MEASUREMENT AND ANALYSIS OF PERSONAL EXPOSURE TO NITROGEN DIOXIDE FROM INDOOR AND OUTDOOR SOURCES

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Abstract

The study of exposure to nitrogen dioxide (NO_2) is important because of its significant health effects. As it is associated with combustion processes, road traffic is one of the main outdoor sources and gas cookers and gas heaters are the main indoor sources. Indoor NO_2 is a significant health problem due to people spending most of their time indoors. Activity patterns and lifestyles vary and, consequently, people may be exposed NO_2 from several different sources during a typical day. In order to understand and quantify total personal exposure, it is, therefore, important to determine both the indoor and outdoor concentration levels.

This thesis reports on two pilot studies, spring and summer 2000 and three full campaigns, autumn, winter 2000 and summer 2001 to investigate the relationship between NO_2 personal exposure of office workers in relation to indoor and outdoor sources and activity patterns. The study has been carried out in the area of Hertfordshire, UK. This region is adjacent to London and has a population of just over one million people. It consists of several major commuter routes connecting medium sized towns to London.

Volunteers using gas cookers and electric cookers in their kitchens were asked to fill in activity patterns records and questionnaires. At the same time, weekly average personal exposure to NO_2 and indoor (bedroom, living room, kitchen and office) and front door NO_2 concentrations were measured by using passive diffusion tubes. Correlation between weekly personal exposures and mean indoor and outdoor concentrations during the same periods were examined.

The results show significant differences in indoor and outdoor concentrations of NO_2 in autumn and winter. The data indicated that NO_2 concentrations in all rooms in houses with gas cookers were significantly higher than those with electric cookers especially in kitchens where levels of NO_2 were 3 to 4 times greater. Interpretation of time activity daily diaries showed that the subjects spent on average 80% of their time indoors. Despite the very high concentrations in kitchens with gas cookers, personal exposure did not increase similarly as volunteers only spent a small amount of time cooking over the 7 day period.

Good correlation was observed between the average indoor NO_2 concentrations, especially in bedrooms and living rooms, and personal exposure. This indicated that indoor levels in areas like the bedroom and living rooms could be used as a proxy for NO_2 personal exposure for this group of volunteers. An empirical time weighted average concentration model was developed based on the NO_2 concentrations measured in the microenvironments and the data on time spent in each microenvironment. This was tested by comparison between time weighted average calculations and the personal exposure measurements of NO_2 concentrations. The comparison yielded good relationships for most of the campaign periods despite the fact that NO_2 concentrations were not similar in the different microenvironments and the fact that subjects spent varying times in these places. Statistical tests were performed for time weighted average concentrations of NO_2 and the personal exposure to NO_2 concentrations and differences were found to be non-significant.

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Chapter 1

Introduction

This chapter provides an introduction to the main concepts of air pollution that are relevant to the topic of the thesis. Outdoor and indoor air pollution are briefly reviewed and information is given on the main sources and health effects of pollution. The chapter then provides a more detailed treatment of NO_2 including its main sources, monitoring and control legislation as well as its health effects. Aim and objectives of this research are also discussed. Finally, a section about how the thesis is organised is presented.

1.1 Air pollution

Air pollution is defined as the presence of gases and non-biological particles of matter in the air that are not natural to the atmosphere (EEA, 1997). Several major air pollutants exist in ambient air such as sulphur dioxide (SO_2), carbon dioxide (CO_2), particulate matter (PM_{10}), ozone (O_3) and the oxides of nitrogen (NO_x). Air pollution can lead to health problems in people but especially to those who are susceptible such and children and the elderly or those suffering from respiratory illnesses (Van der zee, *et al.*, 2000; Garrett, *et al.*, 1998; Mukala, *et al.*, 1996; Sandström, 1995). Health effects from air pollution can vary from coughing, burning eyes and nose, itchy irritated throat, and breathing problems such as bronchitis to heart disease and lung cancer (Thurston and Bates, 2003). Illnesses such as bronchitis, that is, tightness in the chest and wheezing, give rise to acute or short term effects, and can be reversed if air pollution exposures decline (Just, *et al.*, 2002; Venn, *et al.*, 2000). Other effects appear to be chronic, such as asthma, long-term injury to the lungs and breathing passages, lung cancer and cardiopulmonary disease (Gent, *et al.*, 2003; Mortimer, *et al.*, 2002; Oglesby 2000a; Gomzi, 1999). Moreover, air pollution can also cause environmental damage such as to trees, lakes, soil and animals as well as damage to property such as buildings, monuments, statues, and other structures (Benton, *et al.*, 2000; Blake, *et al.*, 1999; Carnol, *et al.*, 1997). It can also lead to haze, which reduces visibility (Thurston, *et al.*, 1997).

