily PM10 concentration and precipitation at DBW from 12th of May to 22nd of September 2005. Red line marks the daily (24-h) European threshold of PM10 concentration. Red dots mark questionable data due to wet filters. Precipitation data were provided by Dr. Cui, CAU, in 2007, and Y. Zhang, CAU, in 2006, field cultivation data including irrigation were provided by S. Qinping, CAU, in 2007.

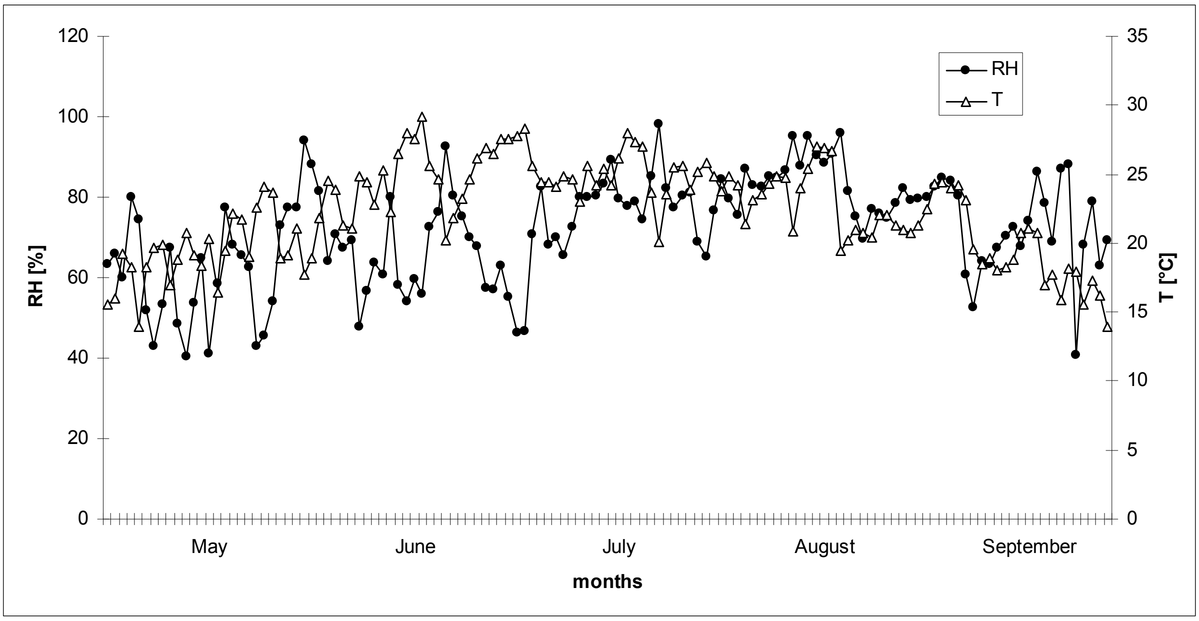

Figure 4.15: Daily Temperature (T) and Relative Humidity (RH) recorded at 1-h intervals at DBW between 12th of May and 22nd of September 2005. Data provided by Dr. Cui, CAU, in 2007.

Analysis of wind data during the study period of PM10 levels in 2005 indicated that winds came mainly from the south or south west (Figure 4.16). This is in agreement with Zhao et al. (2009) and Wu et al. (2009b) for Beijing. The study period of PM10 took place mainly during summer in which high temperatures even at night time normally occurred. The wind flow combined with averaged low wind speed might be different especially during the day when the urban heat island effect is at maximum and influences the regional flow as shown by Guinot et al. (2007) for this season. The author pointed out that “the vertical coupling in summer between the different urban boundary layers is poor and air masses impacting Beijing city predominantly originate from a wide south sector“ (Guinot et al, 2007, p. 7). Consequently, PM pollution over DBW may have been more influenced by the populated and industrialized south and south west surroundings of Beijing region. Moreover, effects of biomass burning during the harvesting seasons in the NCP must be regarded, as well. The PM10 study period covered the harvest of winter wheat and spring maize in the NCP followed by the residue burning of wheat straw and corn residues, respectively. The pollutant emissions resulting from combustion of these crop residues were already discussed in chapter 4.2.3 and are considered to contribute substantially to the PM pollution in rural areas in China (Cao et al., 2008). Since DBW is located in the northern part of Hebei province, the pollutants from burning activities in the NCP may have thus been transported to DBW site from southerly directions. Especially the biomass burning during winter wheat harvest season influences the PM pollution in Beijing area at maximum as shown by Duan et al. (2004) and thus may explain partly the high PM concentration data at DBW during summer.

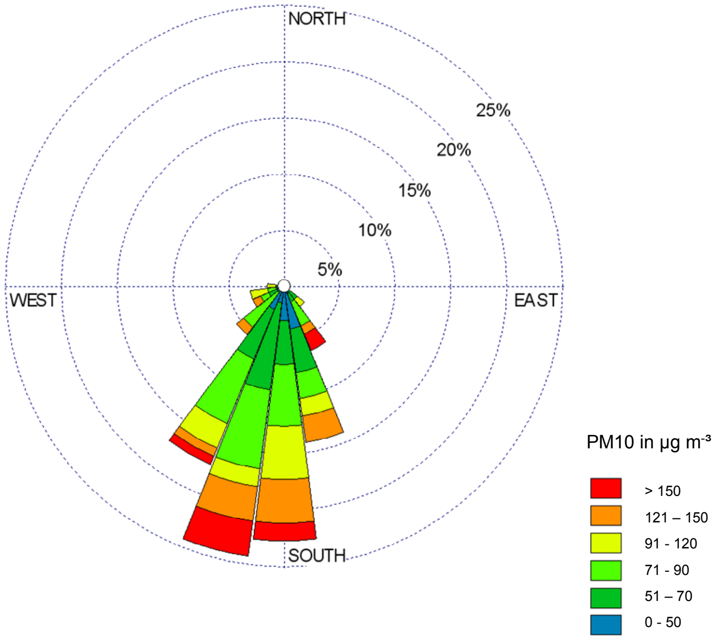

Figure 4.16: Wind rose indicating the frequency of directions along classes of PM10 concentrations recorded at 24-h intervals at DBW from 12th of May to 22nd of September 2005. Wind data were provided by Dr. Cui, CAU, in 2007.

Atmospheric concentrations in 2006

In 2006, observations of daily PM10 levels at DBW were done from August to October only. The results are presented in Figure 4.17 and concentrations ranged from 40 to 341 µg m^{-3}. In total 44 values were reported, less than in 2005 due to the shorter measuring period in this year. The averaged daily PM10 concentration was 187±67 µg m^{-3} and is comparable to the averaged 155±93 µg m^{-3} measured from September to November in Beijing in 2002 by Duan et al. (2005). The daily PM level was again three times higher than the European threshold of 50 µg m^{-3}. In the year 2006, about 98 % of the measured daily PM10 values were higher than the daily European threshold; about 70 % were higher than the daily Chinese threshold. Rain events leading to wash out of particulates can also be observed with lower PM10 levels during or after precipitation. Furthermore, two harvest periods (spring maize and summer maize) were observed whereas the harvesting of summer maize is represented in the Figure with the maximum daily PM10 concentration of 341 µg m^{-3} on 5th of October 2006. This value fits well to the maximum daily PM10 concentration of 356 µg m^{-3} for the same month in 2004 reported by Zhang et al. (2007a) for Beijing. Yang et al. (2008) also reported on daily PM10 exceedances of the Chinese air quality level IVA (250 µg m^{-3}) during harvest and an obvious correlation between the quantity of crop residue burned in the field and PM10 concentration in ambient air. During the whole study period at DBW the air humidity and temperature averaged to 79±10 % and to 20±5 °C, respectively. Analysis of wind data during the study period of PM10 levels in 2006 indicated that wind came mainly from the south or south west similar to the year 2005.

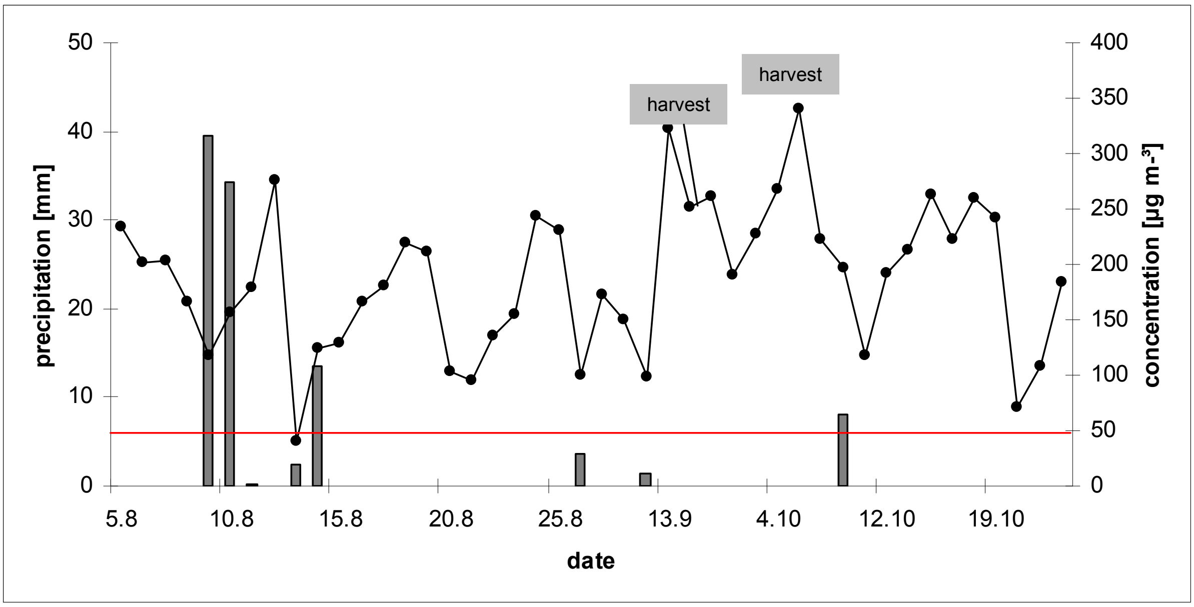

Figure 4.17: Daily PM10 concentration and precipitation at DBW from 5th of August to 26th of October 2006. Red line marks the daily (24-h) European threshold of PM10 concentration. Precipitation data were provided by Dr. Cui and Y. Zhang, CAU, in 2006/2007, field cultivation data were provided by S. Qinping, CAU, in 2007.

4.2.5 PM10 - Temporal variations

Temporal variations in 2005

The distributions of PM10 concentrations over the months May to September are shown in Figure 4.18. The data varied significantly from day to day shown by the large standard deviation for each month. The relatively high mean PM10 concentration of about 195 µg m^{-3} in June may have been due to the harvest of winter wheat as explained above. The influence of the harvest period on the monthly PM10 level for June was much higher than the start of the monsoon season with rainfall. Moreover, the total rainfall of 51 mm in June is relatively low in comparison with the total rainfall of 162 mm in July and 142 mm in August. The long term average of rainfall at Beijing (1961-1991) is listed with 71, 176 and 181 mm for the months June, July and August (Rumbaur, 2009) showing also much lower precipitation in June than in July and August. Thus, the impact of precipitation on decreasing the daily PM concentrations at DBW in June was not as pronounced as during July and August in 2005. The mean PM10 concentration decreased to 178 µg m^{-3} in July up to 150 µg m^{-3} in August. The averaged PM10 concentration from June to August, often classified as wet season in the literature, revealed 174±80 µg m^{-3} (n=91) for DBW site and is in line with recently published PM10 averages of 180±87 µg m^{-3} (n=63) for Beijing during the wet season (Zhang et al., 2010b). The same PM10 average of 180 µg m^{-3} (n=89) was published by Oanh et al. (2006) for several wet seasons in Beijing, whereas wet season is explicitly named for the months May to October by the author. Only Duan et al. (2006) reported on lower summer average of PM10 concentration (119 µg m^{-3}) for Beijing.

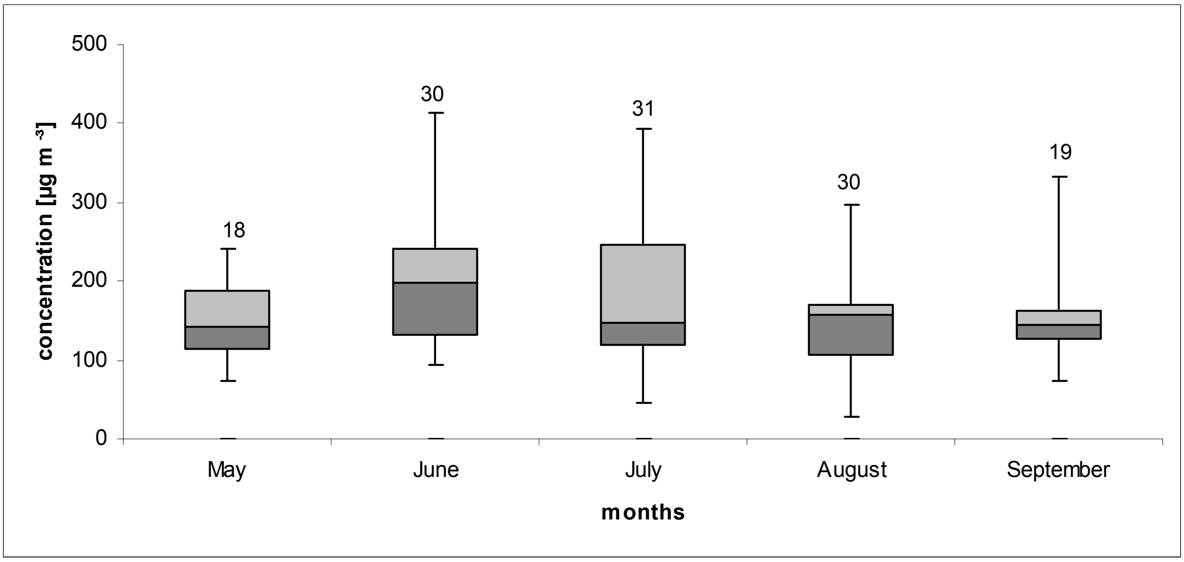

Figure 4.18: Box plots representing PM10 concentrations recorded at 24-h intervals at DBW in 2005. The horizontal line in a box indicates the median, the lower and upper end of a box indicate the 25- and 75-percentile, respectively. Whiskers are drawn to the minimum and maximum values, respectively. The numbers on top of the graphs indicate the number of values that were considered for calculating the corresponding box.

Weekly variations of PM10 concentrations in 2005 are shown in Figure 4.19. The level of PM10 concentrations was distributed homogeneously over the weekdays ranging with minimum 152 µg m^{-3} on Thursday (mean) to maximum 179 µg m^{-3} on Saturday (mean). No significant differences between weekdays regarding daily PM10 concentrations were analysed. Wu et al. (2008) also confirmed similar PM concentration in Beijing on workdays to those of weekends, independent on the season. These results are different from several observations at other cities in the world, such as London (Charron et al., 2007), Milan (Vecchi et al., 2007), Bern (Hueglin et al., 2005) or Pittsburgh (Stanier et al., 2004). In these cities, PM concentration was much higher during workdays and related to more traffic volume, respectively more traffic emissions, than during weekends. The traffic density was clearly lower at weekends than from Mondays to Fridays. The lifestyle in China is completely different to European or American one's and most inhabitants work seven days per week. This leads to similar traffic density each day and no difference of PM concentration on workdays and weekends.

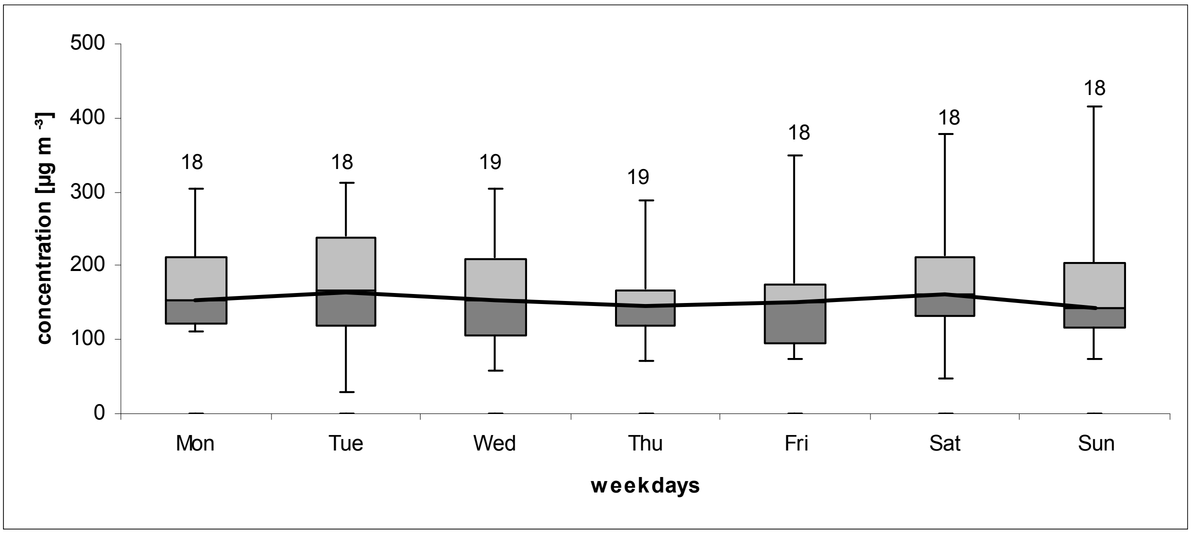

Figure 4.19: Box plots representing the weekday's variation of PM10 concentration at DBW from 12th of May to 22nd of September 2005. The line joints the medians, the lower and upper end of a box indicate the 25- and 75-percentile, respectively. Whiskers are drawn to the minimum and maximum values, respectively. The numbers on top of the graphs indicate the number of values that were considered for calculating the corresponding box.

Diurnal variations of PM10 concentrations were studied using 1-h concentration data. Figure 4.20 shows the diurnal variation of PM10 during autumn in 2005. During the first two weeks of September much higher averaged weekly PM10 concentrations were observed than during the other weeks in autumn. The diurnal measurements were done during the second week of September with averaged weekly PM10 concentration of 181 µg m^{-3}. The observed daily PM10 concentration of 330 µg m^{-3} on 10th of September - the day of the hourly measurements - was an extreme high value but fitted into the high PM10 level in general during the week. The 24-h European threshold for PM10 was far exceeded at any time, on average 6 to 7 times. No rain was recorded during that time. As can be seen in the course of the day, one peak of PM10 occurred in the early morning (7:00-8:00 Hrs.); the second gentle increase of PM10 occurred at 17:00-23:00 Hrs. The occurrence of two peaks was also observed by Shi et al. (2002). The PM10 level at night was not significantly lower than that at daylight but highly variable (±100 µg m^{-3}). In spite, the PM level at daylight was very stable. Only the PM10 value of 260 µg m^{-3} between 18:00 and 19:00 Hrs. was unusual due to its decrease of a third of the evening PM level for only one hour. Such low PM values occurred only from 4:00-6:00 Hrs. during that day. Analysis of wind data showed that wind direction changed in the evening from formerly west to south at exactly the time of the decline of the PM level and one hour later again changed back from south to west. The PM values before and after the described decline were the highest ones of the day and wind came from west as shown in Figure 4.21. In general, the majority of winds during the day came from westerly and north-westerly directions leading air masses to the PM sampler. Only for few hours winds came from north-easterly and easterly directions at 11:00-14:00 Hrs. South and south-east winds prevailed during night switching to west and north-west winds in the early morning. The changes in wind direction are an important aspect due to the fact that on average during PM10 sampling time from May to September wind came mainly from the south as already described in chapter 4.2.4.

In order to interpret the hourly PM measurements more precisely other local meteorological parameters have to be characterised, too. After sunset, the wind speed and temperature decreased and reached the minimum values of almost zero until later night. In contrast, RH values increased in the night until 96 % (see Figure 4.19). The largest difference between daylight and night was noted for the temperature which rose until 27 °C during the day. These meteorological conditions resulted in higher pollutant accumulation during the day. Moreover, the large temperature difference between daylight and night may have led to the adsorption and coagulation of gases on particle surfaces resulting in the formation of secondary particles. When air is cooler near the ground and warmer higher up in the atmosphere, haze accumulates in the region as shown for the NCP in Figure 4.22. The traffic and anthropogenic outdoor activities near DBW are usually concentrated in the morning and evening rush hours and raise the pollutant emission as well. Especially the increasing traffic by heavy trucks in the evening may have caused the second long-term peak of PM10 until midnight. Additionally, west and north-west winds during the day led air masses with PM from surrounded construction sites to DBW. The mountains in the north and north west of DBW play also a role in trapping haze and smog during this time (NASA, 2005b).

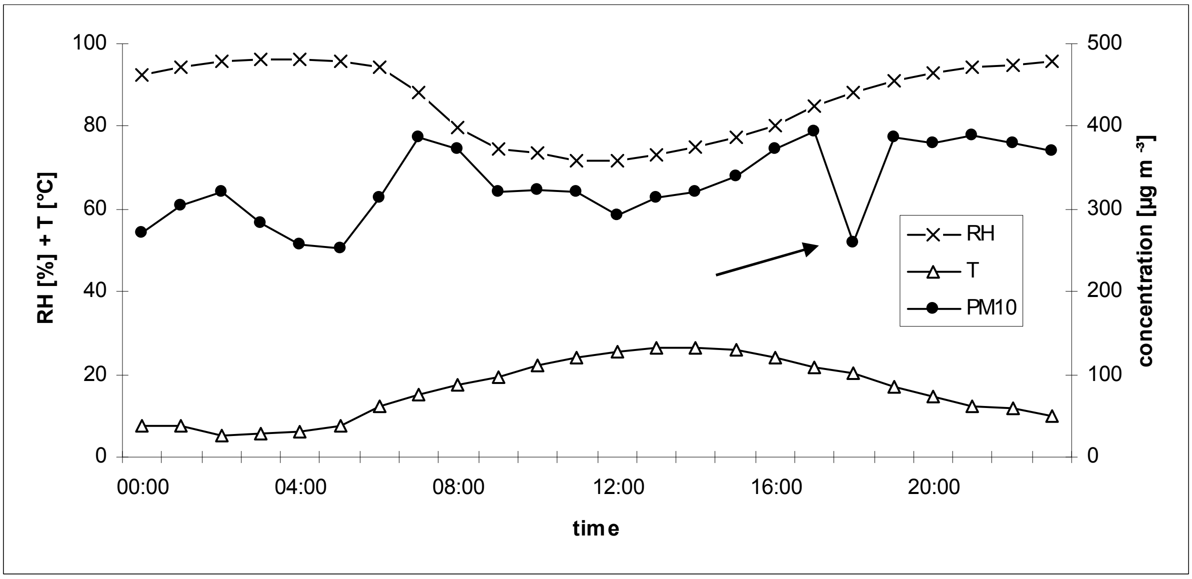

Figure 4.20: Diurnal variations of PM10 concentrations, relative humidity (RH) and temperature (T) recorded at 1-h intervals at DBW on 10th of September 2005. The averaged mass concentration of the day was 330±46 µg m^{-3} (n=24). The arrow marks the decrease of PM level by one third within one hour. RH and T data were provided by Dr. Cui, CAU, in 2007.

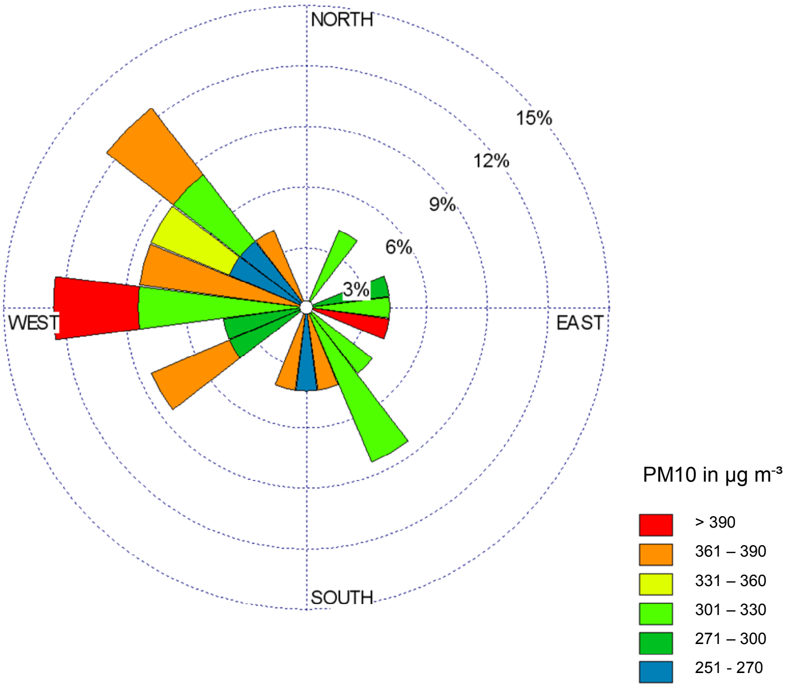

Figure 4.21: Wind rose indicating the frequency of directions along classes of PM10 concentrations recorded at 1-h intervals (from 0:00-24:00 Hrs.) at DBW on 10th of September 2005. Wind data were provided by Dr. Cui, CAU, in 2007.

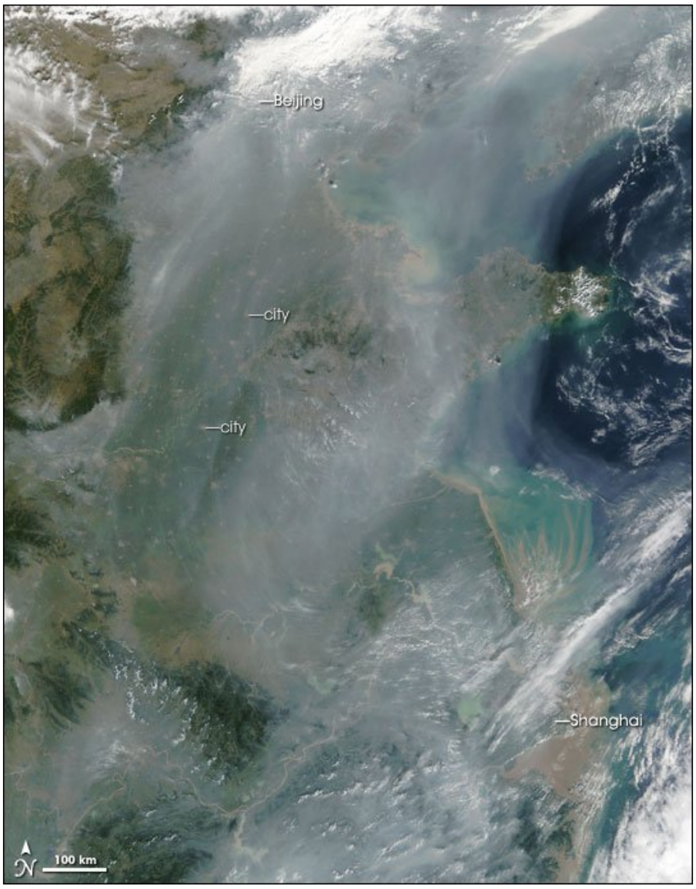

Figure 4.22: Haze covers the NCP from the coastline in the east to the mountains in the west on September 10, 2005 (Source: NASA, 2005b).

Temporal variations in 2006

The variation of PM10 concentration data for the months August to October are shown in Figure 4.23. The relatively high mean PM10 level of September (278 µg m^{-3}) was probably caused by the harvesting of spring maize during the second half of September at DBW. Although there were no PM10 measurements available from 23rd of September (harvest date), some days later high PM concentrations were still recorded on 30th of September with 261 µg m^{-3}. In general, PM10 mass concentrations in September showed a highly negative relationship ($R^2 = 0.95$) to the daily air humidity. Relatively stable weather conditions were observed in September with very low wind speeds (mean 0.76 m s^{-1}) and moderate RH (mean 71 %). Those conditions are usually favourable for pollutants accumulation resulting in high PM10 concentration as described by Duan et al. (2005). They lead to very poor dilution of air masses and dispersion of pollutants and result in the local emissions being trapped in the atmosphere over DBW. Overall, the most polluted PM10 episodes took place in autumn compared with other seasons during both, 2005 and 2006. In 2006, effects of biomass burning must be regarded in autumn, too (see also chapter 4.2.3 and 4.2.4). Wu et al. (2008) mentioned frequent agricultural biomass burning on the fields in the Hebei province in the harvesting season. The produced PM might be transported to DBW site because precipitation was very sparse during autumn.

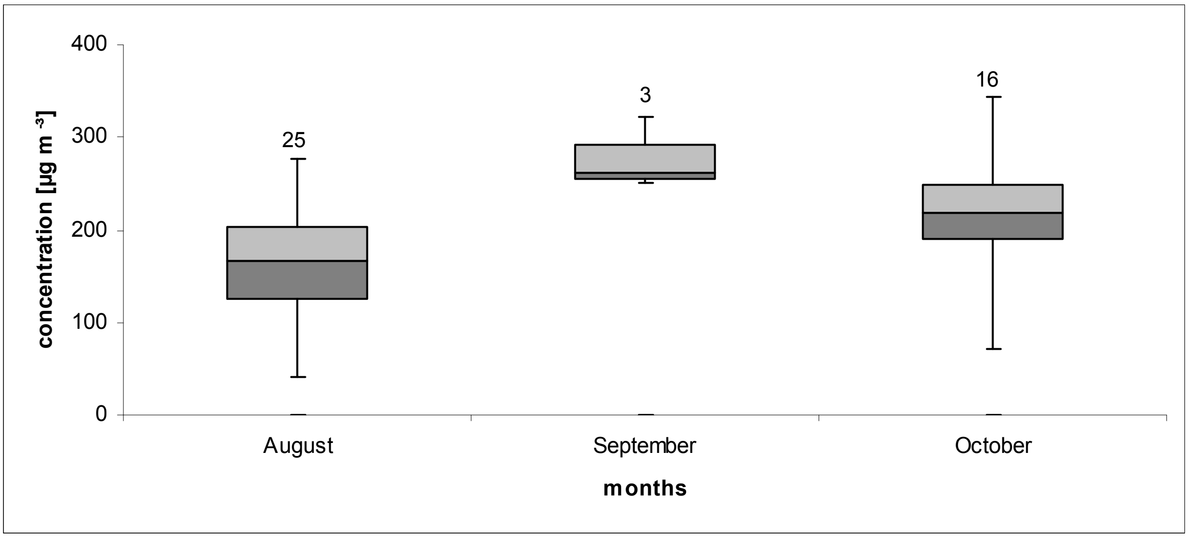

Figure 4.23: Box plots representing PM10 concentrations recorded at 24-h intervals at DBW in 2006. The horizontal line in a box indicates the median, the lower and upper end of a box indicate the 25- and 75-percentile, respectively. Whiskers are drawn to the minimum and maximum values, respectively. The numbers on top of the graphs indicate the number of values that were considered for calculating the corresponding box.

In the present study, the mean PM10 concentration increased from Monday (150 µg m^{-3}) to Thursday reaching the maximum on Thursday (224 µg m^{-3}). After a decrease on Friday the PM concentrations increased again on Saturday. The Sunday showed a strong variability ranging from 263 µg m^{-3} to the overall minimum of 40 µg m^{-3}. Figure 4.24 illustrates box plots indicating the PM concentrations on weekdays. Apart from the described slight increases and decreases of PM concentration - overall there were no significant differences on weekdays. PM concentrations on workdays were again similar to those of weekend-days.

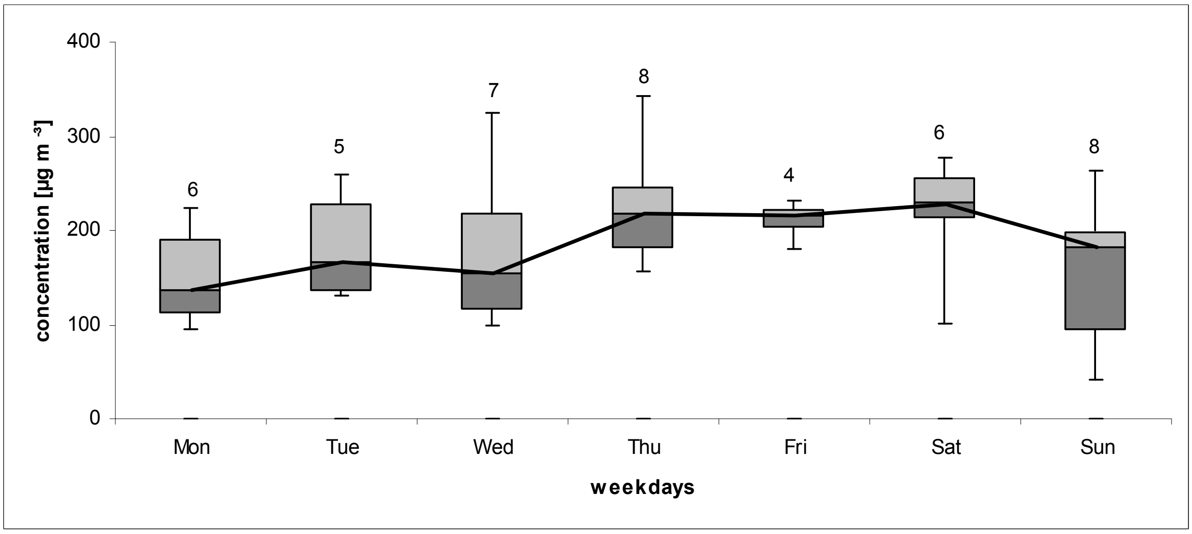

Figure 4.24: Box plots representing the weekday's variation of PM10 concentration at DBW from 5th of August to 26th of October 2006. The line joints the medians, the lower and upper end of a box indicate the 25- and 75-percentile, respectively. Whiskers are drawn to the minimum and maximum values, respectively. The numbers on top of the graphs indicate the number of values that were considered for calculating the corresponding box.

Diurnal variations of PM10 concentrations were again studied based on 1-h concentration data obtained from 30th of August 2006 (Figure 4.25). The hourly PM concentrations ranged from 54 µg m^{-3} at noon to 157 µg m^{-3} at 21:00 Hrs. The PM concentrations during night were remarkably higher than PM concentrations at daylight. The minimum level of PM10 during the day could be explained by the precipitation during the night from 29th to 30th of August lasting until 10:00 Hrs in the morning leading to wash out of PM in the air and to the relatively low averaged daily PM level of 99 µg m^{-3}. Nevertheless, the European threshold for PM10 was again exceeded at any time as shown in Figure 4.25. Several hours after the rainfall an increase of the PM concentrations was observed starting at 18:00 Hrs. with the evening rush hour. After reaching the maximum peak at 21:00 Hrs. the PM level slightly decreased to its "normal" background level. A similar diurnal course of the day was also reported by Zhang et al. (2007a) for Beijing with lowest PM10 concentrations at noon but highest concentrations earlier in the evening, at 19:00 Hrs.

The meteorological conditions on 30th of August 2006 showed extreme values being typical for the monsoon climate. There were almost no differences between night and day concerning air humidity (night: 95 %, day: 86 %), temperature (night: 18 °C, day: 21 °C) and wind speed (night: 0 m s^{-1}, day: 0.3 m s^{-1}). The very low wind flow during the day came mainly from north-westerly direction and was regarded as regional flow strongly influenced by the urban heat island effect. Moreover, it is assumed that DBW site is located in the urban heat island of Beijing since the air temperature perturbation was minimal during the day which is typical for the urban heat island (Liu et al., 2007). Solar heating during the day caused warming and had maybe an effect of generating convective winds within the urban boundary layer. The absence of solar heating during night caused the atmospheric convection to decrease and the urban boundary layer was stabilized (Wikipedia, 2010). Since such meteorological conditions occurred mainly in July and August probably enough stabilization took place until the end of August forming an inversion layer. This layer was as much stable as to result in higher temperatures at night within the urban heat island as well as to prevent mixing of emissions. Only precipitation removed PM efficiently from the atmosphere as has been demonstrated for the 30th of August at DBW.

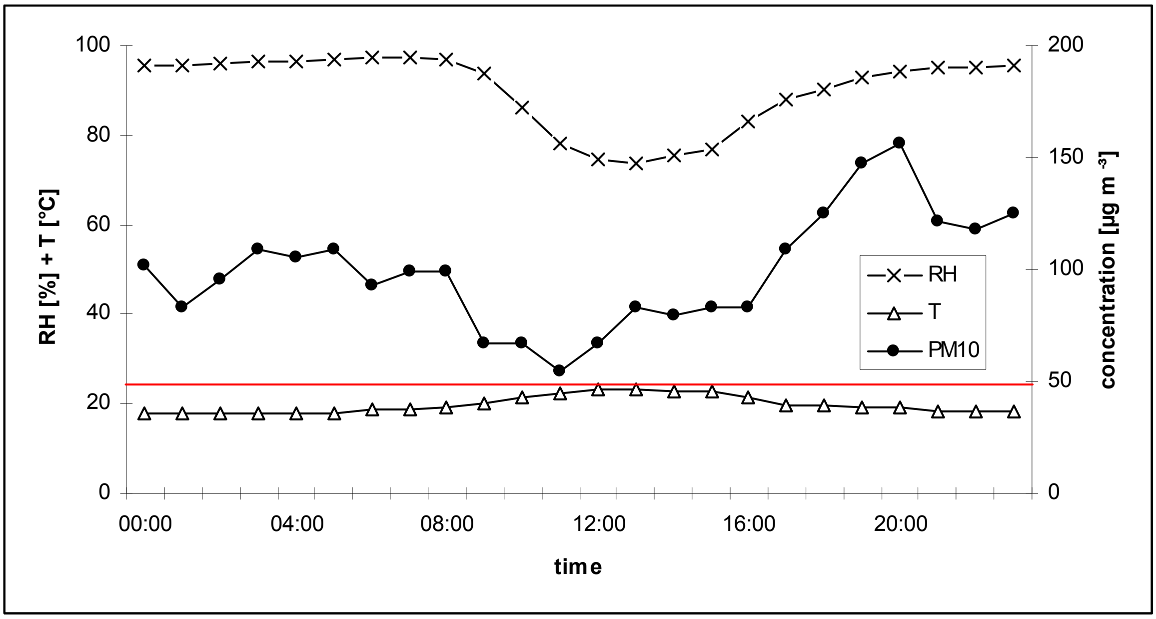

Figure 4.25: Diurnal variations of PM10 concentrations, relative humidity (RH) and temperature (T) recorded at 1-h intervals at DBW on 30th of August 2006. The averaged mass concentration was 99±25 µg m^{-3} (n=24). The red line marks the daily (24-h) European threshold of PM10 concentration. RH and T data were provided by Dr. Cui, CAU, in 2007.

4.2.6 PM2.5 – Atmospheric concentrations

Atmospheric concentrations in 2005

Observations of PM2.5 were done from September to December 2005 at DBW. The results are presented in Figure 4.26. The daily PM2.5 concentrations had an average of 222 µg m^{-3} and varied a lot during the study time as indicated by the standard deviation of 123 µg m^{-3}. The values ranged from a minimum of 31 µg m^{-3} in October until a maximum of 495 µg m^{-3} in November. Precipitation leading to removal of PM from the atmosphere was observed during autumn as can be seen in this Figure. Due to the lack of precipitation data during the winter season, decreases of PM2.5 level caused by rainfall or snow during November and December could be assumed only. Zhao et al. (2009) reported on no precipitation in November and 17 mm in the whole winter period (December-January). The main reason for the remarkable increase of the PM2.5 level during November was the beginning of the heating period. The official start of the heating period in the northern part of China is on the 15th of November but the 1st of November has also to be regarded as the beginning of heating period since private use of coal and biomass as household fuel may be assumed and will be discussed in the section on temporal variations.

Overall, 99 % of the daily PM2.5 concentrations measured in 2005 exceeded the United States daily average air quality standard of 35 µg m^{-3}. The European Union and China still have not yet defined the daily PM2.5 threshold (chapter 2.4). Former studies report on PM2.5 measurements in Beijing which accounted for 86 % of the data exceeded the 'old' daily U.S. standard of 65 µg m^{-3} (Chan et al., 2005).

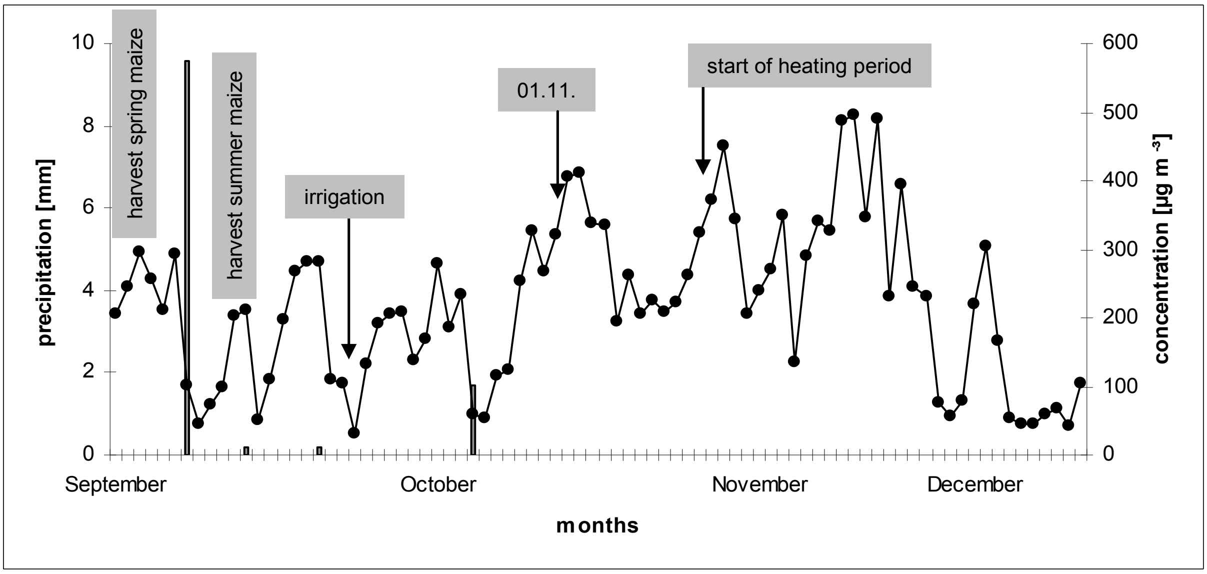

Figure 4.26: Daily PM2.5 concentration (n=82) and precipitation at DBW from 23rd of September to 17th of December 2005. Precipitation data until October were provided by Dr. Cui, CAU, in 2007, precipitation data after October is not available; field cultivation data were provided by S. Qinping, CAU, in 2007.

Atmospheric concentrations in 2006

In 2006, observations of PM2.5 were done from mid of August to the end of October, covering the autumn mostly, at DBW. The results are presented in Figure 4.27. The daily PM2.5 concentrations averaged with 123±53 µg m^{-3}. The values ranged from the minimum of 16 µg m^{-3} measured on 8th of September to the maximum of 311 µg m^{-3} on 6th of October, the time of harvesting of summer maize. Precipitation leading to removal of PM from the atmosphere was observed again during the study time as can be seen especially for the minimum PM2.5 value. The 8th of September was the only day where PM2.5 concentrations measured in 2006 did not exceed the United States daily average air quality standard of 35 µg m^{-3}. Furthermore, air humidity and temperature averaged to 71 % and 16 °C respectively during measurements, less than during the study time of PM10 in 2006. These measurements covered the whole August which is not the case for PM2.5 measurements.

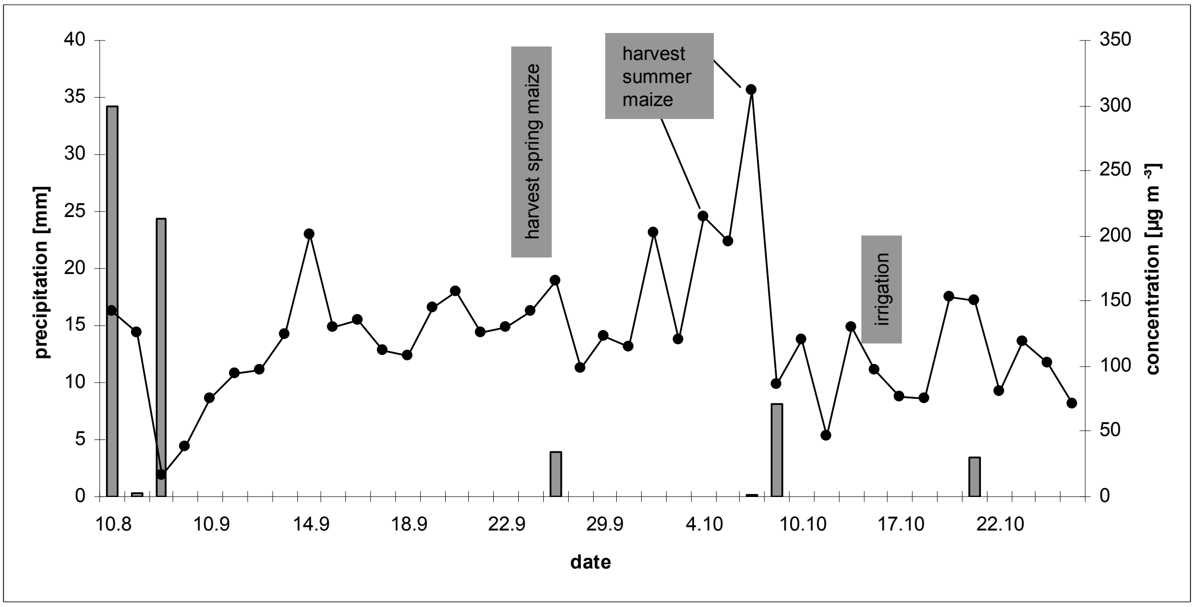

Figure 4.27: Daily PM2.5 concentration (n=40) and precipitation at DBW from 10th of August to 26th of October 2006. Precipitation data were provided by Dr. Cui, CAU, in 2007; field cultivation data were provided by S. Qinping, CAU, in 2007.