1.1.1 Outdoor air pollution

For more than a century, studies have shown that breathing polluted air can be dangerous and harmful to health (COMEAP, 2000). The study of health effects of air pollution began with the study of acute and severe air pollution episodes. As an example there was an incident in 1892, 1000 people died in a smog incident in London. Also, there was an episode in the Meuse Valley, Belgium in December 1930, when air pollution killed 63 people. There followed by a smog episode in a small town in Donora, Pennsylvania, USA in October 1948 killed 20 people. Also, a smog incident in Poza Rica, Maxico killed 20 people. Afterwards, an episode in London in December 1952 killed 4,700 people. Furthermore, a smog incident in New York killed between 170 and 260 people. In addition, another London smog incident in 1962 killed 750 people (Brimblecombe, 1995). These episodes were studied and associated with widespread use of fuels and were catalysts for government efforts to deal with air pollution. Since then, many countries have adopted ambient air quality standards to protect the public against the most common and damaging pollutants. For example, one of the earliest records of air pollution control was in 1306 when King Edward I banned the burning of coal in London due to foul smelling fumes. The Clean Air Act 1956, however, which was later amended and extended by the Clean Air Act 1968, came only after the London smog of December 1952. Since then, the development of air pollution control legislation in the UK has been a gradual process with most of it resulting from the Industrial Revolution of the late 18th and 19th centuries (QUARG, 1996). Also, the European Union Ambient Air Quality Assessment and Management Directive 96/62/EC, known as the Ambient Air Quality Framework Directive, and its associated directives lead to improved air quality in the member states. They contribute to an improved air quality by dealing with atmospheric pollutants at an international level, encompassing the transboundary nature of airborne pollution and by setting standards for industrial and other types of emissions. These directives influenced the UK National Air Quality Strategy (NAQS). In addition there are international standards such as those of World Health Organisation (WHO). The pollutants that are controlled include SO_2, PM_{10}, O_3, nitrogen dioxide (NO_2), carbon monoxide (CO), and lead (Pb). These arise from direct or indirect sources of combustion of fossil fuels as well as other sources. The UK National Air Quality Strategy (NAQS) was published in March 1997. Proposals for amending the Strategy were published in January 1999. A revised version, the current Air Quality Strategy for England, Scotland, Wales and Northern Ireland, published in January 2000 with an addendum in February 2003, provides a framework for air quality control. The strategy gives standards and objectives for eight key air pollutants (benzene, 1,3-butadiene, CO, Pb, O_3, NO_2, PM_{10}, and SO_2) and a timetable for their achievement.

Although substantial investments in pollution control in some industrialised countries have lowered the levels of these pollutants, in many cities, poor air quality is still a major concern throughout the world, a situation driven by population growth, industrialisation, and increased vehicles use. A study by WHO (1992) reported that in megacities, such as Beijing, Delhi, Jakarta, and Mexico City, pollutant levels often exceeded the WHO air quality standards by a factor of three or more, also worldwide, The WHO has estimated that as many as 1.4 billion urban residents were breathing in air exceeding the WHO air guidelines (WHO, 2000). Studies by the European Environment Agency found that 70 to 80 percent of 105 European cities surveyed in 1997 exceeded the WHO air quality standards for at least one pollutant. WHO have estimated that 30-40% of Europeans living in cities were exposed to average concentrations of air pollutants such as sulphur dioxide, nitrogen dioxide that were above WHO or EU guidelines (WHO, 2000). However, not everyone who lives in such areas will have health problems. Some people will experience pollution-related health problems due to various factors including level, extent, duration of exposure, susceptibility and age.

Attention in the UK has focused on monitoring and controlling a range of key pollutants including PM_{10}, SO_2, NO_x, NO_2, O_3, CO. Airborne particulate matter is a complex mixture of different substances measuring the size fraction of particles with median diameter up to 10 micrometers (PM_{10}). It is produced by both primary and secondary sources. Primary particles are directly emitted to the atmosphere from many sources such as road traffic, coal burning, industry, windblown soil and dust and sea spray. On the other hand, secondary particles are particles formed within the atmosphere by chemical reaction or condensation of gases. The major contributors are sulphate and nitrate salts formed from the oxidation of SO_2 and NO_x (APEG, 1999).

Since 1952 there has been a sharp fall in levels of particulate matter, but this downward trend appears to have ceased due to the increase in road traffic, and in particular diesel-powered vehicles (DoE, 1997). Whilst the complex toxicological mechanisms of particles are not yet fully understood, documented evidence from episodes such as the London smog, along with recent clinical and epidemiological studies indicate a clear association with respiratory morbidity and mortality (Schwartz, 2000).