Analysis of wind data during the study period of PM2.5 levels in 2006 confirmed the observations made in 2005 during same time. On average wind came mainly from the south or south west (Figure 4.28) indicating that the populated and industrialized regions to the south and south west of Beijing exerted a great influence over atmospheric pollution in DBW. Non-Beijing sources play also an important role in the PM2.5 concentration of Beijing, respectively DBW. Wu et al. (2009b) identified for PM2.5 pollution during summer in Beijing that the largest contribution of sulphate is made by some regions of the NCP, namely Hebei and Shandong provinces and Tianjin city, located southerly of DBW. The most frequent southerly air flow of Beijing then is connected with high secondary water soluble ions concentrations he pointed out. In general, about 70 % of PM2.5 pollution in Beijing can be attributed to sources outside Beijing during southerly wind flows (Streets et al., 2007). These results might explain partly the PM2.5 pollution in DBW. The very low wind speed (on average 1 m s^{-1}) during study time is another important aspect and may have prevented the dispersion of pollutants resulting in shorter conversion times of secondary ions and more PM2.5 accumulation, especially during autumn.

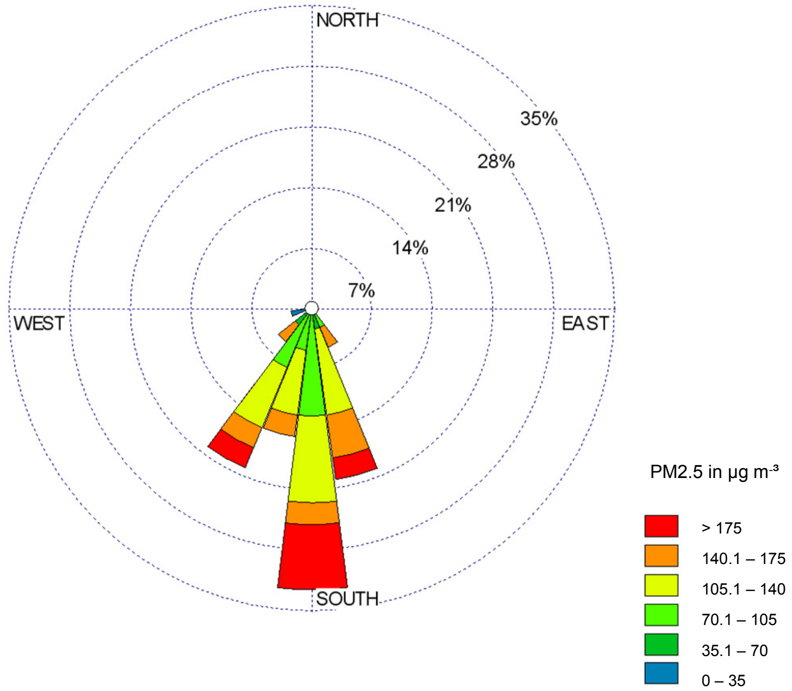

Figure 4.28: Wind rose indicating the frequency of directions along classes of PM2.5 concentrations recorded at 24-h intervals at DBW from 10th of August to 26th of October 2006. Wind data were provided by Dr. Cui, CAU, in 2007.

4.2.7 PM2.5 – Temporal variations

Temporal variations in 2005

The variation of PM2.5 concentration data for the months September to December are shown in Figure 4.29. The different PM2.5 levels covered two seasons in 2005, namely autumn and winter with averaged PM2.5 concentration of 183 µg m^{-3} and 253 µg m^{-3}, respectively. The PM2.5 level during autumn (September – October) may be related to harvest period and pollution of biomass burning as already discussed for TSP and PM10 levels during autumn. Obtained filters during this time are shown in Figure 4.30. Biomass burning at Hebei province was already discussed in chapter 4.2.3 mentioning that corn residue (besides wheat straw) is considered to have one of highest emission factors from all crops in China. Two harvests of maize at the end of September and at the beginning of October probably caused a lot of corn residue at DBW and in Hebei province in general. Due to the fact that in recent years corn residue lost its value as household fuel, crop residue burning took place to get rid of the material. Therefore, the higher PM2.5 concentrations at DBW in the autumn are likely due to biomass burning emissions as confirmed by Zhao et al. (2009) who measured PM2.5 during autumn in the same year. Due to the suburban character of DWB, urban local emission sources of Beijing city leading to the increase of PM2.5 level must be considered, too. Other authors reported lower PM2.5 concentrations during autumn such as 112 µg m^{-3} (He et al. 2001) or 122 µg m^{-3} (Zhao et al., 2009) but the observations took place in urban areas of Beijing. However, DBW was influenced strongly by both rural and urban emission sources.

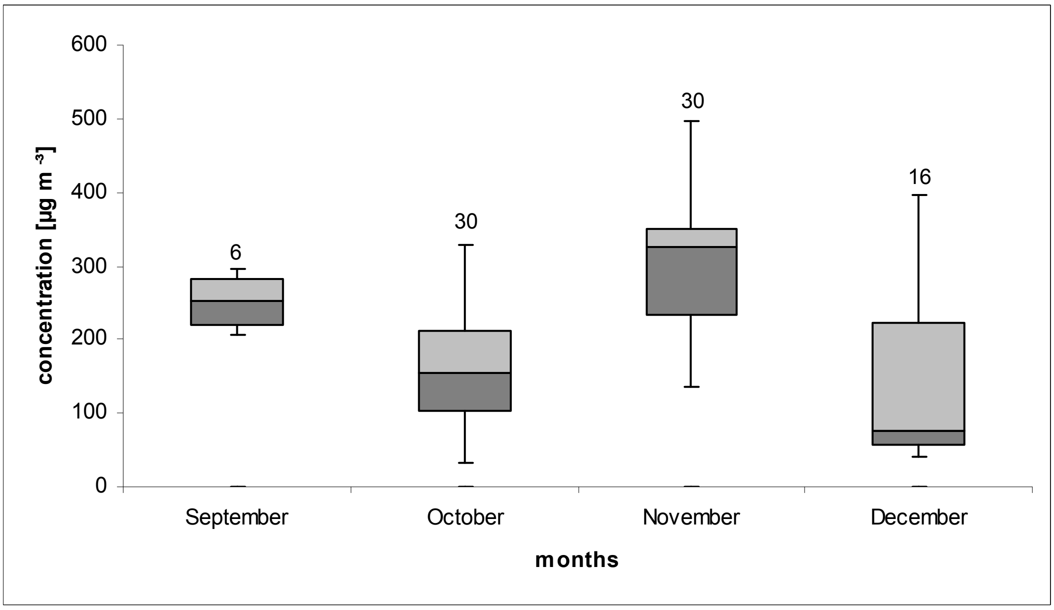

Figure 4.29: Box plots representing PM2.5 concentrations recorded at 24-h intervals at DBW in 2005. The horizontal line in a box indicates the median, the lower and upper end of a box indicate the 25- and 75-percentile, respectively. Whiskers are drawn to the minimum and maximum values, respectively. The numbers on top of the graphs indicate the number of values that were considered for calculating the corresponding box.

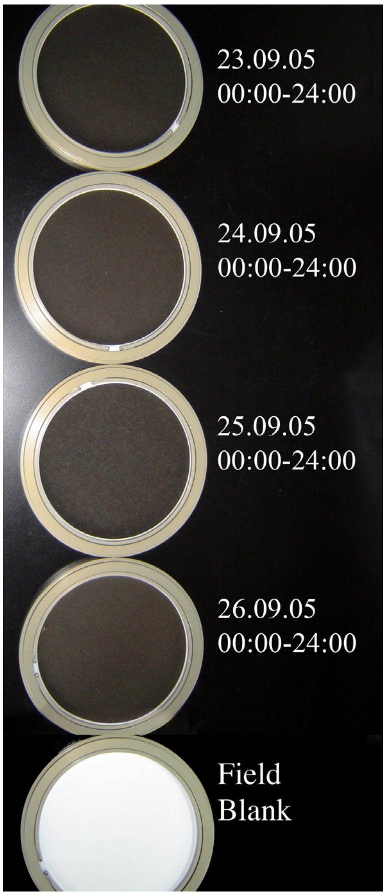

Figure 4.30: Collected filters representing PM2.5 concentrations recorded at 24-h intervals at DBW from 23rd to 26th of September 2005.

Regarding the PM2.5 level observed during winter at DBW, He et al. (2001) also reported that PM2.5 concentrations to be in Beijing were highest during the winter. Averaged PM2.5 concentrations during winter in Beijing were reported by Zhao et al. (2009) to be 180 µg m^{-3} or by Oanh et al. (2006) to be 168 µg m^{-3}. Own measurements showed remarkably higher PM2.5 concentration during November (on average 312 µg m^{-3}) than during December (on average 137 µg m^{-3}) with extreme peaks up to 350-450 µg m^{-3}. According to NASA (2005c) the Beijing's pollution index reached the highest level on the scale between November 4-5, and residents were warned to spend as little time as possible outdoors. Figure 4.31 illustrates the thick atmospheric pollution over Beijing and the NCP during this month. Zhao et al. (2009) also discovered that PM2.5 concentrations were highest during November 2005 and Oanh et al. (2006) observed PM2.5 levels above 400 µg m^{-3} during December in Beijing.

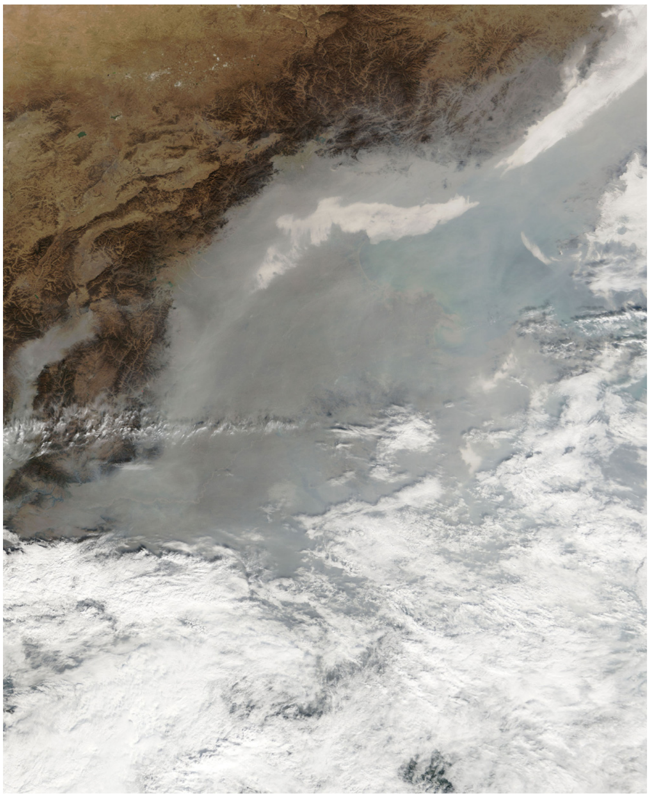

Figure 4.31: A nearly opaque band of thick smog obscures the view of Beijing and the NCP on November 4, 2005 (Source: NASA, 2005c).

Two main aspects must be regarded while discussing the observed high PM2.5 level during November at DBW. On the one hand biomass burning must again to be taken into account because the biomass burning activity of crop residues around Beijing normally was recorded to peak during mid-October to mid-November (Zheng et al., 2005). Local burning including the burning of fallen leaves in early November may have also caused remarkably higher PM2.5 concentrations as mentioned by Duan et al. (2004). On the other hand the official start of the heating period on 15th of November caused the second peak of PM2.5 levels in the month. It is known that coal is used in Beijing and other urban areas in the North China Plain, not only for power generation, industry, and heating systems, but also for heating in many old houses which applies more for rural areas in North China Plain and suburban areas of Beijing such as DBW.

Moreover, the anomalously low level of precipitation during November as reported by Zhao et al. (2009) and temperature inversions favoured the accumulation of pollutants in the atmosphere. The daily PM2.5 levels in November and December differ in their relation to the meteorological parameters wind speed and relative humidity; but they were unrelated to temperature. An overview on daily values of these parameters is given in Figures 4.32 and 4.33, respectively. While almost no relationship between PM2.5 and air humidity or wind speed was found during November, PM2.5 and RH showed a positive relationship ($R^2 = 0.7$) during December (Figure 4.34). Additionally, PM2.5 and wind speed correlated slightly negative ($R^2 = 0.4$) in December. The wind speed during December was significantly higher than in November blowing clean north-westerly winds to the study site. Figure 4.35 illustrates that the low wind speeds were related to south and south-westerly directions moving slowly air masses from the populated and industrialized south of Beijing as well as long-range transported pollutants from Hebei province to DBW. These wind flows are strongly related to November indicating that the influence of biomass burning and the start of heating period were much more related to the enhancement of PM2.5 concentration than the meteorological parameters. In December, the wind direction changed and stronger winds transported clean air from north-west to DBW and removed significant amounts of PM2.5 from the air.

Overall, no differences between weekdays were found similar to PM10 data analysis. Daily PM2.5 concentrations were homogeneously distributed during the week with a slightly higher PM2.5 level on Friday than during the other weekdays.

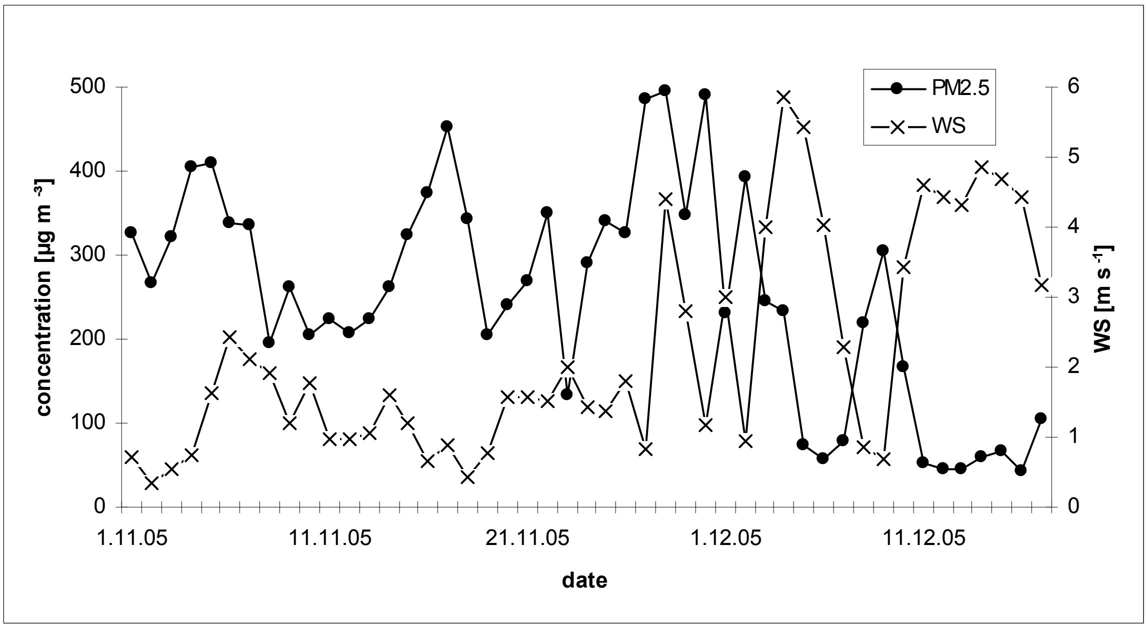

Figure 4.32: Daily PM2.5 concentrations and wind speed (WS) at DBW during the winter season of 2005. Wind data were provided by Dr. Cui, CAU, in 2007.

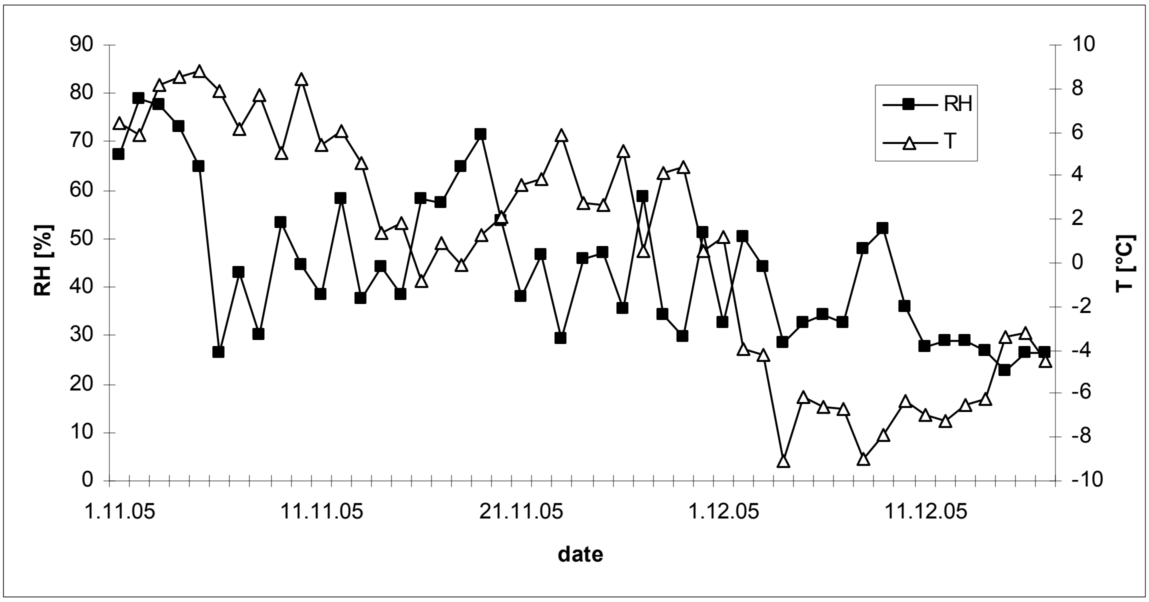

Figure 4.33: Daily relative humidity (RH) and temperature (T) at DBW during the winter season of 2005. Data were provided by Dr. Cui, CAU, in 2007.

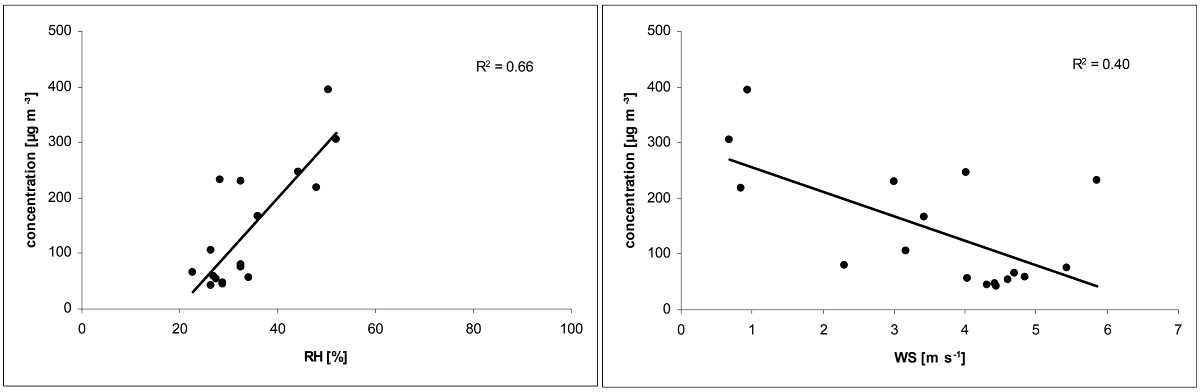

Figure 4.34: Relationship between PM2.5 concentrations and relative humidity (RH) (left) and wind speed (WS) (right) determined at DBW during December 2005. Data are based on 24-h values (n=17). RH and WS data were provided by Dr. Cui, CAU, in 2007.

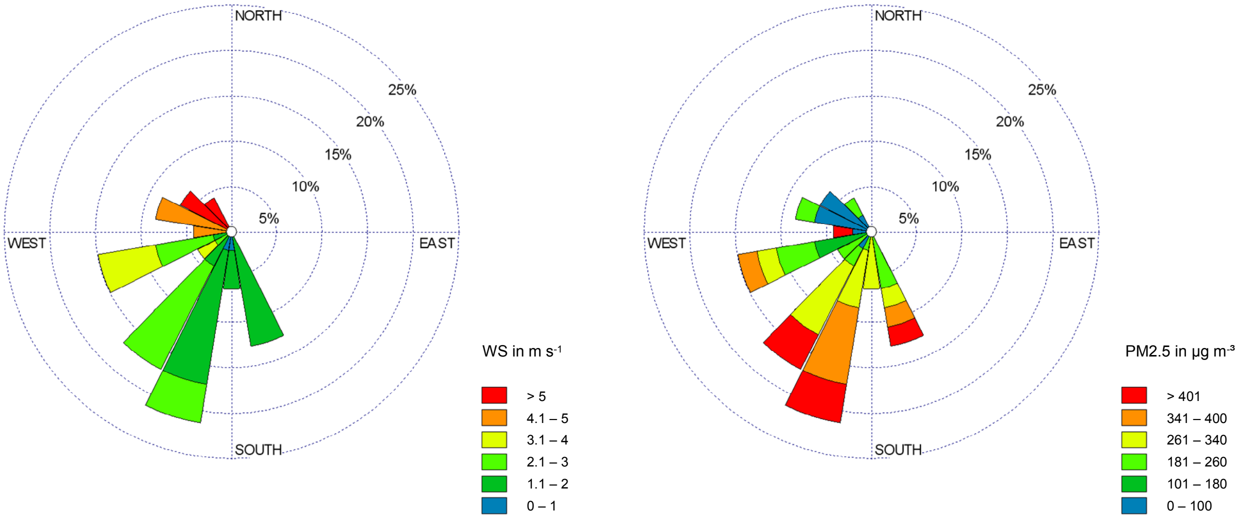

Figure 4.35: Wind roses indicating the frequency of directions along wind speed (WS) classes (left) and classes of PM2.5 concentration (right). Data are based on 24-h values between 1st of November and 17th of December 2005. Wind data were provided by Dr. Cui, CAU, in 2007.

In 2005, the diurnal variation of PM2.5 concentrations was studied based on 1-h concentration data from 28th of September (Figure 4.36). The hourly PM concentrations ranged from a minimum of 173 µg m^{-3} at 4:00-5:00 Hrs. to a maximum of 433 µg m^{-3} at 13:00-14:00 Hrs. The averaged daily PM2.5 concentration was recorded to be 292 µg m^{-3} and corresponds with high diurnal variations of PM10 during September 2005 as discussed in chapter 4.2.5. The described midday peak was also mentioned by Wu et al. (2008) occurring around 13:00 Hrs. in autumn. Higher temperatures and moderate relative humidity were related to increasing PM2.5 level during the day (Figure 4.37). These climate conditions obviously supported the formation of secondary particles as also described by He et al. (2002) contrary to lower temperatures which might be not favourable for the secondary particle formation. Especially the formation of sulphate and ammonium is forced by these appropriate meteorological conditions (Han et al., 2007b) in combination with high concentrations of their precursors SO_2 and NH_3. Another much smaller peak occurred between 18:00-19:00 Hrs. and was associated with the evening rush hour. The average night-time PM2.5 concentrations were not significantly lower than PM concentrations at daylight. The lowest PM2.5 concentrations occurred before sunrise, between 4:00-6:00 Hrs. The overnight PM2.5 minimum at 4:00 Hrs. was also observed by Zhao et al. (2009). The author found that PM2.5 concentrations decreased during night due to reduced source activities and removal of particles by dry deposition, a mechanism enhanced for hygroscopic particles by the increase in relative humidity which was also noticed at DBW and shown as negative correlation in Figure 4.37.

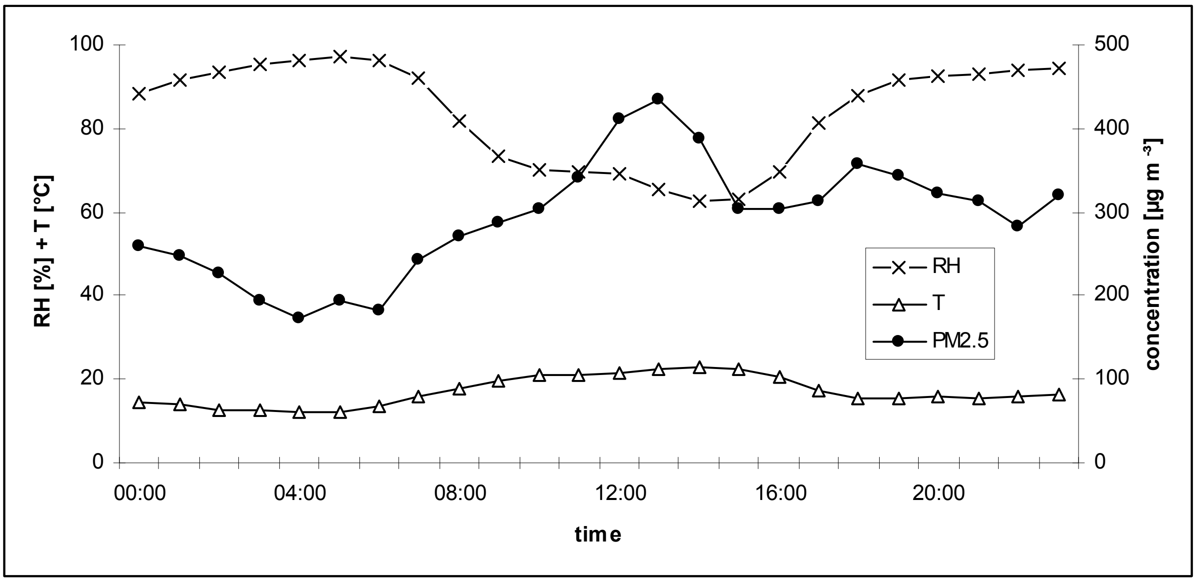

Figure 4.36: Diurnal variation of PM2.5 concentrations, relative humidity (RH) and temperature (T) recorded at 1-h intervals at DBW on 28th of September 2005. The averaged daily mass concentration of the day was 292 ±69 µg m^{-3} (n=24). RH and T data were provided by Dr. Cui, CAU, in 2007.

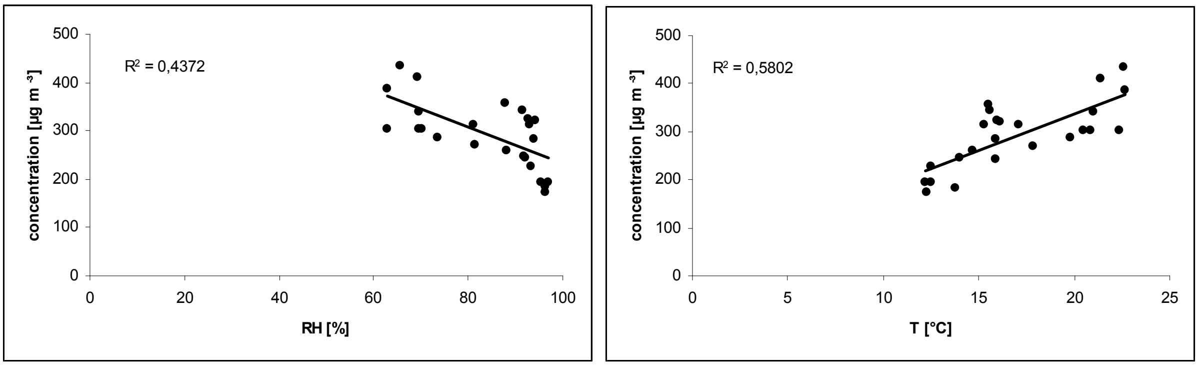

Figure 4.37: Relationship between PM2.5 concentrations and relative humidity (RH) (left) and ambient temperature (T) (right) determined at DBW on 28th of September 2005. Data are based on 1-h values. RH and T data were provided by Dr. Cui, CAU, in 2007.

Temporal variations in 2006

The variation of PM2.5 concentration data for the months August to October 2006 are shown in Figure 4.38. The study time of PM2.5 in 2006 covered almost the season of autumn only. The averaged PM2.5 level of 123 µg m^{-3} during autumn is nearly the same as of averaged PM2.5 level during whole study time in 2006. In September, PM2.5 level averaged with 117 µg m^{-3} which was not significantly lower than the PM2.5 level of October with 131 µg m^{-3}. As already shown for 2005, also the PM2.5 level during autumn in 2006 might have been a direct link between harvest period and pollution of biomass burning. Combustion of crop residues and fallen leaves during autumn has been already discussed for TSP and PM10 concentration data. Two harvests occurred during autumn 2006 showing clearly the PM2.5 peaks during harvesting time (see also chapter 4.2.6).

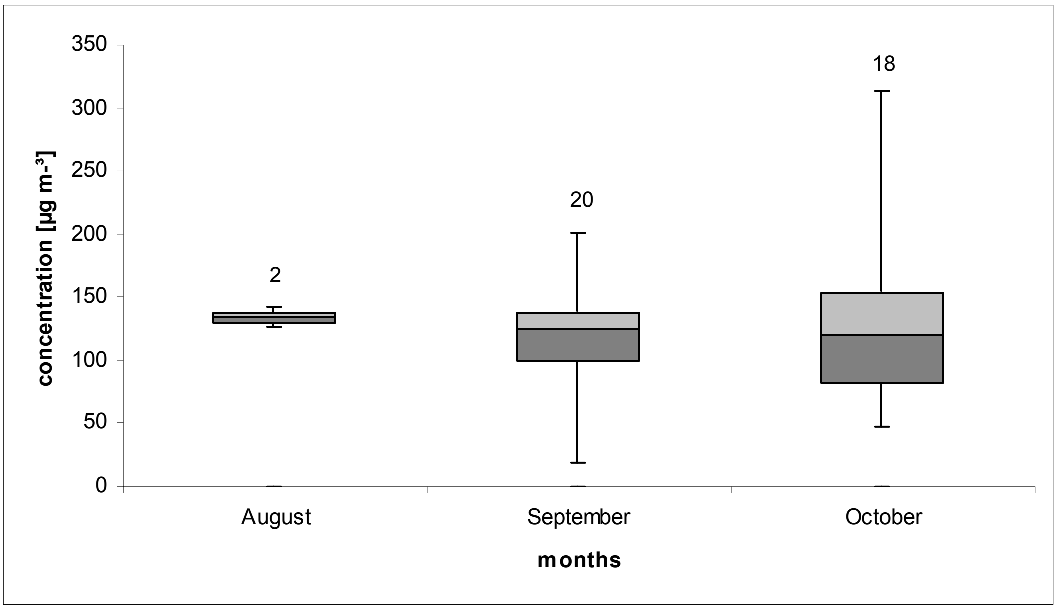

Figure 4.38: Box plots representing PM2.5 concentrations recorded at 24-h intervals at DBW in 2006. The horizontal line in a box indicates the median, the lower and upper end of a box indicate the 25- and 75-percentile, respectively. Whiskers are drawn to the minimum and maximum values, respectively. The numbers on top of the graphs indicate the number of values that were considered for calculating the corresponding box.

Again, no differences between weekdays were found similar to 2005. Daily PM2.5 concentrations were homogeneously distributed over the week.

In 2006, diurnal variations of PM2.5 concentrations, wind speed, air humidity and temperature were studied based on 1-h concentration data on 8th of September (Figure 4.39 and 4.40). The hourly PM2.5 concentrations ranged from a minimum of zero at 5:00-6:00 Hrs. and 9:00-11:00 Hrs. to a maximum of 74 µg m^{-3} at 2:00-3:00 Hrs. The averaged PM2.5 concentration of the day was recorded with an extreme low level of 16 µg m^{-3} which was the minimum daily value during whole PM2.5 study period in 2006. The level also corresponded with low diurnal and daily PM10 levels during same time period as discussed in chapter 4.2.6. Nevertheless the low PM2.5 concentrations were exceptional and caused by heavy storm and rain (total sum of precipitation was 24.4 mm) the night and day before. Therefore the diurnal pattern of PM2.5 concentrations did not show a “normal” diurnal variation of PM2.5; it was more an example of PM2.5 concentrations after wash out of fine particulates from the atmosphere. A slight positive relationship between the PM2.5 level at DBW to RH ($R^2 = 0.45$) was observed. Furthermore, strong winds during the daylight of 8th of September prevented PM2.5 accumulation as can be seen in the peak at 10:00-11:00 Hrs. with wind flows of 5 m s^{-1} and zero PM2.5. As shown in

Figure 4.41 the strongest wind flows came mainly from westerly and north-westerly directions indicating that fresh and clean air was transported from mountainous regions and favoured the pollutant dispersion at DBW. In total, only 12 % of the hourly PM2.5 concentrations measured on that day exceeded the United States daily average air quality standard of 35 µg m^{-3}. Those exceedances occurred after midnight when the wind flows were relatively low and fine particulates at DBW accumulated and were not blown out. Additionally, air masses with PM2.5 pollutants may have entered DBW from the south east as shown in the Figure since the whole Beijing city area is located south-east of DBW.

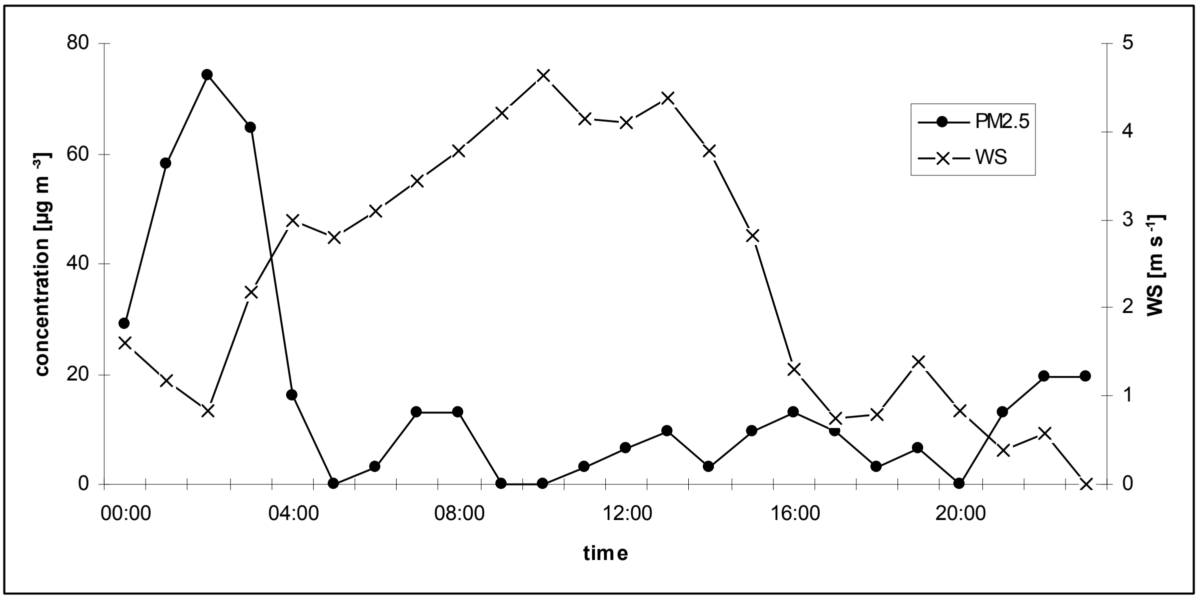

Figure 4.39: Diurnal variations of PM2.5 concentrations and wind speed (WS) recorded at 1-h intervals at DBW on 8th of September 2006. The averaged mass concentration of the day was 16±21 µg m^{-3} (n=24). Wind data were provided by Dr. Cui, CAU, in 2007.

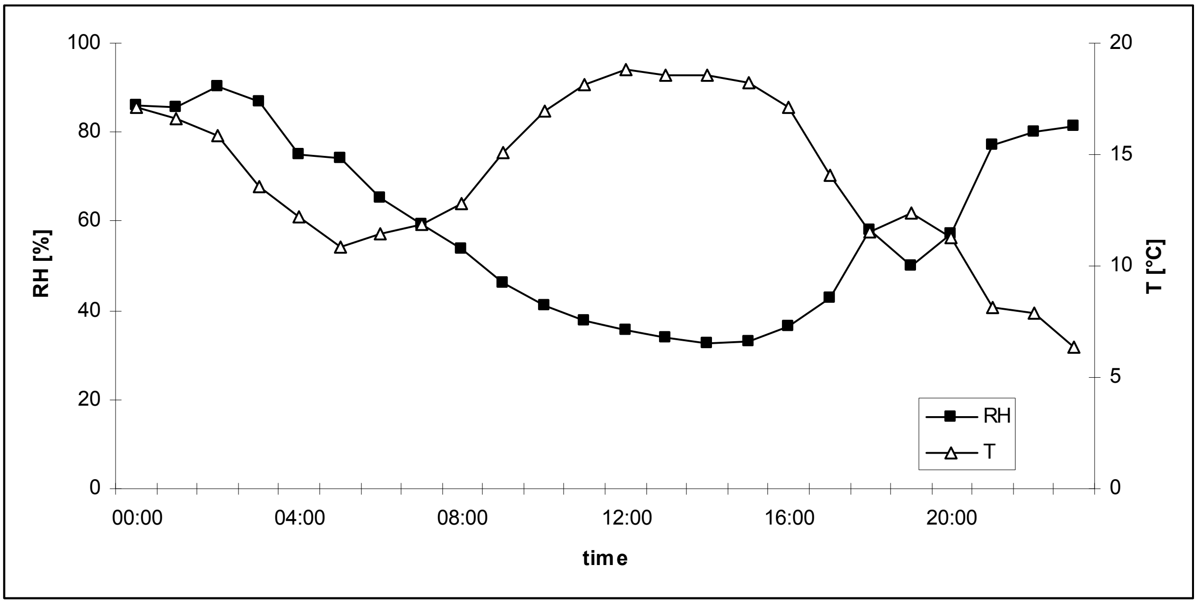

Figure 4.40: Diurnal variations of Relative Humidity (RH) and Temperature (T) recorded at 1-h intervals at DBW on 8th of September 2006 (n=24). Data were provided by Dr. Cui, CAU, in 2007.

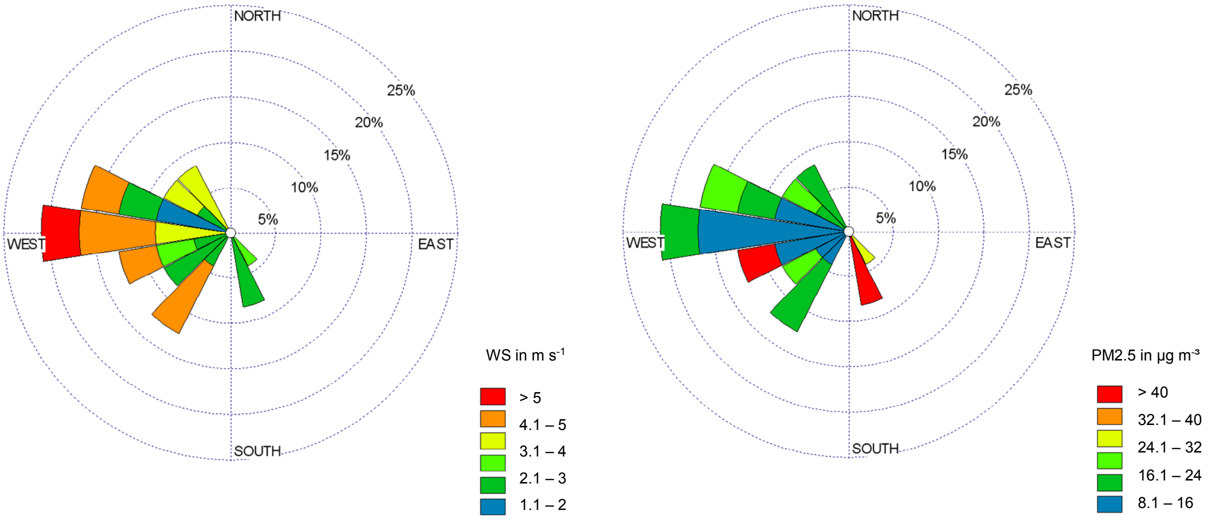

Figure 4.41: Wind roses indicating the frequency of directions along wind speed (WS) classes (left) and classes of PM2.5 (right). Data are based on 1-h values on 8th of September 2006. Wind data were provided by Dr. Cui, CAU, in 2007.

4.2.8 Particle size distribution and PM2.5 to PM10 ratios

The diurnal contribution of the three PM fractions during one day in August 2006 is shown in Figure 4.42. Measurements took place on a rainy day (total sum of rainfall was 34.2 mm) with high air humidity (98 %) and extreme low wind speeds (0.3 m s^{-1}) which is typical for the wet season. The temperature averaged to 23 °C and did not differ between day and night. PM2.5 constituted a larger fraction of PM10 during the course of the day, also shown with averaged PM2.5/PM10 ratio of 0.9. Slightly lower PM2.5/PM10 ratios of 0.8 were only observed in the afternoon and late evening. The high PM2.5/PM10 ratios may be related to relatively high contributions from secondary particles and combustion sources as shown by Oanh et al. (2006). The author described such ratios also for Asian cities during wet season being attributed to the emission from the vehicular fuel combustion or from the surrounding residential fuel combustion. Due to the fact that fine particles mainly consist of secondary particles which are formed in the atmosphere by chemical reactions, they may have contributed substantially to the high PM2.5/PM10 ratio at DBW. The high air temperature at night and the high RH indicated that DBW was probably influenced by the urban heat island during the PM measuring period. It is assumed that the formation of secondary particles was forced by the urban emissions such as vehicular exhaust, air conditioning, industry, and others. Moreover, due to the time period required for their formation, the secondary particles were expected to have a rather uniform distribution in cities (Oanh et al., 2006). The PM2.5/PM10 ratios obtained at DBW only varied slightly independently from the course of the day. The slightly lower PM2.5/PM10 ratio during the afternoon and late evening might therefore be related to primary emissions. Therefore it can be assumed that primary sources nearby DBW such as truck traffic during late evening and fuel combustion from rural households during the afternoon contributed more to coarse particles. Moreover, TSP made up about one third on average of the dust in the morning and the strong construction activities nearby DBW may have contributed to particles larger than 10µm. Throughout the day, the PM2.5 fraction represented 73 % on average, PM10 about 9 % and TSP about 18 %. This result indicated that several sources contributed to atmospheric pollution at DBW during the day.

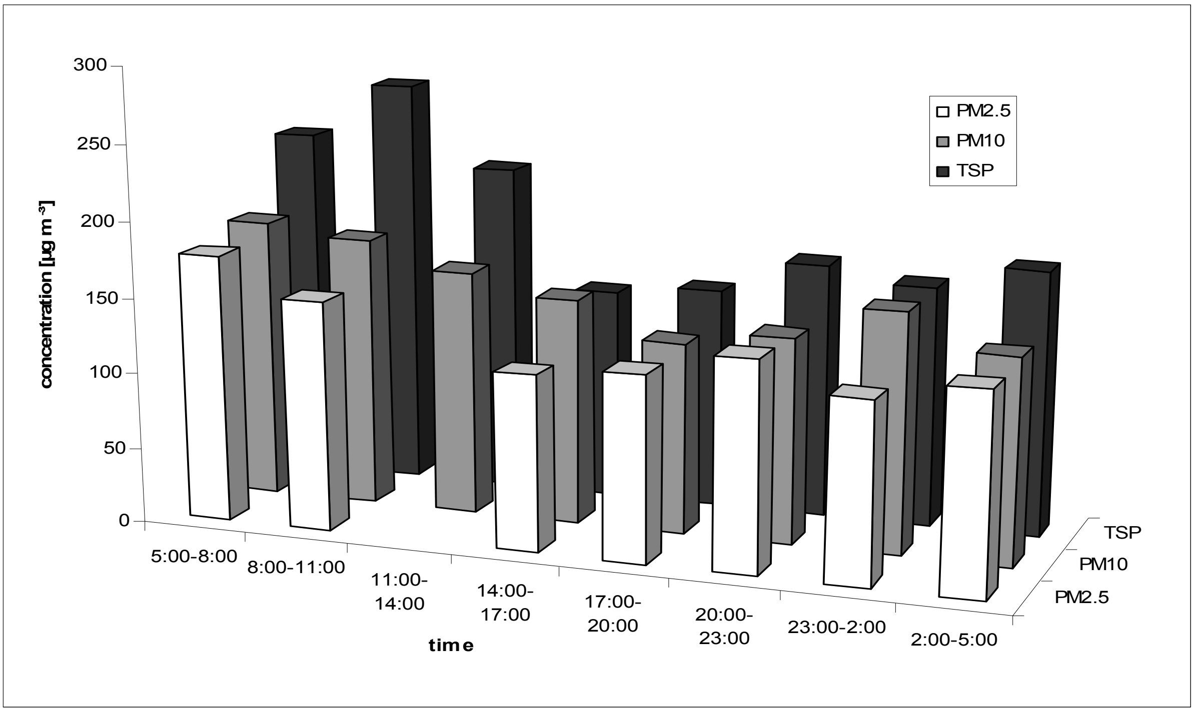

Figure 4.42: Particle size distribution at DBW on 10th of August 2006. Data are based on 1-h values of PM2.5, PM10 and TSP concentrations. PM2.5 was not recorded between 11:00-14:00 Hrs.

The diurnal changes of the three PM fractions during 24 hours in September 2006 are shown in Figure 4.43. Measurements took place between 13th and 14th of September 2006, with high PM concentrations generally and no rainfall. PM2.5 constituted again a larger fraction of PM10 during the course of the day, also shown with averaged PM2.5/PM10 ratio of 0.8. The lowest PM2.5/PM10 ratio of 0.5 and the largest contribution of TSP with about 43 % can be seen at 18:00-21:00 Hrs. The beginning of the "truck time" and thus the increase of activities at construction sites during late evening nearby DBW may be regarded a primary source for the larger amount of coarse particles and thus the lower ratio. Additionally, the temperature decreased from 20 °C to 14 °C during this time period and may have interrupted the formation of secondary particles. Throughout the day, the PM2.5 fraction represented 55 % of the dust load on average, PM10 about 17 % and TSP about 28 %.