Sulphur dioxide (SO_2) is a colourless gas occurs in volcanic gases, combustion of iron pyrites which is contained in coal and also is produced from various metallurgical and chemical processes. In the UK, power stations are the main source of SO_2 (Environment Agency, 2000). The study by NEGTAP (2001), on transboundary of air pollution in UK, reported that emissions of SO_2 in 1999 had declined by 80% of its peak emissions over the UK. This decrease was initially achieved through controls on coal burning, introducing cleaner solid fuels, taller power station stacks and relocating power stations into rural areas. In recent years further decreases have been achieved through generating more electricity from gas and nuclear power stations (Environment Agency, 2000).

Oxides of nitrogen or nitrogen oxides (NO_x) is commonly used to described the sum of nitric oxide or nitrogen monoxide (NO) and nitrogen dioxide (NO_2) concentrations (AEA Technology, 2003). Even though nitrous oxide (N_2O) is the most common oxide of nitrogen in the atmosphere, and important as a greenhouse gas, it is not harmful to human health at ambient concentrations and will not be discussed in this thesis. Both NO and NO_2 are formed in high temperature combustion processes, although NO is in the big majority, at ambient temperatures it is oxidised with sunlight, reactive hydrocarbons and ozone to NO_2 which is a more toxic secondary pollutant (more details are discussed in section 1.2). The study by NEGTAP (2001) on transboundary of air pollution in UK reported that road transport is the largest source of NO_x emissions in the UK, contributing 49% of total emissions in 2000, with coal combustion including coal fired power stations accounting for 18%. However, emissions from road transport have fallen by 34% between 1990 and 2000. NEGTAP also report that overall emissions of NO_x have declined by 37% from 1990 to 2000. Similarly, the recent study of AQEG (2004) on nitrogen dioxide in the United Kingdom estimated the time series of NO_x emissions in the UK from 1970 with predictions through to 2020 (Figure 1.1). It also reported that overall emissions of NO_x fell by 37% from 1990 to 2000 and were expected to reduce by a further 25% by 2010.