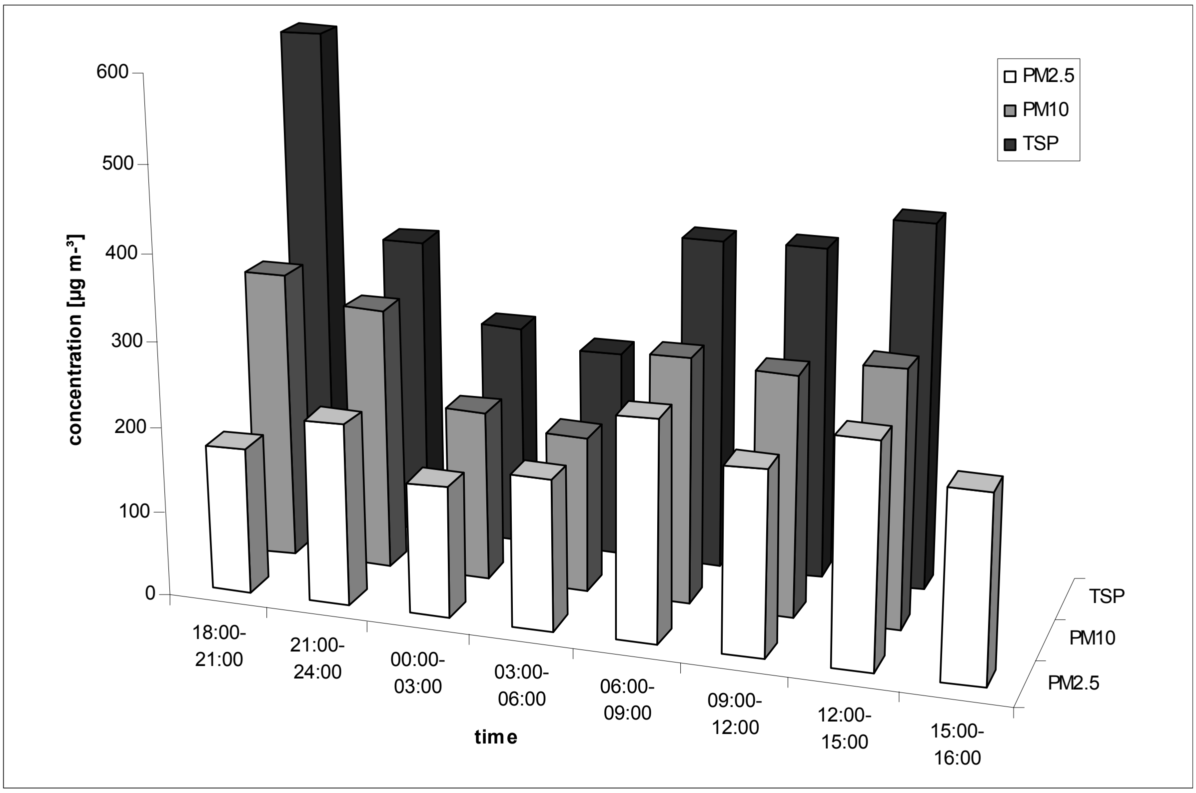

Figure 4.43: Particle size distribution at DBW between 13th and 14th of September 2006. Data are based on 1-h values of PM2.5, PM10 and TSP concentrations.

The diurnal contribution of the three PM fractions during 24 hours in October 2006 is shown in Figure 4.44. Measurements took place between 4th and 5th of October 2006 covering the harvesting time of summer maize at DBW. The PM2.5/PM10 ratio on that day was 0.6 and was somewhat lower than in September and August. Throughout the day, the PM2.5 fraction represented 50 % of the dust load on average, PM10 about 35 % and TSP about 15 %. This finding indicates that coarse particles contributed 50 % to measured PM levels. Obviously, mechanical activities such as harvesting, tillage and ploughing as well as biomass burning during and after harvest on experimental sites in DBW may have caused this distribution of particle sizes and the high PM level in general. The slightly higher PM10 than TSP concentration between 21:00 and 24:00 Hrs. occurred due to the one by one impactor change on hourly basis as described in chapter 3.2 and the comparison of the three PM fractions might be therefore not as accurate as in a parallel measurements.

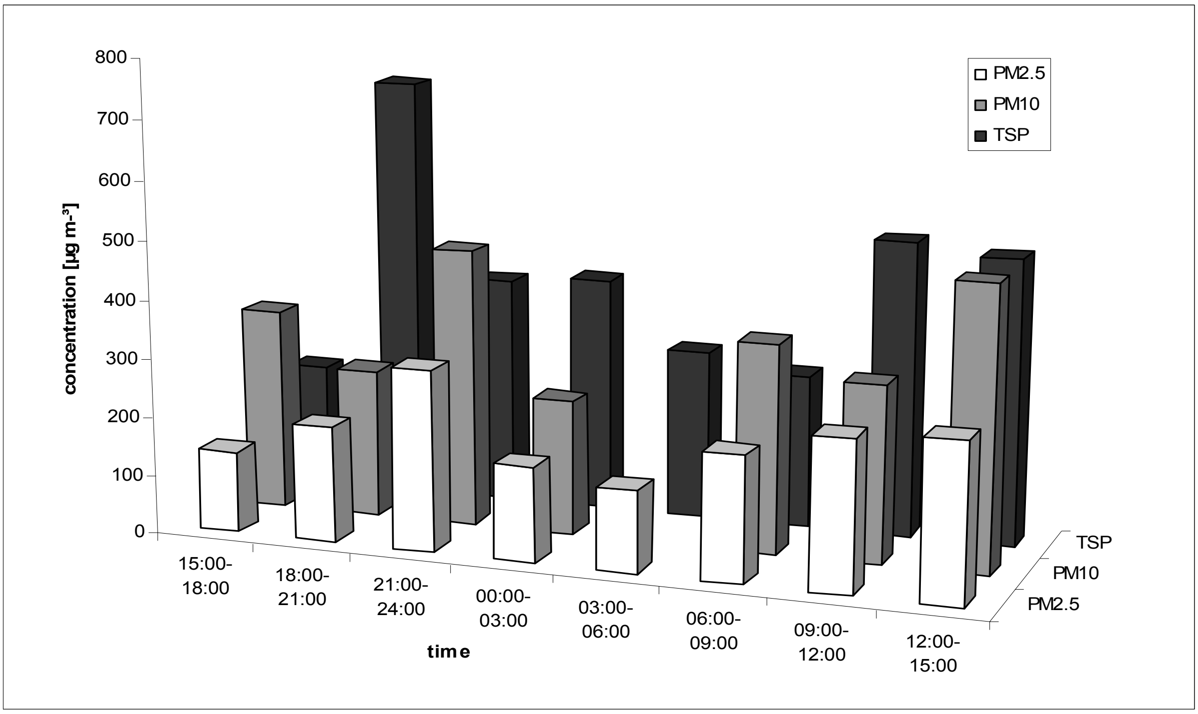

Figure 4.44: Particle size distribution at DBW between 4th and 5th of October 2006. Data are based on 1-h values of PM2.5, PM10 and TSP concentrations. PM10 was not recorded between 3:00-6:00 Hrs.

The contribution of the three PM fractions with the PM2.5/PM10 ratio of 0.6 during three weeks in October 2006 at DBW is shown in Figure 4.45. The daily change of impactors took place between 5th and 26th of October 2006 at 9:00 Hrs. Throughout these three weeks, the PM2.5 fraction represented 35 % on average, PM10 about 19 % and TSP about 46 %. The Figure shows that from 5th to 8th of October TSP constituted almost two third of dust load. Especially on the 6th of October visibility was extremely low. From 4th to 7th of October tillage and ploughing on most of the experimental fields at DBW took place as confirmed by own observations. Obviously, dust particles caused by these agricultural activities had been incorporated in the measurements. From 21st to 23rd of October TSP constituted even more than two third of dust load probably affected by the meteorological conditions. Rainfall occurred on that day when PM10 was measured and led to removal of particles from the atmosphere. The day after, strong winds (3 m s^{-1} on average) came from north-west and caused a blue-sky day (own observations) and it may be assumed that coarse particles from north-west regions were transported and blown to DBW site. The higher PM2.5 than PM10 concentration during this time occurred due to the one by one impactor change on daily basis as described in chapter 3.2 and the comparison of the three PM fractions might be therefore not as accurate as in a parallel measurements.

Analysis of the obtained PM2.5/PM10 ratios ranging from 0.3 to 0.8 did not display a clear distribution of PM fractions over the study period. From 5th – 11th of October PM2.5/PM10 ratios of 0.8 were obtained and can probably be related to the crop residue burning after the harvest at DBW. As stated above, such high PM2.5/PM10 ratios suggest relatively high contributions from secondary particles and the combustion sources (Oanh et al., 2006). Lower ratios indicate a higher contribution from primary sources such as re-suspended soil and road dust and other mechanical activities.

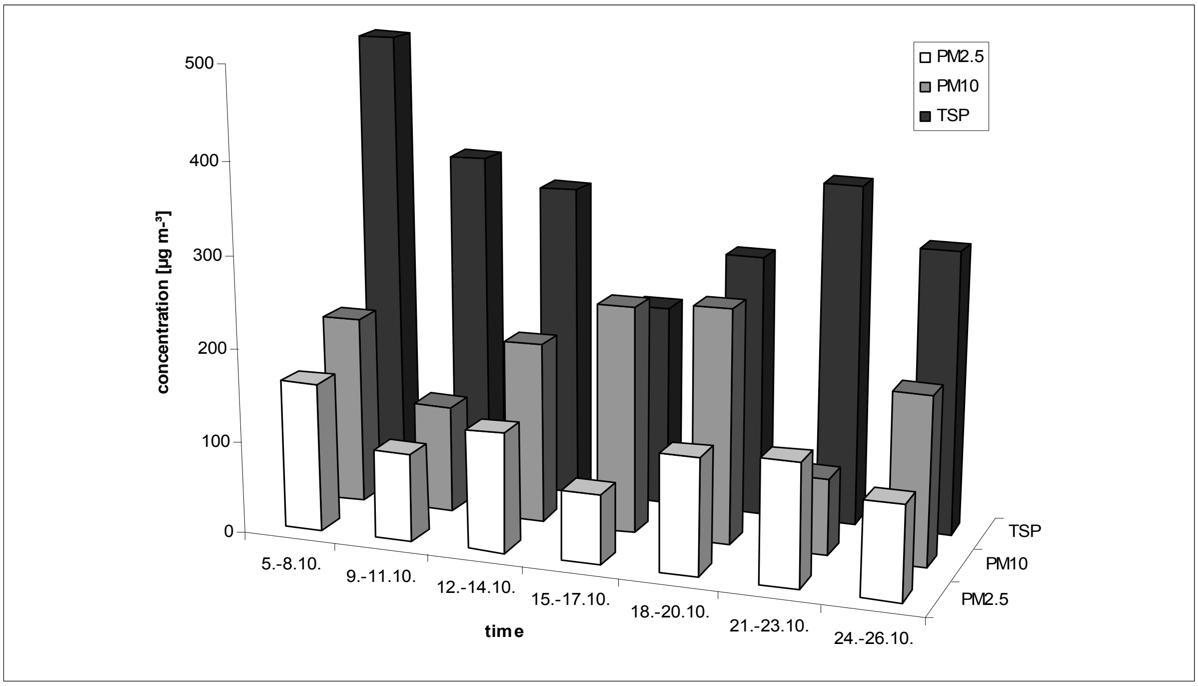

Figure 4.45: Particle size distribution at DBW between 5th and 26th of October 2006. Data are based on 24-h values of PM2.5, PM10 and TSP concentrations.

The contribution of the three PM fractions during August, September and October in 2006, respectively summer and autumn, is shown in Figure 4.46. Throughout the study period, PM2.5/PM10 ratios ranged from 0.8 in August and 0.4 in September to 0.6 in October. The PM2.5/PM10 ratio on average during the study period (0.6) is in agreement with the annual PM2.5/PM10 ratios observed in Beijing (0.6) and other Asian cities as reported by Oanh et al. (2006). Yang et al. (2002b) reported on ratios of 0.66 in winter and 0.49 in summer at Beijing implying that the coal combustion used for the heating of buildings produces many ultra fine particles in the winter. The high PM2.5/PM10 ratio in summer at DBW may be attributed to different sources. It can only be assumed that more secondary particles may be formed due to more intensive photochemical reactions or the emission from the vehicular fuel combustion may be increased due to more traffic during summer which has been reported for two other

Asian cities during the wet season (Oanh et al., 2006). Overall, PM2.5 occupied about 70 % of the total PM in August whereas its contribution was decreasing from 42 % in September to 38 % in October. The contribution of coarse and total suspended PM was about two times larger in autumn than in summer.

Overall, similar to the daily PM levels, highly fluctuating PM2.5/PM10 ratios are the reflection of the changes in the meteorology and emission throughout a time period with sources that are discontinuous and episodic in nature, and sources that are not. The PM2.5/PM10 ratio values obtained did not display a clear seasonality. Few studies on PM2.5/PM10 ratios in the Beijing region and other Chinese locations reported different ratios (Yang et al., 2002b; Niu et al., 2006) and similar ratios (Cao et al., 2003; Cao et al., 2004) in different seasons. In general, concentration data increases from August to October 2006 for all three PM fractions being a part of the annual course of PM pollution at DBW. The slightly higher PM10 than TSP concentration in September occurred due to the one by one impactor change on daily basis as described in chapter 3.2 and the comparison of the three PM fractions might be therefore not as accurate as in a parallel measurements.

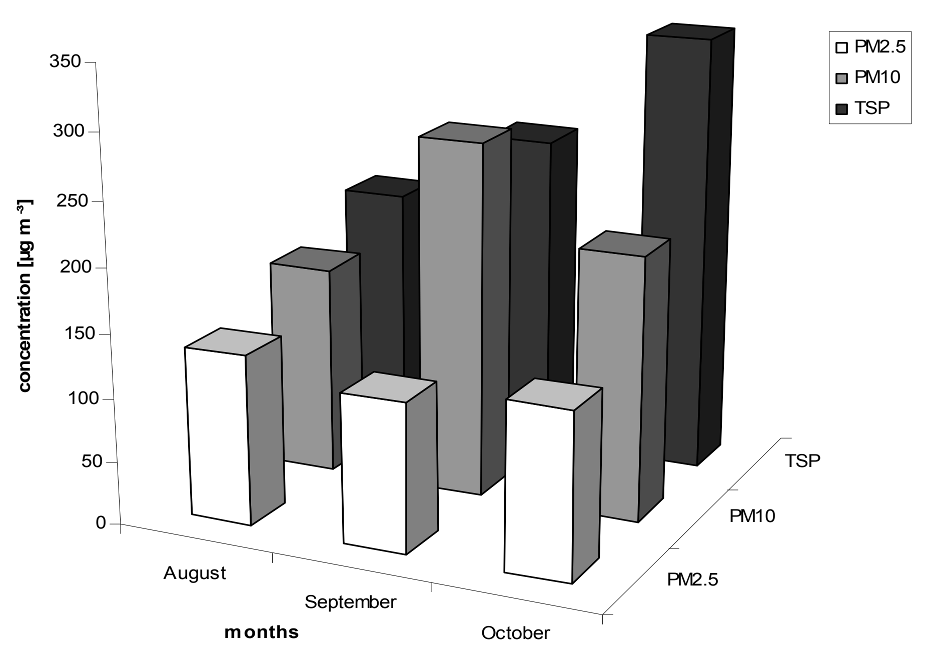

Figure 4.46: Mean concentration for PM2.5, PM10 and TSP at DBW in August, September and October 2006. Data are based on 24-h values of PM2.5, PM10 and TSP concentrations. Data were available for 42 days (PM2.5), for 44 days (PM10) and for 26 days (TSP).

4.2.9 Filter analyses (test phase)

Results of the determination of particulate ammonium and nitrate are shown in Table 4.2. As can be seen higher nitrate than ammonium values were obtained which seems to be contradictory to other published annual data (Shen et al., 2009). It should be repeated that only a small part of the loaded filters were tested covering the time period from the end of April to the end of May 2005. The high nitrate values were obtained from those TSP samples which are clearly related to the dust event which was described in chapter 4.2.2. Such high nitrate concentrations during dust storms may be due to gas phase and/or particle phase. Nitrogen can be transported into DBW with the soil dust or gas phase partitioning of nitrogen species to the particle phase due to the large amount of particulate matter in the atmosphere. This finding might be the reason for the increased nitrate concentrations which was also described during dust storm events in Beijing by Dillner et al. (2006). Moreover, low ammonium and nitrate concentrations during rain events are listed in the Table indicating the wash out of these N species with particulates.

Table 4.2: Particulate ammonium and nitrate measured on glass fibre filters at DBW in 2005

	date	daily concentration	pNH_4^+	pNO_3^-
		[µg m^{-3}]	[µg m^{-3}]	[µg m^{-3}]
TSP	26.4.05	379	5.3	33.6
	27.4.05	510	6.7	26.9
	28.4.05	905	4.5	6.2
	29.4.05	452	3.4	30.8
	1.5.05	357	2.2	7.8
	2.5.05	482	2.2	15.4
	3.5.05	569	3.1	19.3
	4.5.05	504	3.6	27.4
	5.5.05	113	0.6*	1.4*
	7.5.05	235	1.1	12.3
	8.5.05	205	1.7	2.0
	9.5.05	134	0.8	0.8
PM10	12.5.05	148	11.2	28.0
	15.5.05	208	28.0	21.8
	16.5.05	135	33.6	10.6
	17.5.05	97	0.6*	1.4*
	18.5.05	73	0.8	5.6
	19.5.05	112	1.4	8.4
	20.5.05	170	3.1	21.6
	21.5.05	115	6.2	14.6
	22.5.05	73	1.1	4.8
	23.5.05	111	1.7	9.5
	24.5.05	131	7.6	14.8
	25.5.05	241	1.1	10.1

* rain event

4.2.10 Measurements of ^{15}N

The mass spectrometric measurements were a challenge due to the filter material. Especially the combustion of the glass fibre filters limited the measuring runs of the IRMS leading to more often changes of the oxidation pipe than during normal measurements or an uncompleted combustion of the samples in general. The $\delta^{15}N$ values of the quartz fibre filters seem to be therefore more reliable. In fact, a lot of filter material with a small amount of dust load was combusted resulting in low total nitrogen amounts which related to both filter types. Acetanilide with 10.36 N % was thus not the optimum standard to calculate total N and $\delta^{15}N$. Especially the isotopic measurements of PM samples collected on hourly basis must therefore be regarded very critically due to the low PM load on the filter compared with daily samples. These results are not shown. Overall, observed total nitrogen on the samples ranged from 0.0 – 22.4 % (data not shown) and ^{15}N ratios were found to be very heterogeneous ranging from -3.0 ‰ to 44.3 ‰ (n=216), including both filter types. The statistical summary is given in Table 4.3. As can be seen, there is the high standard deviation between daily samples and obviously a difference in results depended on the filter materials used which makes it difficult to get a clear picture. Thus, Figure 4.47 is only a trial to illustrate the isotope ratios of PM10 on a time scale.

Table 4.3: Nitrogen isotope ratios ($\delta^{15}N$) in PM2.5, PM10 and TSP collected at DBW, China, on daily basis in 2005 and 2006

		PM2.5		**PM10**		**TSP**	
		$\delta^{15}N$ ratios [‰]		$\delta^{15}N$ ratios [‰]		$\delta^{15}N$ ratios [‰]	
	Filter	Range	Mean±SD	Range	Mean±SD	Range	Mean±SD
2005	GF10	-3.0 to 19.9	8.6±4.0	0.7 to 16.3	8.2±4.0	2.0 to 5.7	3.6±1.4
2006	QMA	3.1 to 44.3	20.2±9.2	3.2 to 39.8	20.9±7.3	0.8 to 31.4	18.4±7.7

SD = Standard Deviation

The variations of the ^{15}N ratios (Figure 4.47) suggest that they are controlled by several parameters including changes in air mass origins, their transport and contribution of local source. It is e.g. known that particles emitted from the combustion of fossil fuels such as unleaded gasoline, diesel, fuel oil and coal show $\delta^{15}N$ ratios between -19.4 ‰ and +5.4 ‰ (Pavuluri et al., 2010; Widory, 2007). In contrast, a significant contribution from biomass burning (C3 and C4 plants) in Brazil was shown by Martinelli et al. (2002) with ^{15}N values ranging from 8.3 ‰ to 18.7 ‰.

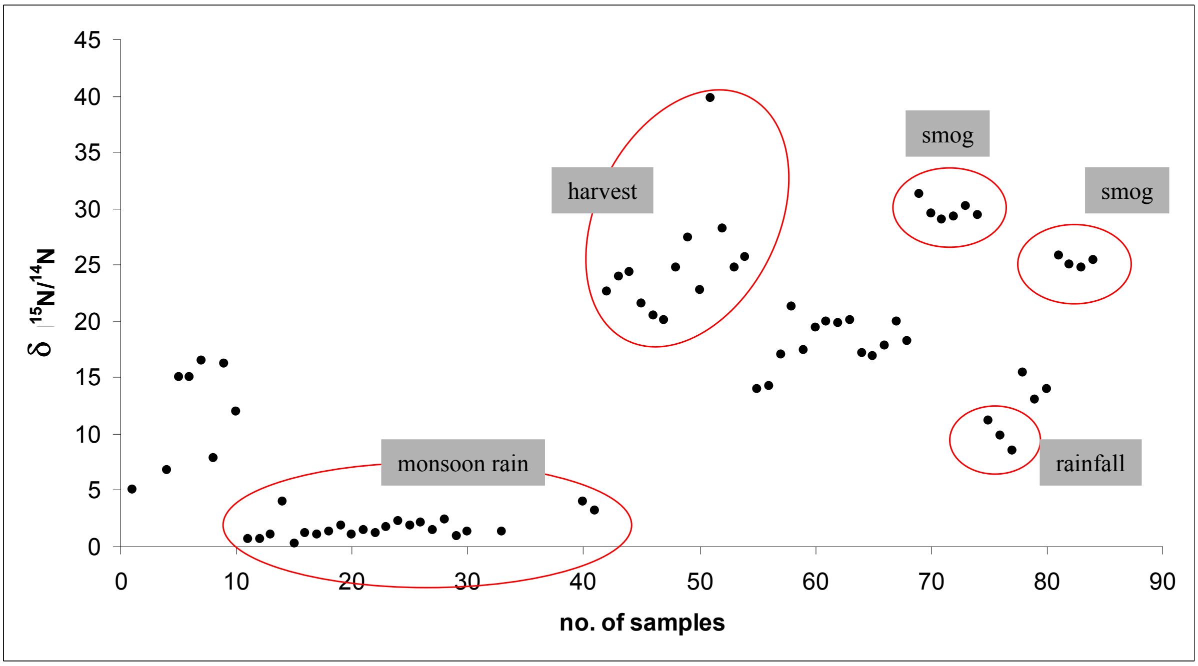

Figure 4.47: Nitrogen isotope ratios (δ^{15}N) in PM10 collected with glass fibre filters (no. 1-42, in summer) and quartz fibre filters (no. 43-84, in autumn) at DBW, China, in 2006. Ratios are based on two replicates of isotopic analysis, at least.

Similar δ^{15}N ratios to DBW were found in India by Pavuluri et al. (2010) clearly indicating that bio-fuel/biomass burning and animal excreta were the two major sources of atmospheric N species in the South and South East Asian region. Furthermore, recent measurements of aerosols in Jeju Island, Korea, showed a significant enrichment in ^{15}N with δ^{15}N values of 6.8‰ to 26.9‰, and attributed to significant atmospheric processing of N species, mainly emitted from China, during long range transport (Kundu et al., 2010). The author obtained the highest δ^{15}N values (mean 20.2±5.2 ‰) during summer and autumn and explained them partly by an enhanced contribution of ^{15}N- enriched emissions from agricultural straw burning in China in a harvest season (summer and autumn). These findings correspond very well with the δ^{15}N values of this study during the same time. Overall, the Asian 15^{N} ratios are remarkable higher compared with other ratios in the world as shown in Table 4.4.

Table 4.4: Nitrogen isotope ratios ($\delta^{15}N$) in atmospheric aerosols collected at different locations over the world

Location/Source	Form of N	$\delta^{15}N$ ratios [‰]			Reference
		Range	Mean±SD		
DBW, China	TN	0.8 to 44.3	20.0±8.4	n=160*	this study
Chennai, India	TN	15.7 to 31.2	23.9±3.3	n=49	Pavuluri et al., 2010
Jeju Island, Korea	TN	6.8 to 26.9	15.1±3.4	n=84	Kundu et al., 2010
Jeju Island, Korea	TN	-3.7 to 12.4	10.6		Kawamura et al., 2004
Piracicaba, Brazil	TN	7.0 to 18.7			Martinelli et al., 2002
Paris, France	TN	5.3 to 15.9			Widory, 2007

TN = Total Nitrogen; SD = Standard Deviation; * only quartz fibre filters

(adapted from Pavuluri et al., 2010)

4.2.11 Synthesis

Other authors also reported on the high PM levels in Beijing (Wang et al., 2008b) and on the exceedances of air quality limits (Zhang et al., 2007b). The inter city comparison in Asia by Oanh et al. (2006) showed the highest levels of PM2.5 and PM10 in Beijing supporting the findings of present study.

In comparison, the **quantity of exceedances** of the European daily mean PM10 threshold in rural European regions is less than 20 times per year (BUWAL, 2005). PM10 concentrations at European rural sites normally range between 5 and 19 µg m^{-3} (Gnauk et al., 2005; Jones & Harrison, 2006; UBA, 2009b) which is similar to the range of PM2.5 concentrations at rural sites (Hueglin et al., 2005; Putaud et al., 2004). Long-term measurements at a European rural site by Held et al. (2008) recorded highest median PM values during spring and autumn with PM10 up to 35 µg m^{-3} and PM2.5 up to 25 µg m^{-3}. Only in extreme situations in wintertime the daily PM10 in the rural background of Europe can reach values > 50 µg m^{-3} as described for Eastern Germany by Spindler et al. (2010). The main sources for those extreme situations are the long-range transport of polluted continental air masses and secondary particle mass formation in combination with low mixing volume and wind velocity. The study by Spindler et al. (2010) was carried out at a rural background site in Europe with semi-natural grassland but was surrounded by agricultural land. Moreover, PM samples within that study were taken by the same High Volume Sampler which had been used at DBW and thus can be compared with. The measured mean PM values (PM10 with 24 µg m^{-3} and PM2.5 with 19 µg m^{-3}) were the highest at a rural site in Europe in 2006. In contrast, the mean PM values in 2006 at DBW (PM10 with 187 µg m^{-3} and PM2.5 with 123 µg m^{-3}) were seven to six times higher than the European ones.

Although the PM monitoring site was located in an agricultural setting it must be noted that the air quality at DBW is much affected by air masses from the nearby Beijing mega city. In Europe, the quantity of exceedances of the PM10 threshold at **urban** sites is often more than 35 times per year (Charron et al., 2007; Jones & Harrison, 2006, UBA, 2009b). Mol et al. (2008) reported for 2017 stations in Europe that the PM10-limit value for daily values generally is exceeded frequently at urban (more than 35 %) and traffic stations (more than 60 %) and occasionally at **rural** background stations. High local and regional contributions may also be responsible for those exceedances as Moreno et al. (2006) reported for an industrial site, where a total of 113 days was recorded exceeding the daily European PM10 threshold during one year. In Europe, high daily PM peak concentrations at urban sites also exist but the PM pollution level differs quite a lot from those in Asia, respectively China. According to Table 2.7, urban daily PM10 concentrations in China may range from 59 to 262 µg m^{-3} without dust storm events. Values for rural sites in China range from 66 to 118 µg m^{-3}. These ranges imply that the daily European PM10 threshold is exceeded almost each day at the Chinese PM monitoring stations, no matter if the station is located at a rural or urban site. The PM10 concentrations at DBW site confirmed this picture. Only under extreme meteorological conditions such as heavy rainfalls PM levels of less than 50 µg m^{-3} were detected at DBW.

The PM2.5 network in Europe is not comparable with the existing PM10 network since there are still a limited number of operational PM2.5 measurements. While PM10 mass concentrations have been monitored by national and international air pollution networks for two decades (see e.g. EMEP and AirBase data banks), PM2.5 measurements are still being started up at many sites in Europe (Putaud et al., 2010). Results of 217 European stations generally showed an increase from rural background to urban background to traffic locations, in accordance with increasing proximity to PM sources (Mol et al., 2008). High annual PM2.5 concentrations at urban sites in Europe can range between e.g. 30 µg m^{-3} for Prague (Sillanpää et al., 2006) and 45 µg m^{-3} for Turin (Götschi et al., 2005) and thus exceed the 25 µg m^{-3} limit value of the new Air Quality Directive of the European Union (EC, 2008). In China, annual PM2.5 concentrations were reported between 31 and 106 µg m^{-3} according to Table 2.6. Overall, daily PM2.5 concentrations may range from 53 to 303 µg m^{-3} at urban sites depending on time and location which is similar to the range of observed PM2.5 concentrations at DBW in 2005 and 2006. At Chinese rural sites daily PM2.5 concentrations were reported to be much lower than in cities with values up to 24 µg m^{-3} (see Table 2.6). The PM2.5 levels of own measurements at DBW clearly showed results similar to reported ones for Chinese urban sites. However, the PM2.5 pollution level there is still about three times higher in comparison with urban sites in Europe.

The **traffic**-related particulates are one of the most important sources of air pollution deteriorating the air quality of Beijing. Since cars are the most important source of urban air pollution worldwide (Fenger, 2009), Beijing became aware of the explosive increase of emissions by vehicles latest before hosting the Olympic games in 2008 (Watts, 2005). Actually, 15.500 new cars are registered every week and the number of cars in Beijing are estimated to reach five million by the end of the year 2010 (Geo TV, 2010; see Figure 1.1). For urban areas in highly industrialized countries of the world, Han & Naeher (2006) reviewed that traffic-generated emissions were estimated to account for more than 50 % of the total emissions of PM, but for China they noted that PM10 and PM2.5 levels at traffic sites were generally much higher than those found in the U.S. and Europe and the highest ones among four other Asian sites. Knowledge on PM characterization of emissions of gasoline and diesel cars in China is not available in comparison with EU and U.S. (Yao et al., 2009) and no concrete number of total traffic-generated emissions of PM for China was found in literature.

With regard to PM measurements at DBW the influence of traffic on particle concentration was clearly demonstrated. Results obtained by Gros et al. (2007) also showed that the PM nighttime peak measured in Beijing was closely related to diesel emissions from trucks which are allowed to circulate only during the night. It is assumed that this source also strongly influenced the increase of particle concentration in the night at DBW as shown with the hourly measurements of TSP, PM10 and PM2.5. The peaks observed in the evenings and at night in 2005 and 2006 at DBW occurred between 17:00 and 1:00 Hrs. and were often maximum peaks of the day. After 17:00 Hrs., the traffic density in the rush hour tends to lead to increasing vehicle emissions and more road dust suspension and finally increasing secondary aerosols concentrations. The reported night peaks at 20:00 Hrs. by Wu et al. (2008) or at 19:00 Hrs. by Zhang et al. (2007a) for PM10 and PM2.5 at Beijing were also associated with evening-rush-hour traffic. At DBW, the majority of observed maximum peaks for TSP, PM10 and PM2.5 also occurred between 17:00 and 21:00 Hrs., only some occurred later until 1:00Hrs. The results thus demonstrate that road traffic is a significant source for the air pollution at DBW. Also morning peaks observed between 7:00 and 8:00 Hrs. for the three PM fractions at DBW are assumed to be related at least partly to the morning traffic rush hour. Moreover, analyses of weekly variations of PM2.5 and PM10 showed homogeneously distributed concentrations over the weekdays due to similar traffic density each day.

PM nighttime peaks for Beijing were not only related to diesel emissions from trucks, but also stemmed from industries located in the south of the city (Gros et al., 2007). Some of the plants are allowed to work only during the night and thus are also assumed to strongly influence the increase of particle concentration in the night at DBW depending on meteorological conditions. **Coal** is still the major source of energy in China (Kan et al., 2009) and also the major source for industrial activities including heat generation in winter (Zheng et al., 2005). The coal-fired power plants are still dominant in the power generation sector in China occupying about 45 % of total PM emissions whereas in Beijing, all coal combustion sources contribute to 15-20 % to fine particles according to Yao et al. (2009). Indeed, own measurements of PM2.5 during winter 2005 showed not only increased but the highest concentrations ever of the study time with the beginning of the **heating** period in November. The monthly mean of PM2.5 in November was remarkable higher than in other months. High PM2.5 emissions in the winter resulting from increased emissions from heating sources were also reported by Zhao et al. (2009) or He et al. (2001). Duan et al. (2006) detected the PM2.5/PM10 ratio of 0.8 during winter in Beijing concluding that the combination of increased emission for heating supply and the favourable meteorological conditions had strengthened the fine particle formation.

The wide-spread **construction activities** are one special urban aspect since they have also exacerbated Beijing's air pollution problems (Chan & Yao, 2008). In 2004, over 3.600 construction sites were simultaneously underway within Beijing area (National Bureau of Statistics of China, 2004) and new ones were allowed to be established until the end of the year 2006 taking into account the air quality policy before the Olympic Games in 2008. Therefore it can be assumed that the number of construction sites in Beijing area might have been increased during the study time at DBW since 2005 and 2006. These were the last years before some air policy measures regarding the Olympic Games were set up. During own hourly observations of PM at DBW, several construction activities nearby the study site and a permanent flow of heavy trucks, often uncovered, driving to construction sites were observed at night. The sampled PM peaks during late evenings might therefore strongly be influenced by these sources. Hourly measurements in September showed that especially the PM10 level was even slightly higher at night than at day. Moreover, the lowest PM2.5/PM10 ratio of 0.5 and the largest contribution of TSP with about 43 % as shown between 18:00 and 21:00 Hrs. of the same day may be explained by the elevated generation of road dust. Re-suspended road dust is estimated to account about 25 % of the total PM at urban sites in Germany (UBA, 2005).

Amato et al. (2009) showed for Barcelona that traffic of uncovered heavy trucks, as also observed at DBW, played the biggest part in controlling the spatial variation of load of PM10 road dust and construction activities within an urban area sharply increased the levels of PM10 road dust. It can be concluded that the dust developed from the intensive construction activities near DBW, especially during night, was subsequently re-suspended by road traffic. “Moreover, the deposited PM load at construction sites [can] act as a reservoir or trap for traffic-related particles, which gives rise to large amounts of hazardous pollutants available for resuspension” (Amato et al., 2009, p. 1650). A European PM study done in the Western Mediterranean area dealing with PM contributions in relation to construction activities concluded the same (Pey et al., 2010). The author reported on large contributions of the coarse fraction of sampled PM due to the extremely abundant construction activities combined with the special adverse climatology of the Mediterranean region. Long dry periods favoured the dust accumulation and resuspension, additionally. The combination of dry conditions and construction activities also referred to the study site at DBW. The limited wet removal of air particulates during the dry season mainly affected the contributions of each PM fraction leading to a twice times larger contribution of coarse particles and total suspended PM than in the wet season.

Since DBW is an agricultural setting, the **influence of agriculture** on the PM measurements is another important aspect to taken into account. Agricultural operations on open fields such as ploughing, harrowing, disking and harvesting “are known to lift particles into the air” as described by Winiwarter et al. (2009, p. 3822) and own PM measurements strongly reflected the agricultural activities at DBW. The highest daily PM10 concentrations in both study years were measured during harvest times of winter wheat (412 $\mu g\ m^{-3}$ in 2005), spring maize (262 $\mu g\ m^{-3}$ in 2005) and summer maize (341 $\mu g\ m^{-3}$ in 2006). It is known that emissions of PM from agricultural operations are significant and constitute an emerging air quality issue especially in the transition zones between rural and urban environments (Qiu & Pattey, 2008) which is the case at DBW. In 2005, the Canadian Criteria Air Contaminants (CAC) emissions inventory estimated that agriculture accounted for 12 % of TSP, 19 % of PM10 and 5 % of PM2.5 emissions in Canada (Environment Canada, 2007). In Europe, the contribution of agriculture to the primary PM2.5 emissions is about 5 % and 25 % for the PM10 emissions as reported by Erisman et al. (2008). Current investigations show that PM emissions from agriculture in intensive emission areas might be underestimated and probably are more important than previously estimated.

Since the PM peaks at DBW were obtained during harvest time it must be assumed that sampled PM derived from **field preparation** and **harvesting operations** which occurred on the days during harvest time. Up to now, only several studies have quantified the particle size distributions and plume dynamics of agriculturally-derived field preparation and harvesting operations. Dust plumes generated by agricultural field preparation and planting operations on a cotton field were measured by Holmen et al. (2006). The author found that approximately 45-50 % of the measured mass consisted of PM2.5 and 85-95 % could be associated to PM10 during disking and harvesting. Peak levels of ambient particulate concentrations coinciding with the peak agricultural harvest season were also reported by Giles et al. (2006). These findings correspond to own results. In October 2006, during harvest time of summer maize 85 % of the measured mass was PM10 whereas in the months before and after harvest PM10 accounted for only 72 % respectively 65 %. In the same period, PM2.5 accounted for 50 % of the mass.

Another important source of PM related to agriculture is **crop residue burning**. Its influence on the ambient air quality in China is seldom studied (Yang et al., 2008). On the one hand, crop residue energy is still an important part of the rural energy for cooking or heating in China, even though the energy conversion efficiency is only 10 to 20 % as reviewed by Cao et al. (2008, p. 50). On the other hand, there is also crop residue burning in the NCP to get rid of the residue material. Crop residue burning in the field mostly occurs at night (Yang et al., 2008) which was also confirmed by own observations. Therefore Yang et al. (2008) concluded that ambient air quality at night is more serious than at daytime in this period. Own hourly PM measurements during harvest of summer maize in October 2006 confirmed this conclusion. The highest PM2.5 concentration of the day was sampled with 308 µg m^{-3} between 22:00 and 23:00 Hrs. and PM10 with 472 µg m^{-3} between 23:00 and 24:00 Hrs. being remarkably higher than during non-harvest times in October. On the second day of the harvest, high hourly PM concentrations, with TSP of 501 µg m^{-3} between 9:00 and 10:00 Hrs. or with PM10 of 479 µg m^{-3} between 14:00 and 15:00 Hrs. were observed. These peaks may be not only related to crop residue burning but more to soil suspension due to agriculturally-derived harvesting operations. In general, during the four days of harvest of summer maize the PM level for the three fractions was high with 496 µg m^{-3} for TSP, 206 µg m^{-3} for PM10 and 161 µg m^{-3} for PM2.5.

The PM2.5/PM10 ratio of 0.8 of the harvest time indicates that crop residue burning influenced the PM level compared to the average ratio of 0.5 in autumn. Moreover, there is an obvious correlation between the quantity of crop residue burned in the field and PM concentration as stated by Yang et al. (2008). Duan et al. (2004) also stressed that the pollution by biomass burning affects the whole region thus affecting residential areas inside Beijing and the areas inside of a radius of 50 km. Combustion tower experiments by Cao et al. (2008) indicate that wheat straw has the highest PM emission factor which corresponds with the highest daily PM10 concentration during wheat harvest. Yang et al. (2008) found higher PM10 emissions due to crop residue burning in summer than in autumn. Comparisons with European countries are difficult because data in the EU are lacking

As already mentioned the daily **weather patterns** need to be considered in the discussion of own measurements at DBW since they are strongly related to the seasonal and diurnal variations of PM concentrations. On the one hand, the meteorological parameters themselves showed a seasonal and diurnal variability which on the other hand also influenced the PM levels in the atmosphere. Several authors (Guinot et al. 2007; Duan et al., 2006; Chan & Yao, 2008) also reported on the contrasted seasonal climate conditions of Beijing area. Furthermore, the climate conditions at DBW showed a significant day-to-day and night-day variability. The concentrations of the three PM fractions at DBW did not follow a weekly pattern but more a diurnal and seasonal one. For instance, the precipitation pattern showed a clear seasonality from dry winter seasons to rainy summer seasons and rain events leading to wash out of particulates were often reported. Especially during the wet season, the daily PM levels remained below European thresholds after heavy monsoon rainfalls. However, high PM concentration episodes at DBW were mainly related to meteorological conditions during which pollution dispersion was reduced, leading to an increase of PM concentrations as shown for those times when relative humidity was between 60 and 80 %, no rainfall and low wind speeds occurred.

The **wind pattern** is a special parameter regarding the atmospheric PM levels at DBW, especially during the **spring** season. Own observations at DBW during spring showed the influence of dust storm events to PM air pollution in the NCP. The highest wind speeds correlated with the highest TSP concentrations and came from north-westerly directions leading PM masses from the desert regions of China to the NCP. As has been shown before, the dust storms contribute significantly to PM in the spring (Oanh et al., 2006). The extreme high PM loads up 905 $\mu g\ m^{-3}$ sampled during dust events at DBW even called for a more frequent filter change of the High Volume Sampler than during normal days. Data on other fractions are not available but a recent study by Zhang et al. (2010b) in Beijing reported on average mass ratios of PM2.5, PM10 and TSP accounting for 29, 20 and 61 % of the dust load with standard deviations of ±14-15 %, respectively, in spring. Chan & Yao (2008) also observed lowest PM2.5 and PM10 concentrations in Beijing during spring season. Even there were no PM measurements at DBW during spring season in 2006, it should be noted that regional transport of TSP particles definitively occurred while the worst dust storm in at least five years hit Beijing in April leading to 300.000 tons of sand and dust in the city and along the coastlines. These brownish sediments (ABC's) from China-Mongolian deserts clouded the Yellow Sea (CNN, 2006; Natural Hazards, 2006).

Besides the north-westerly winds, southerly winds were also predominant at DBW leading polluted air masses from the southern part of the NCP and Beijing area to the study site. Strong southerly and south-westerly winds connected with high PM loads were also observed at DBW during spring season. Guinot et al. (2007) pointed out that the diversity of the regional wind directions in Beijing region is leading to the homogenization of air pollutants of different origins. The regional PM background of DBW thus originated either from the Beijing source point area, from the densely populated and from the industrialized south and south west of Beijing, respectively Hebei region or from the agricultural used rural areas of Hebei region. Strong winds during spring only suggested that the secondary organic aerosols formation was not so much forced and primary coarse particles such as soil probably contributed a large percentage to the PM levels due to the high wind speeds. In fact, high shares of soil dust during spring were also reported by He et al. (2002) or Duan et al. (2006) and the yellow coloured filter samples from the study site supported this suggestion. With respect to the whole year, particulate soil matter has become the largest part of TSP in Chinese areas such as the NCP with an average level of 40 to 50 % (He et al., 2002). Wang et al. (2008b) even reported on soil as the major source of PM10 in Beijing. These findings indicate that not only in spring the winds blow and transport coarse particles to DBW. In fact, the southerly wind flows were also the most frequent during the other seasons at DBW. These predominant wind flows may have also transported particulate soil matter from agricultural fields of the NCP and other regions in the south to DBW. Modelling results showed that during sustained wind flow from the south, Hebei Province can contribute 50–70 % of the PM2.5 load measured in Beijing (Streets et al., 2007).

The most frequent southerly winds were also described by Wu et al. (2008) during a **summertime** study in Beijing. By using trajectories cluster analysis, the authors described that the southerly air flows are connected with high secondary aerosol loads. The largest contribution of sulphate is generated in the Hebei and Shandong provinces and Tianjin City (all located south of DBW) whereas trajectories with northwest directions were associated with low concentrations of secondary aerosols. This is in line with the estimations made by Streets et al. (2007) for the summertime in Beijing that 34 % on average of PM2.5 came from sources outside of Beijing, including Tianjin municipality, Hebei and Shandong province. Own observations during summer showed a high PM2.5/PM10 ratio of 0.8 in combination with southerly wind flows indicating larger amounts of secondary aerosols than during autumn as indicated by a mean PM2.5/PM10 ratio of 0.5. In combination with the high RH of about 80 % as detected for DBW during July and August, ultra fine particles coagulate with pre-existing particles, and grow through the condensation of water and other gases via gas-particle-conversion and the adsorption on the particle surface to fine particles. Especially the formation of secondary species such as sulphate and nitrate can be accelerated from their precursors SO_2 and NO_x through the high humidity (Zhang et al., 2010b). Additionally, the stronger and longer "solar radiation during summer time [also favours] the photochemical formation of secondary aerosol particles" (Wang et al., 2008b, p. 1324; Guinot et al., 2007). Moreover, the detected high T and RH as well as the low wind speeds in summer at DBW prevented the horizontal and vertical diffusion in the atmosphere and may have forced the formation of secondary particles. In summertime, high T and RH are normal climate conditions caused by subtropical anticyclones that suppress the uplifting of the lower-troposphere as reported specifically for August by Gao et al. (2005). This meteorological condition favours the secondary formation of particles and is relevant also at DBW in August. These conditions explain why there was almost no dispersion of air pollutants in the atmosphere and that the observed PM2.5 level during August 2005 (wet season) was not remarkable lower than during September and October (dry season) of the same year.

The observed PM level in **autumn** at DBW was partly still related to the prevailing meteorological conditions. Stable weather conditions such as intense sunlight, moderate air humidity and less precipitation probably still strengthened the formation of secondary particles but other sources such as agriculture (harvest and crop residue burning) must also be taken into account as can be seen in the PM2.5/PM10 ratio of 0.5. Especially in September, the low PM2.5/PM10 ratio of about 0.4 indicates that coarse particle is the predominant form in DBW. Results obtained by Duan et al. (2006) during autumn in Beijing confirmed this conclusion. Moreover, analyses of PM2.5 concentrations sampled in September showed that obviously low temperatures led to lower PM2.5 concentrations. Indeed, Duan et al. (2006) found that low temperature is not favourable for secondary sulphate formation.

In **winter**, the meteorological parameters wind flow and strength became more important. The prevailing strongest wind flows at DBW came from north-west, similar to spring, as also noted by Chan & Yao (2008) for Beijing. As shown, the north-westerly wind flows were responsible for the "cleaning effect" of the air through the dispersion of particles leading to lower PM levels at the study site during wintertime. Another meteorological aspect during wintertime is that “relatively low temperature and wind speed … [can] favour the formation of … temperature inversions, stable [atmospheric layers] and low mixed boundary layers, which would … lead to the accumulation of pollutants” (Sun et al., 2006, p. 3153). As already shown by Duan et al. (2006) persistent temperature inversions and increases in emissions related to heating in wintertime usually leads to the increases in ambient pollutant concentrations. For Beijing it is known that the boundary layer height is at minimum during winter and therefore strongly influencing the enhancement of atmospheric concentrations (Guinot et al., 2007).

Finally, wind shifts during the sampling period were not only observed on a seasonal basis but occurred also on diurnal and even hourly basis as shown during PM10 sampling in 2005. These shifts could generally lead to mixtures of aerosols from different sources.

PM long-term datasets from Europe illustrate how local concentrations of anthropogenically emitted pollutants are closely linked to daily weather patterns so that source recognition will be difficult (Putaud et al., 2010; Bigi & Harrison, 2010; Viana et al., 2008; Moreno et al., 2006). Velders et al. (2009, p. 3859) pointed out that “meteorological fluctuations to a large degree determine surface concentrations of air pollutants in European countries”. Exceedances of PM thresholds in Europe are often associated with low wind speed and/or stable anticyclonic situation (Charron et al., 2007) and high PM concentration episodes are reported to be mainly related to meteorological situations in which pollution dispersion is reduced (Putaud et al., 2004). Since the last decade, several studies have identified the characteristics of air pollution concentrations in China but only few in terms of sources and sinks in relation to the meteorological processes. Overall, the observed PM results at DBW are closely related to meteorological fluctuations.

Due to its complex meteorological and topographic situation air pollution in Beijing can not be explained only by singular sources as Guinot et al. (2007) noted. This finding is also true for DBW and **multiple sources** are assumed to interplay at the study site. Emissions from the greater Beijing region must be taken into account as well as several combustion sources, industrial pollution from the south east to south west of Beijing and the agricultural sources of Hebei and Shandong province. The high PM levels and the $\delta^{15}N$ values at DBW may be attributed to both natural and anthropogenic factors showing distinct seasonal trends. Extensive coal burning in the NCP during the winter, with limited dispersion, may cause high PM levels during this period of the year, and the dust storms may contribute significantly to PM in the spring. Regarding PM2.5 and PM10 six common sources were defined by Wang et al. (2008b) for Beijing namely, local dust, secondary aerosol, mobile source, biomass burning, coal combustion, and minor industrial emission. Interestingly, the source apportionments of PM2.5 are greatly different among investigations of various research groups (Yao et al., 2009) and especially the variations of PM2.5 concentrations in China are still poorly understood (Zhao et al., 2009). It should be noted that PM2.5 is still regarded as an unspecific measure for a mixture of scores of particulate air pollutants even in Europe (Götschi et al., 2005).

Another aspect is that, besides seasonal changes PM varies along diurnal cycles indicating that fine and coarse particles are different from one day to the other similar to the results reported for Beijing by Gros et al. (2007) or Wu et al. (2008). In general, diurnal variations of PM levels can occur due to local events (such as harvest), episodes linked to enhanced general atmospheric pollution during regional stagnation of air masses including the heat island effect, the arrival of long-range transported air pollutants (such as industrial pollutants from Beijing area, pollutants from Hebei and Shandong province, deserts,) and the described seasonal meteorological changes. Variations of particulate ammonium and nitrate concentrations completed this picture for a part of the study time.

4.3 Ammonia (NH_3)

Due to the fact that the Radiellos® were changed every 14 days, the columns in the Figures consequently represent two weeks, respectively. Overall, ammonia levels were in the range from 9 $\mu g\ m^{-3}$ (Wuqiao) to 43 $\mu g\ m^{-3}$ (Changping). During the first test phase in May 2005, the NH_3 concentrations were clearly highest at the climate station in Wuqiao as can be seen in Figure 4.48. The monthly mean concentration of 18 $\mu g\ m^{-3}$ was measured there. The lowest monthly NH_3 concentration of 11 $\mu g\ m^{-3}$ was also measured at Wuqiao but on the second site, the winter wheat field. At both DBW plots monthly mean NH_3 concentrations of 14 $\mu g\ m^{-3}$ were remarkable higher than at both sites in Quzhou (12 $\mu g\ m^{-3}$), respectively. The most important factor explaining the variation at Wuqiao is that the climate station is located in a distance of 15 m to the toilets of the research station. These toilets are similar to those which are widely used in rural areas in China, with open doors and windows and open pits for the excrements. It is therefore assumed that this source contributed to the high ammonia concentrations. The laboratory blanks showed averaged standard deviation of 0.4 $\mu g\ m^{-3}$ for all three sites together (including the three replicates per site) indicating a high plausibility of the obtained results. Transport blanks showed averaged zero NH_3 concentrations indicating the accurate handling with the Radiellos® and no contamination by storage and transport.

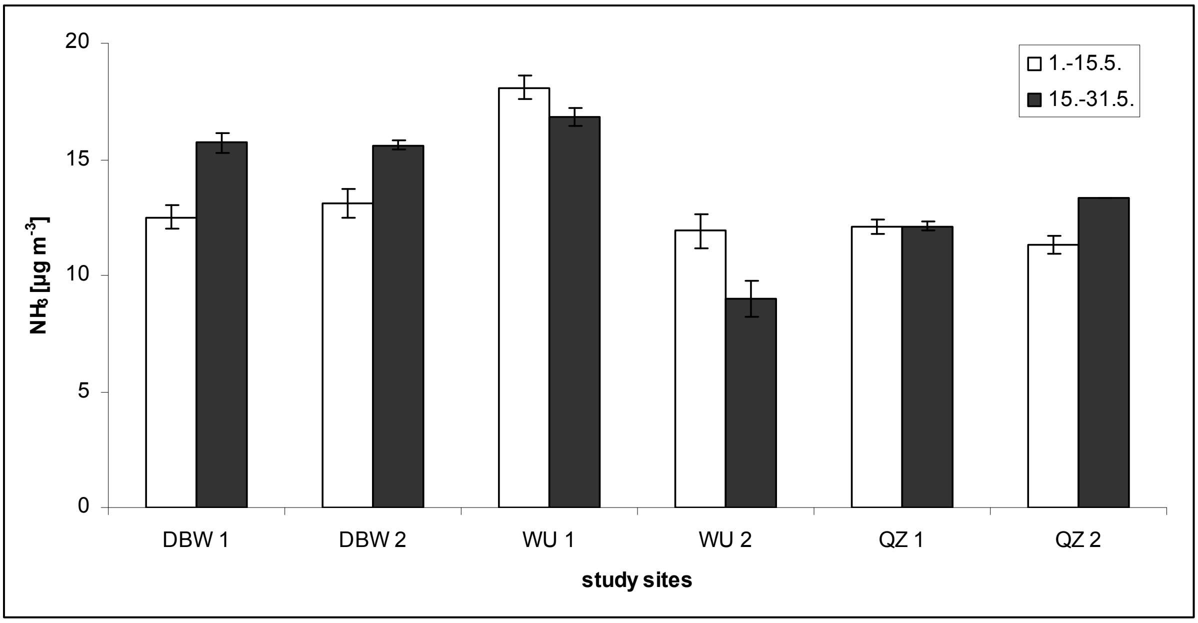

Figure 4.48: Bi-weekly ammonia concentrations measured in the North China Plain in May 2005 (DBW=Dongbeiwang, WU=Wuqiao, QZ=Quzhou; 1=climate station, 2=agricultural field). Error bars representing the standard deviation over three parallels.

At Changping site, the NH_3 concentrations were highest and averaged to 27±1.1 µg m^{-3} between June and October. Parallel NH_3 measurements at DBW were remarkable lower with averaged 22±0.9 µg m^{-3}. Animal production is known to be the main source of ammonia emissions (Hinz & Scholz-Seidel, 2005) and therefore the NH_3 concentrations at the Changping site may be attributed to the livestock production located nearby.

As shown in Figure 4.49, at both sites the highest concentrations were in summer on average 24±0.8 µg m^{-3} at DBW, respectively 30±1.3 µg m^{-3} at Changping. Highest NH_3 concentrations at DBW were also reported in summer the years after by Shen et al. (2009). The seasonal course of the NH_3 concentrations from May to September 2005 at DBW followed the air temperature is shown as positive correlation ($R^2 = 0.68$) in Figure 4.50. This pattern may be attributed to the increased volatility of ammonia at higher temperatures.

Besides the seasonal and spatial variability of the monthly ammonia levels in 2005, a strong relationship to the PM10 loads ($R^2 = 0.80$) at the DBW site was also found according to Figure 4.50. This finding indicates that air pollution may be strongly affected by agricultural activities at that site.

In 2006, NH_3 concentrations at DBW were slightly lower than one year before as shown in Figure 4.51. The mean monthly NH_3 concentrations were 12±0.7 µg m^{-3} in August, 12±0.5 µg m^{-3} in September and 14±0.3 µg m^{-3} in October 2006. Transport blanks showed again averaged zero NH_3 concentrations.

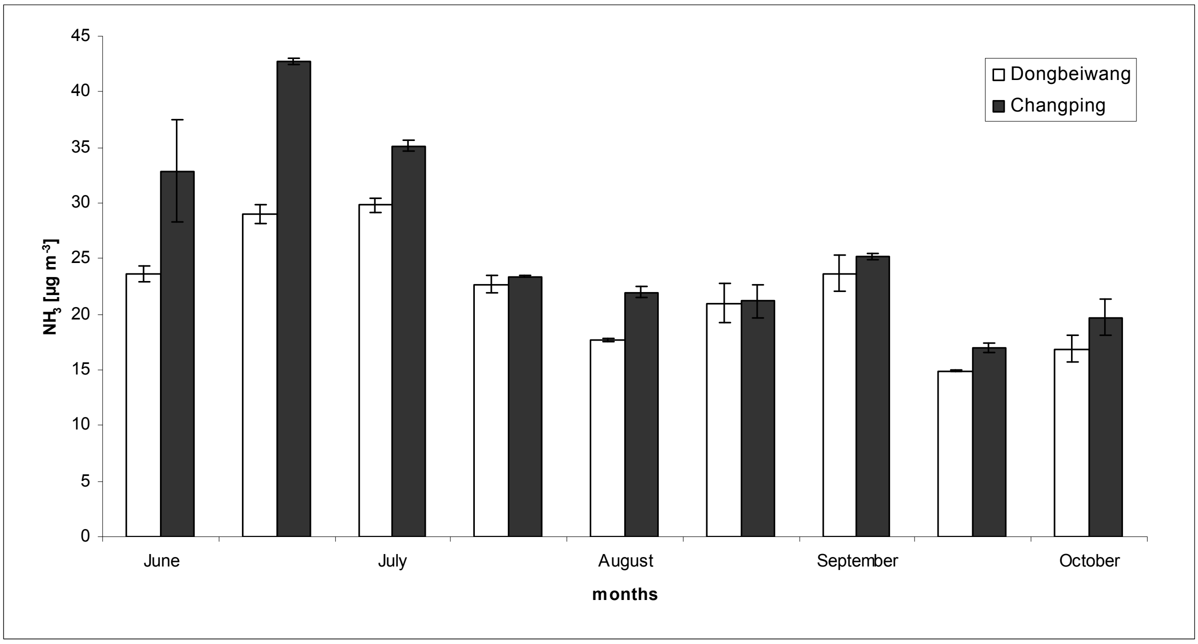

Figure 4.49: Bi-weekly ammonia concentrations measured in the North China Plain in 2005. Error bars representing the standard deviation over two parallels. Data were provided by J. Shen, CAU, in 2006.

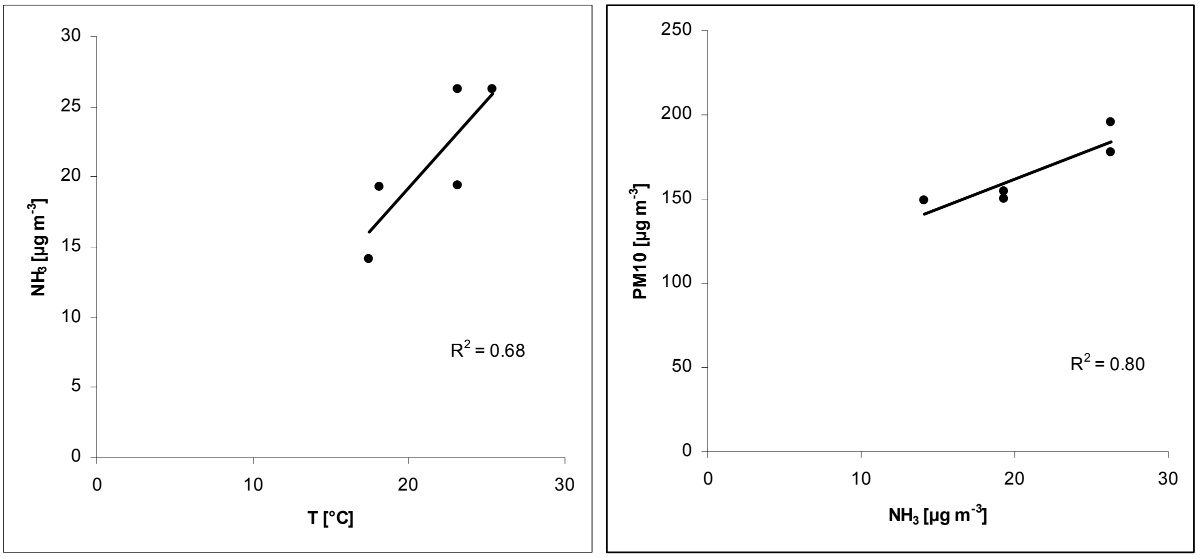

Figure 4.50: Relationship between monthly ammonia concentration (NH_3) and temperature (T) (left) and PM10 (right) determined at DBW from May to September 2005. T data were provided by Dr. Cui, CAU, in 2007.

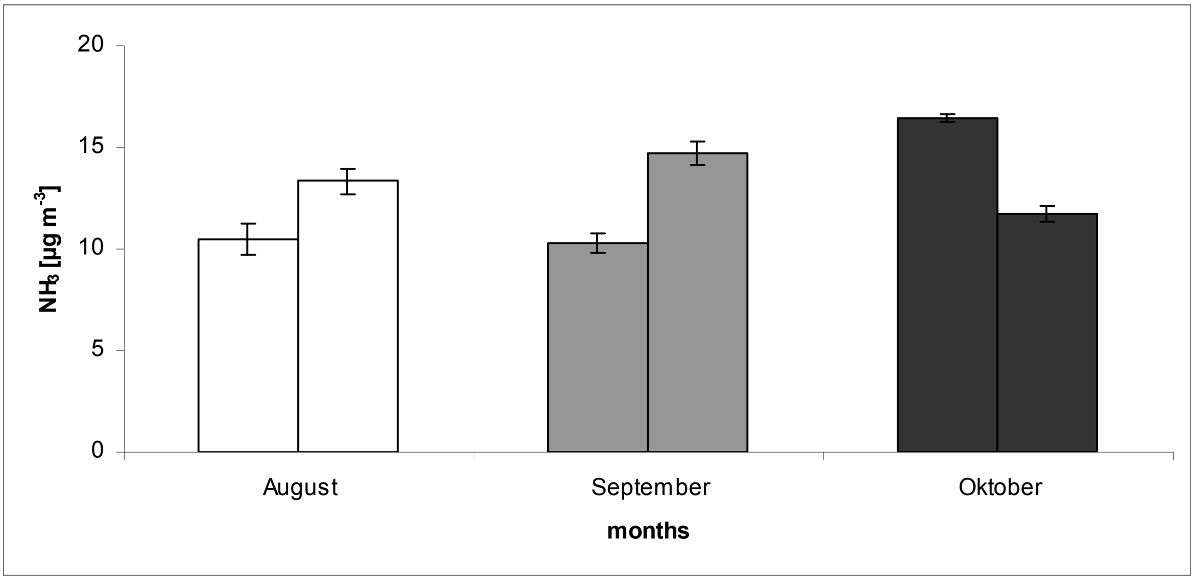

Figure 4.51: Bi-weekly ammonia concentrations measured at DBW from August to October 2006. Error bars representing the standard deviation over three parallels.

Bi-weekly ammonia concentrations at agricultural European sites may also show rates up to 35 µg m^{-3} often indicating specific agricultural activities such as manure application (Van Pul et al., 2008; Bleeker et al., 2006) whereas background concentrations of agricultural areas may range between 3 and 11 µg m^{-3} (Thöni et al., 2004). Only in the Netherlands a higher range between 11 and 22 µg m^{-3} was reported which corresponds with the preliminary mean NH_3 concentrations in the NCP. Long-term NH_3 measurements at urban areas in Switzerland showed also few seasonal fluctuations and the average concentrations measured were similar to those of crop farming or extensive cattle farming areas (Thöni & Seitler, 2009).

Ammonia concentrations obtained at three different heights in the summer maize field in 2005 and 2006 are shown in Figure 4.52. The concentrations declined by averaged 38 % with the distance from 2 m height to 20 cm above ground. This decline of concentrations may give a measure of the NH_3 levels deposited onto vegetation. In both study years, the harvest of summer maize started on 4th of October and it can be seen that the decline of NH_3 concentrations is more distinct in those measuring times when harvest date was not close and plants were still in the growth and mature stage.

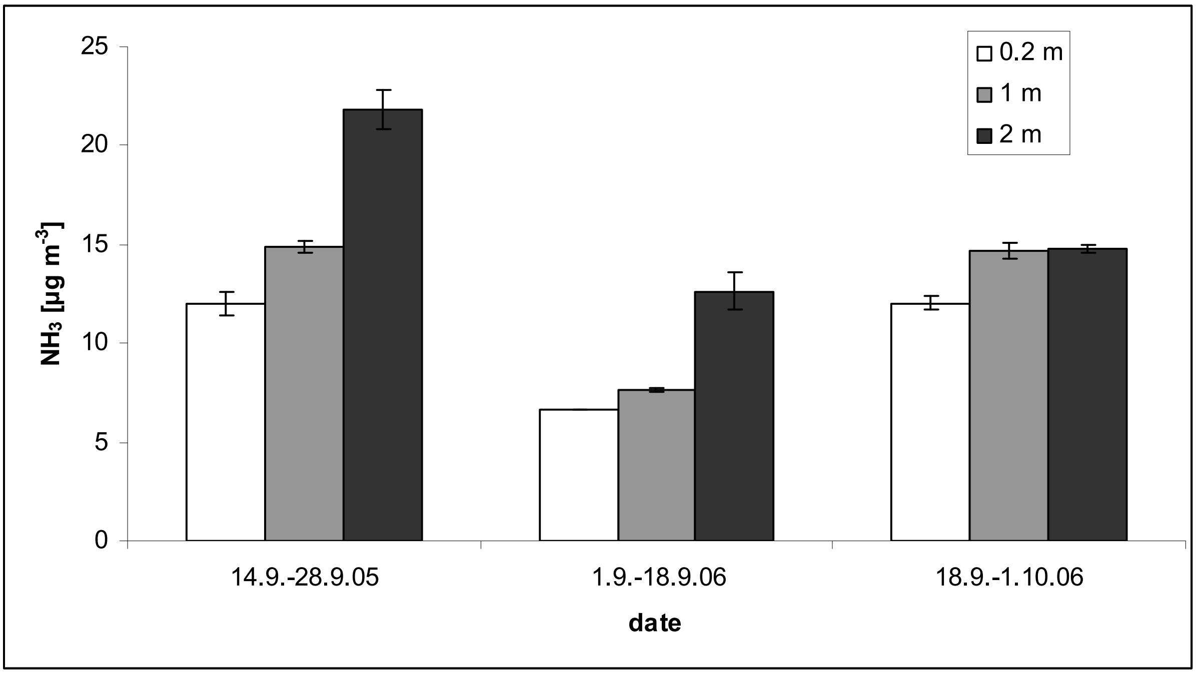

Figure 4.52: Ammonia concentrations measured at different heights on summer maize field at DBW in September 2005 and 2006. Error bars representing the standard deviation over two (1.9.-18.9.06 and 14.9.-28.9.05), respectively three parallels (18.9.-1.10.06).

Overall, high NH_3 levels were observed in the NCP with peak seasonal values. Concentrations were higher at sites characterized by predominant livestock farming. Local sources and sinks have a strong influence on the ambient ammonia concentrations measured as shown for Wuqiao.

Several factors may influence the ammonia measurements, such as e.g. different types of weather protection systems for the passive sampler against meteorological influences. The PVC shelter used at DBW which protected the samplers from precipitation and direct sunlight was recommended by the Radiello® company but the shelter is not the optimum. A weather protection system for passive samplers made by THIES is recommended by the NH_3 working group in Germany (Rienecker, 2005) in order to minimize the influences by temperature, humidity, incident air flow, and bird or fly faeces. Contamination of the Radiellos® by humans might have also occurred, especially at DBW, because the exposed samplers were new and visible for everybody and humans were interested in to touch them. At Wuqiao and Quzhou the Radiellos® were hidden and not visible for the village population. Furthermore, the standard deviations of ammonia measurements during the first test phase at DBW and Changping with two replicates were remarkable higher than those with three replicates. Therefore, three replicates per site were performed during the following studies as done by Shen et al. (2009) in order to ensure data quality.

Finally it should be noted, that there is still an ongoing discussion about the uncertainty in the concentrations measured with the passive samplers. Different types of passive samplers show different NH_3 concentrations during parallel measurements (Rienecker & Helmholz, 2005). Concerning the applied passive samplers within this study, Seitler & Thöni (2009) proved Radiellos® to be the qualitative better passive samplers than others.

4.4 Bioindication study

Although not native to China, plants of the grass survived the exposure in the three NCP locations. However, plants were tallest in the northernmost location (Germany) and also plant weight somewhat declined from north to south (Fig. 4.53) due to higher average temperatures and shorter day length at lower latitudes, which seem to affect growth and phenology of the grass. The latter is also indicated by the fact that only one plant at 36 °N produced a stem and that in the Chinese plants there was no relationship between the initial weight of the ramets and the leaf number at harvest (data not shown). Average ammonia concentrations at the German sites varied from 2.3 to 7.3 µg m^{-3}, which are rather low concentrations just above the background levels. Ammonia levels in China were discussed in chapter 4.3. It is assumed that different growth of the plants at the four sites is primarily related to the different climatic conditions and these have larger effects than different chemical climates at these sites.

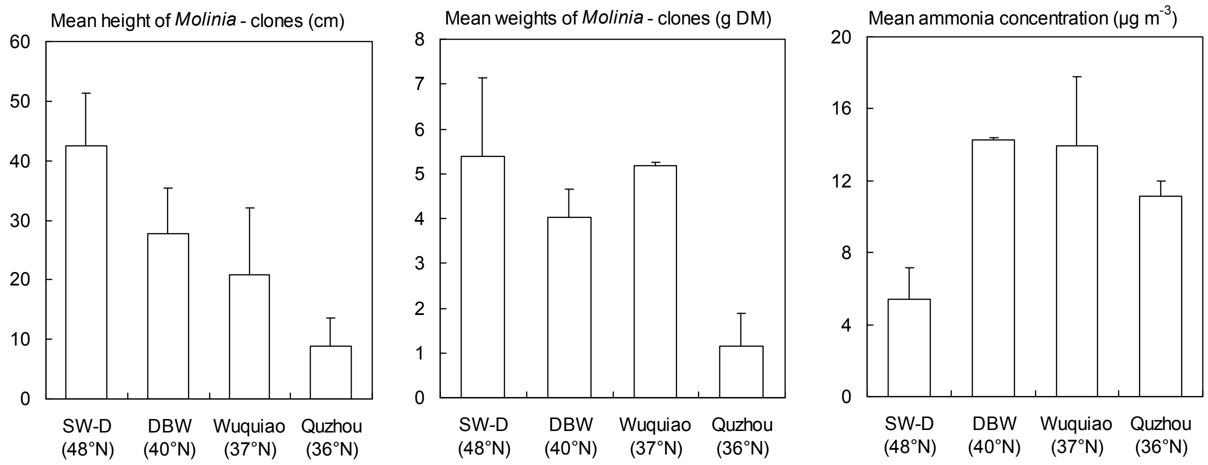

Figure 4.53: Mean plant heights (left) and biomasses (centre) of *Molinia*-biomonitors and ammonia concentrations (right) in the summer 2005 at one German and three Chinese test sites. Note: Data on NH_3 in China relate to May alone, while in Germany they represent the average values from May to July. Ammonia data from SW Germany with permission from Landesamt für Umweltschutz (LfU) Baden-Württemberg (Franzaring, 2006).

At each site, however there may still be differences in growth and vitality of the biomonitors that may be related to a different supply of atmospheric nitrogen. While in Germany plant growth parameters (height, dry weight) were not related to the (low) ammonia concentrations, senescence proved to be somewhat lower in plants exposed to higher ammonia levels. It seems that the availability of airborne reduced nitrogen may increase the vitality or reduce senescence in this plant species. At the same time, shoot:root ratio (SRR) was slightly increased in those plants which received higher ammonia concentrations (data not shown). It remains unclear whether these responses would become more pronounced at higher ammonia concentrations. At the Chinese sites, however, where higher ammonia concentrations were recorded, no correlations between ammonia, growth parameters and senescence were identified.

5 Conclusions and Outlook

DBW represents a suburban area that is typical for the Beijing region and the northern part of the North China Plain. While discussing both PM measurements at rural and urban sites it became clear that DBW is definitively not only a rural site. DBW is still a village with agricultural fields but Beijing city with its construction sites, skyscrapers and streets is coming closer. The area around DBW site changed dramatically even within the PM measuring period of two years and the contrast of rural versus urban areas had been strengthened there. Since the concentrations of the three PM fractions are in the same range of reported ones for urban sites in China, PM levels at DBW must therefore strongly be influenced by different sources from Beijing city. It is known that coarse particles in urban areas usually tend to be mechanically generated and are composed of materials such as tyre dust while fine particles tend to be produced either directly from combustion sources (black carbon and organics of primary origin), or by gas-to-particle conversion involving reaction products of sulphates, nitrates, ammonium, and organics. Due to the fact that the High Volume sampler was located on the agricultural field PM contributions including $\delta^{15}N$ values seem to be very representative for the North China Plain during harvesting time. Overall, it is only possible to give assumptions on the responsible pollution source. As Widory (2007, p. 2388) already stated “scientific understanding of the nitrogen budget requires further studies of its isotopic behaviour along the different chemical reactions leading to the formation of solid nitrogen in air particles”.

The seasonal ammonia levels were in the range from 9 to 43 $\mu g\ m^{-3}$, which indicates intensive agricultural activity in the whole NCP. Overall, the observed PM and NH_3 concentrations were closely related to meteorological fluctuations which was also observed partly for the bioindication experiment. It was shown that the plants of the temperate grass species were taller in the German locations than in China and plant weights generally declined from north to south of the NCP due to higher average temperatures and presumably the shorter day length at lower latitudes.

PM long-term datasets in China do not yet exist and there is no routine monitoring especially of PM2.5 in China. Several authors stressed that continuous studies covering longer times and concerning both the coarse and fine fractions of PM are lacking. Even though there are some air quality studies using satellite data for predictions and assessments, real air quality observations in China are still limited. “A good understanding of air pollution concentrations and fluxes at regional or national scale requires the integration of observations from field campaigns…” (Streets et al., 2003).

PM research in the NCP started within this study and the presented results covering two years are a first milestone in order to understand the characterization of particles and their interactions in the atmosphere of the NCP. The PM monitoring operated on an agricultural study site was a key element of the field campaign in order to study pollutant concentrations in the NCP but also the influences of the nearby megacity. Since the NCP is a highly populated region including the two megacities Beijing and Tianjin, it is assumed that other sites, at least in the northern part of the NCP, would reflect similar PM profiles. Especially the fact that the potential for rural depopulation is extremely high in the NCP drives major concern about PM pollution in suburban areas as represented by DBW.

Another important aspect regarding PM research in China is the lack of data comparability. There are currently no reference methods for measuring PM mass concentrations in China. In general, diverse American or Chinese measuring devices were used for data collecting (see chapter 2.5). However, this was the first study on continuous PM sampling in China with European and/or German measuring devices. Sampling with the High Volume Sampler Digitel DHA 80 proved to be suitable for the conditions in the NCP. Especially the standardized measuring method, the robustness of the measuring device in the field as well as the accurate calibration of the device ensured reliable PM data. Therefore the High Volume Sampler can be highly recommended for long-term PM measurements in China. Future research on PM in China should emphasize the use of standard measuring methods such as the High Volume Sampler which was applied already in long-term research studies in Europe. The differences among measuring methods in China and a lack of strict air quality control in carrying out PM monitoring make it difficult for the published findings to be generalized and the comparisons to be made between studies.

The simple and low-cost passive sampling method used (Radiellos®) also proved to be an appropriate tool for evaluating ammonia exposure in the NCP. In future, monitoring the long-term development of ambient ammonia concentrations will be essential to document the efficiency of measures aimed at reducing ammonia emissions. It is therefore crucial to choose the monitoring sites very carefully and to take the characteristics of each site into consideration when interpreting the data.

Moreover, a gap of knowledge regarding the categorization of representative study sites was observed in various publications on air pollution measurements in China. Difficulties in the interpretation and source recognition of PM air pollution in urban and rural sites were recognized. A categorization of urban, suburban, rural, natural site as the European

Environment Agency proposed (Larssen et al., 1999) is recommended also for China in order to allow a better comparability across individual sites as well as to obtain reliable background data.

In the future, exposure assessment and epidemiologic studies are necessary in China to address different sources, different physiochemical composition, and their varying biological potentials. Up to now, “there has been no air pollution cohort study in China examining the long-term effects of air pollution, nor any data assessing the relation between air pollution and cardiovascular morbidity and sub-clinical indicators” (Kan et al., 2009, p. 71).

With respect to the atmospheric environmental protection, China has implemented a series of measures to control PM emissions. After the Olympic Games measures have been implemented in Beijing, that is e.g., private vehicles are restricted not to operate within the 5th ring road between 6:00 and 21:00 Hrs. which is assumed to positively affect the air pollution situation in Beijing’s suburban areas such as DBW. A compressed natural gas bus program has been introduced in Beijing and the new measure of subsidies for retirement of vehicles with yellow labels is to accelerate the elimination of old vehicles. However, it is unclear to date whether measures will be effective with regard to the explosive increase of new registered cars in Beijing since China is the sale market leader worldwide with currently 10.5 million cars per year. First cost-benefit analyzes of pollution control measures in China were performed in order to illustrate the rising economic costs of the health impacts from air pollution. It is therefore assumed that investigations in both gaseous air pollutants and PM will be of increasing interest in the future. One very important air policy measure with real effects on pollutant concentrations in China would be that the Chinese air quality standards become legally binding.

6 Summary

The thesis presented here was conducted at the Institute of Landscape and Plant Ecology at the University of Hohenheim within the scope of the first Sino-German International Research Training Group (IRTG) “Modeling Material Flows and Production Systems for Sustainable Resource Use in Intensified Crop Production in the North China Plain”. The project is jointly performed by the University of Hohenheim and the China Agricultural University (CAU) Beijing and financed by the German Research Foundation and the Chinese Ministry of Education. The present study was performed in the framework of subproject 1.3 of the IRTG which had the major aim to study air pollution and atmospheric nitrogen deposition in the North China Plain (NCP). For that purpose data on concentrations of atmospheric pollutants were required in order to assess the level of exposure to pollution of both population and environment in the NCP.

This study represents the initial work in the NCP in 2005 and 2006 in order to monitor air pollution and dry nitrogen deposition and its effects. Within this work experiments were conducted to monitor concentrations of PM2.5, PM10, TSP, NO_x and NH_3 in the NCP. Ammonia monitoring and biomonitoring were synchronised in order to study the potential effects of nitrogen deposition on *Molinia caerulea*. Since there was no air monitoring network existing in the NCP at the onset of this study, one major part of the work consisted of setting up and testing of European measuring devices under the special conditions in the NCP. The measurements have been therefore the starting point of field observations in the NCP and especially the PM monitoring operated at the agricultural study site Dongbeiwang (DBW) was a key element of the field campaign in order to study pollutant concentrations in the NCP but also the influences of the nearby megacity Beijing.

Sampling with the High Volume Sampler Digitel DHA 80 proved to be suitable for the conditions in the NCP. The levels of daily PM10 measured in this study exceeded European (50 $\mu g\ m^{-3}$) and Chinese (150 $\mu g\ m^{-3}$) thresholds by far. Also the EU standard for the number of tolerated daily exceedances (35 times per year) was not met in the Beijing area. Results of PM10 measurements at DBW showed 126 exceedances of the daily mean European threshold in only 128 days in 2005 and 43 exceedances in 44 days in 2006. The maximum daily mean of 412 $\mu g\ m^{-3}$ also reflects the high PM10 peak concentrations in the study region. Results of daily PM2.5 measurements at DBW in 2005 and in 2006 showed exceedances of the U. S. daily average air quality standard of 35 $\mu g\ m^{-3}$ for 99 % of the data (mean value in 2005: 222 $\mu g\ m^{-3}$ and in 2006: 123 $\mu g\ m^{-3}$). High daily PM2.5 peak concentrations were observed especially during the winter. Overall, only under extreme meteorological conditions such as heavy rainfalls PM levels of less than 50 µg m^{-3} were detected at DBW. Diurnal and hourly variations of PM levels were demonstrated. Glass fibre filters proved to be suitable for the collection of high PM loads whereas quartz fibre filters are much more suitable for the laboratory analysis of N species. Determination of particulate ammonium and nitrate on glass fibre filters of spring season was tested and showed averaged concentrations of 2.4 and 13.1 µg m^{-3} (TSP) and 8.0 and 11.6 µg m^{-3} (PM10), respectively. The mass spectrometric measurements were challenging due to the filter material and $\delta^{15}N/^{14}N$ ratios were found to be very heterogeneous ranging from -3.0 ‰ to 44.3 ‰, referring to both filter types.

The simple and low-cost passive sampling method used (Radiellos®) also proved to be an appropriate tool for evaluating ammonia exposure in the NCP. The seasonal ammonia levels were in the range from 9 to 43 µg m^{-3} at DBW, Wuqiao and Quzhou, which indicates intensive agricultural activity in the whole NCP. No relationship was found between atmospheric ammonia levels and plant growth parameters of *Molinia caerulea* and thus, growth of these test plants was not related to gaseous dry deposition of ammonia. The NO_x measurements in NCP did not yield reliable data within given time.

Overall, multiple sources are assumed to interplay at the study site namely, local dust (such as harvest), traffic, biomass burning, coal combustion, secondary aerosol and industrial emissions from Beijing area. Long-range transported air pollutants such as pollutants from Hebei and Shandong province or deserts as well as the weather pattern greatly influence the atmospheric pollution at DBW and NCP in general.

7 Zusammenfassung

Die vorliegende Forschungsarbeit wurde im Rahmen des ersten deutsch-chinesischen internationalen Graduiertenkollegs (IRTG) „Modeling Material Flows and Production Systems for Sustainable Resource Use in Intensified Crop Production in the North China Plain“ am Institut für Landschafts- und Pflanzenökologie der Universität Hohenheim angefertigt. Das Graduiertenkolleg ist ein Gemeinschaftsprojekt der Universität Hohenheim und der Chinesischen Agraruniversität Peking (CAU), welches von der Deutschen Forschungsgemeinschaft und dem Chinesischen Bildungsministerium finanziert wird. Die vorliegende Studie fand im Rahmen des Teilprojekts 1.3 statt, welches als übergeordnetes Ziel die Untersuchung von Luftverschmutzung und atmosphärischer Stickstoffdeposition in der Nordchinesischen Tiefebene (NCP) hat. Um Wirkungen von Luftschadstoffen auf die Bevölkerung und Umwelt analysieren und beurteilen zu können, sind Messungen von Luftschadstoffkonzentrationen vor Ort notwendig. Die Erhebung und Analyse relevanter Kennwerte im Bereich der trockenen Deposition in der NCP bildet den Kern dieser Arbeit.

Im Rahmen dieser Forschungsarbeit wurden in den Jahren 2005 und 2006 hierzu erstmalig Daten in der Nordchinesischen Tiefebene erhoben. Im Speziellen wurden Experimente zur Untersuchung von PM 2.5, PM10, TSP, NO_x und NH_3 durchgeführt. Ammoniakmessungen in der Umgebungsluft und Biomonitoringexperimente fanden parallel statt, um die potentiellen Auswirkungen von Stickstoffdepositionen auf *Molinia caerulea* zu untersuchen. Da es in der NCP zu Beginn dieser Studie keine Luftmessstation gab, bestand ein Hauptteil der Arbeit darin, europäische Messgeräte unter den besonderen Bedingungen im Forschungsgebiet einzurichten und zu testen. Die Untersuchungen stellen daher den Beginn der Messkampagne in der NCP dar. Insbesondere Staubmessungen auf dem landwirtschaftlichen Untersuchungsstandort Dongbeiwang (DBW) waren ein Schlüsselelement der Messkampagne, um Luftschadstoffkonzentrationen in der NCP zu untersuchen sowie Einflüsse der Metropolregion Peking zu erfassen.

Die Probenahme mit dem Staubsammler Digitel DHA 80 erwies sich als geeignet für die Bedingungen in der NCP. Die in dieser Studie gemessenen täglichen Feinstaubwerte PM10 überstiegen die europäischen (50 $\mu g\ m^{-3}$) und chinesischen (150 $\mu g\ m^{-3}$) Grenzwerte um ein Vielfaches. Die in der EU jährlich zulässigen 35 Überschreitungen des Tagesgrenzwertes wurden in der Region Beijing nicht eingehalten. Im Jahr 2005 überschritten die in DBW an 128 Tagen gemessenen PM10 Werte 126 mal den EU Grenzwert. Im Jahr 2006 gab es 43 Überschreitungen an 44 Messtagen. Der maximal gemessene Tageswert von 412 $\mu g\ m^{-3}$

reflektiert die allgemein hohen PM10 Konzentrationen im Untersuchungsgebiet. Täglich gemessene PM2.5 Konzentrationen in DBW zeigten in den Jahren 2005 und 2006 Überschreitungen des U.S. Grenzwertes von 35 µg m^{-3} für 99 % der Daten (Mittelwert für das Jahr 2005: 222 µg m^{-3} und für das Jahr 2006: 123 µg m^{-3}). Besonders hohe PM2.5 Tageswerte wurden vor allem in den Wintermonaten beobachtet. Insgesamt wurden nur unter extremen meteorologischen Bedingungen in DBW, wie z.B. schweren Regenfällen, Feinstaubwerte unter 50 µg m^{-3} gemessen. In dieser Studie werden ebenfalls Tagesverläufe und stündliche Abweichungen der Staubmessungen gezeigt. Für die Messung hoher Feinstaubkonzentrationen erwiesen sich Glasfaserfilter als geeignet, während Quartzfaserfilter weitaus besser für die Laboranalyse von Stickstoffspezies geeignet sind. Die Bestimmung von staubgebundenem Ammonium und Nitrat auf Glasfaserfiltern wurde getestet und zeigte durchschnittliche Konzentrationen für TSP und PM10 von jeweils 2.4 und 13.1 µg m^{-3} beziehungsweise 8.0 und 11.6 µg m^{-3}. Die massenspektrometrischen Messungen waren aufgrund des Filtermaterials eine Herausforderung. Die gemessenen $\delta^{15}N/^{14}N$-Werte erwiesen sich als sehr heterogen und lagen - bezogen auf die benutzten Filtertypen – in einem Bereich von -3.0 bis 44.3 ‰. Die in den Untersuchungen verwendeten einfachen und kostengünstigen Passivsammler (Radiellos®) erwiesen sich ebenfalls als ein geeignetes Instrument zur Messung von Ammoniak in der Umgebungsluft der NCP. Die Ammoniakkonzentrationen in DBW, Wuqiao und Quzhou schwankten jahreszeitlich im Bereich von 9 bis 43 µg m^{-3} und weisen auf eine intensive Landbewirtschaftung in der NCP hin. Allerdings konnte kein Zusammenhang zwischen den gemessenen Ammoniakkonzentrationen und der angenommenen trockenen gasförmigen Ammoniakdeposition und den Pflanzenwachstumsparametern des verwendeten Bioindikators *Molinia caerulea* festgestellt werden. Die NO_x Messungen in der NCP ergaben keine verlässlichen Daten innerhalb der vorgegebenen Zeit.

Insgesamt wird von einer Wechselwirkung zahlreicher Faktoren hinsichtlich der Luftverschmutzung im Untersuchungsgebiet ausgegangen. Insbesondere lokale Staubquellen (z.B. Ernte), Verkehr, Verbrennung von Biomasse und fossiler Brennstoffe, sekundäre Aerosolpartikel sowie Industrieemissionen der Metropolregion Peking werden diskutiert. Ferner haben Luftschadstoffe, die aus den Provinzen Hebei und Shandong und aus den chinesischen Wüsten über weite Strecken transportiert werden, neben den meteorologischen Faktoren großen Einfluss auf die atmosphärische Verschmutzung in DBW und der Nordchinesischen Tiefebene insgesamt.

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Abbreviations, Acronyms and Units

ABC	Atmospheric Brown Clouds
AirBase	European Air quality dataBase
API	Air Pollution Index
asl.	above sea level
BUWAL	Bundesamt für Umwelt, Wald und Landschaft (Switzerland)
CAC	Canadian Criteria Air Contaminants
CAU	China Agricultural University
CAWAS	Centre for Atmosphere Watch and Services
CH_4	Methane
CMA	China Meteorological Administration
CNAAQS	Chinese National Air Quality Standards
CNN	Cable News Network
CO	Carbon monoxide
CO_2	Carbon dioxide
CuO	Copper oxide
$C_2H_3NO_5$	Peroxyacetyl nitrate
DBW	Dongbeiwang (experimental site)
DFG	German Research Foundation (Deutsche Forschungsgemeinschaft)
DIN	German Institute for Standardization (Deutsches Institut für Normung)
EA	Elemental Analyzer
EANET	East Asian NET
EC	European Commission
EMEP	European Monitoring and Evaluation Programme
EMPA	Swiss Federal Laboratories for Materials Testing and Research (Eidgenössische Material-Prüf-Anstalt, Switzerland)
EPA	United States Environmental Protection Agency
ERSEC	Ecological Research for Sustaining the Environment in China
EU	European Union
FAO	Food and Agriculture Organization of the United Nations
FUB	Research Group for Environmental Monitoring (Forschungsstelle für Umweltbeobachtung)
GDP	Gross Domestic Product
GF	Glass fibre
HCl	Hydrochloric acid
HLUG	Hessisches Landesamt für Umwelt und Geologie
HNO_2	Nitrous acid
HNO_3	Nitric acid
Hrs.	Hours
H_2O	Distilled water
H_2S	Hydrogen sulphide
H_2SO_4	Sulphuric acid
$h\upsilon$	Sunlight
IPCC	Intergovernmental Panel on Climate Change
IRMS	Isotope Ratio Mass Spectrometer
IRTG	International Research Training Group
ISO	International Organization for Standardization
LfU	Landesamt für Umweltschutz (Baden-Württemberg)
LUA	Landesumweltamt Nordrhein-Westfalen
MPG	Max Planck Gesellschaft

N	Nitrogen
NAAQS	National Ambient Air Quality Standards (United States of America)
NASA	National Aeronautics and Space Administration
NCP	North China Plain
NH_3	Ammonia
NH_4	Ammonium
NH_x	Reduced nitrogen (NH_3 + NH_4)
NH_y	Reduced nitrogen compounds
NH_4NO_3	Ammonium nitrate
NMVOC	Non-methane VOC
NO	Nitric oxide
NO_2	Nitrogen dioxide
NO_3	Nitrate
NO_x	Nitrogen oxide (sum of nitrogen monoxide, NO, and nitrogen dioxide, NO_2)
Nr	reactive nitrogen (Nr is not a chemical element. It is the term for all chemical forms of nitrogen, except N_2.)
NO_y	NO + NO_2 + NH_3
N_2	Di-nitrogen (unreactive nitrogen)
N_2O	Nitrous oxide
N_2O_5	Di-nitrogen-pentaoxide
O	Oxygen atom
O_2	Oxygen molecule
O_3	Ozone
OH	Hydroxyl radicals
PE	Polyethylen
pH	Electrical conductivity
PM	Particulate Matter
PM1	Ultra fine particles with an aerodynamic diameter less than 0.1 µm
PM2.5	Fine particles with an aerodynamic diameter less than 2.5 µm
PM10	Coarse particles with an aerodynamic diameter less than 10 µm
QMA	Quartz microfibre
QZ	Quzhou (experimental site)
R_c	Canopy resistance
RH	Relative Humidity
SEPA	State Environmental Protection Agency (China)
SO_2	Sulphur dioxide
SRR	Shoot:Root Ratio
T	Temperature
TSP	Total Suspended Particulate Matter
UBA	German Federal Environmental Agency (Umweltbundesamt)
UMEG	Zentrum für Umweltmessungen, Umwelterhebungen und Gerätesicherheit Baden-Württemberg
UNEP	United Nations Environment Programme
U.S.	United States of America
V_d	Deposition velocity
VDI	Verein Deutscher Ingenieure
VOC	Volatile organic compounds
WHO	World Health Organization
WMO	World Meteorological Organization
WS	Wind speed
WU	Wuqiao (experimental site)

Units

cm	centimetre
d	day
g	gram
h	hour
ha	hectare
µg	microgram
m	meter
min	minutes
mm	millimetre
ng	nanogram
ppb	parts per billion
ppt	parts per trillion
s	second
Tg	Teragram

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