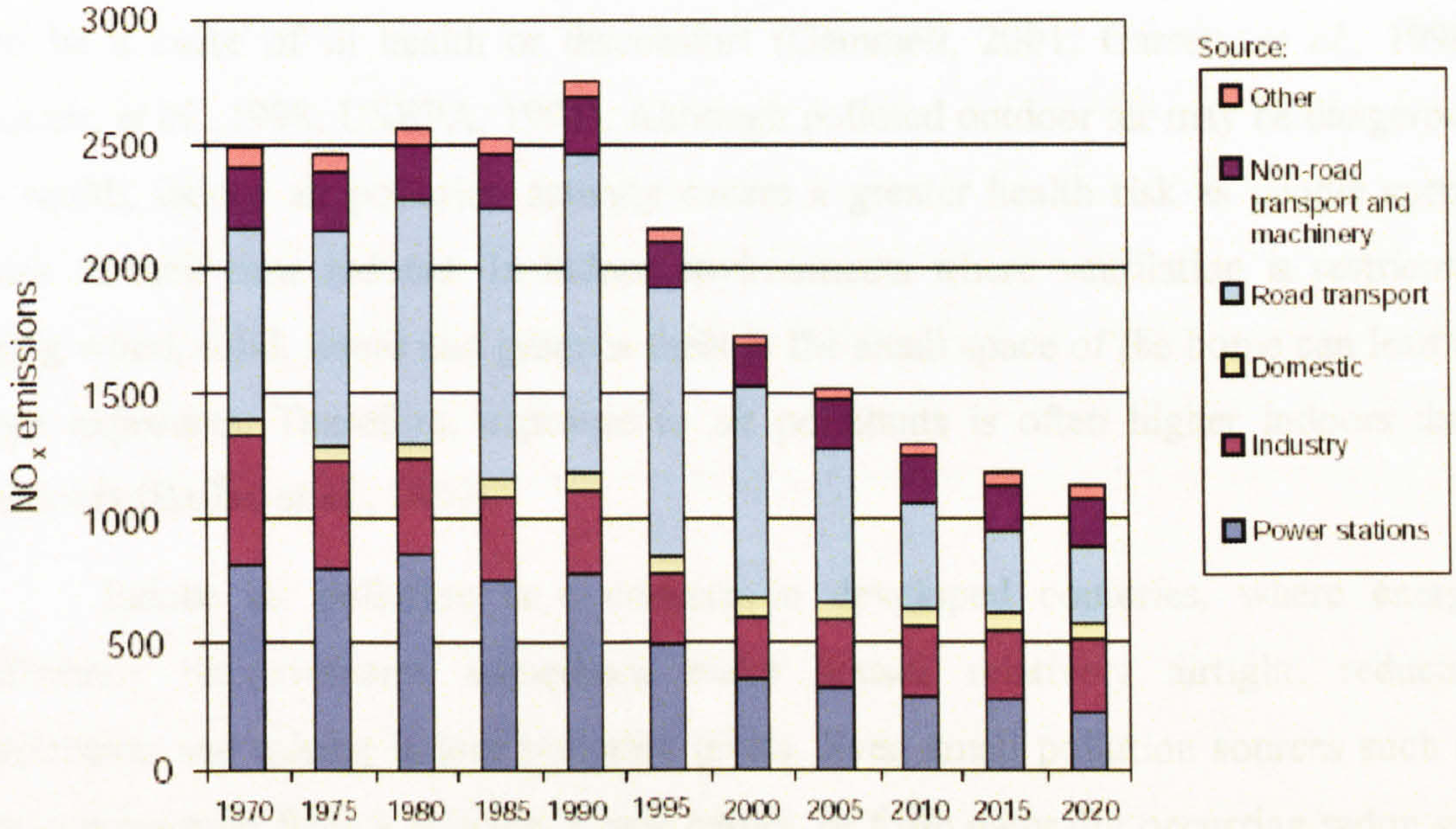


Figure 1.1 NO_x emissions in kilotonnes in the UK by source from 1970 to 2020.
Source: AQEG, 2004. Nitrogen Dioxide in the United Kingdom. p.22.

Ground level ozone (O_3) is mainly a secondary pollutant, formed by the action of sunlight on NO_2 in the presence of hydrocarbons and volatile organic compounds (VOCs). Ozone levels are dependent on meteorological factors, optimal conditions for production being high temperature, sunlight, and low wind. Therefore, ozone levels in the UK vary seasonally, and are subject to wide fluctuations (NEGTAP, 2001). The NEGTAP (2001) study on transboundary air pollution in the UK also reported that even though the peak concentrations declined by 30% between 1986-1999, however, the mean ozone concentrations show signs of increase trend.

1.1.2 Indoor air pollution

Air pollution has been recognised as a serious problem for human health not only in outdoor environment but also in indoor environment (Baek, *et al.*, 1997; Arashidani, *et al.*, 1996; Alberts, 1994; Dijkstra, *et al.*, 1990). Indoor air pollution is the presence within buildings of toxic or other substances, which directly or indirectly can be a cause of ill health or discomfort (Gemmell, 2001; Garrett, *et al.*, 1999; Garrett, *et al.*, 1998; USEPA, 1991). Although polluted outdoor air may be dangerous to health, indoor air pollution actually causes a greater health risk as people spend most of their time indoors. In indoor environments where ventilation is restricted, using wood, solid, liquid and gaseous fuels in the small space of the home can lead to high exposures. Therefore, exposure to air pollutants is often higher indoors than outdoors (Bailie, *et al.*, 1999).

Indoor air pollution is a concern in developed countries, where energy efficiency improvements sometimes make houses relatively airtight, reducing ventilation and raising indoor pollutant levels. Even small pollution sources such as those emanating from a furnace, a new carpet, or from naturally occurring radon gas can lead to significant human exposures (UKCCS, 2002; Steinbuch, *et al.*, 1999). Moreover, high air pollution concentrations from outdoors, air exchange rates, the use of combustion sources, chemical reactions and adsorption of air pollutants in the indoor environment can all influence indoor air pollution.

Some researchers have found that burning wood and solid fuels produces large amounts of smoke and other air pollutants (Bailie, *et al.*, 1999). Liquid and gaseous fuels such as kerosene and bottled gas are also less polluting than those unprocessed solid fuels (Bailie, *et al.*, 1999). The World Bank has designated indoor air pollution in developing countries as one of the four most critical global environmental problems (Alberini, *et al.*, 1997). Epidemiological studies in developing countries have linked exposure to indoor air pollution from solid fuels with at least four major categories of illness: acute respiratory infections (ARI) in children, chronic obstructive lung diseases such as asthma and chronic bronchitis, lung cancer, and stillbirths and other problems at birth (Alberini, *et al.*, 1997). ARI appears to have the greatest health impact in terms of the number of people affected and the time lost due to illness, especially in children younger than age 5 (Boezen, *et al.*, 1999). Many studies in different countries have examined the link between personal exposures to smoke from cooking stoves with the development of ARI in children. In South Africa, investigators found that Zulu children living in homes with woodstoves were almost five times more likely to develop a respiratory infection severe enough to require hospitalization (Garrett, *et al.*, 1998). Likewise, a study in the Gambia found that children carried on their mothers' backs as they cooked over smoky cooking stoves contracted pneumococcal infections one of the most serious kinds of respiratory infections at a rate 2.5 times higher than nonexposed children (Alm, *et al.*, 1994). A study in Tanzania found that children younger than 5 years of age who died of ARI were 2.8 times more likely to have been sleeping in a room with an open cooking stove than healthy children. Overall, studies indicate that exposure to wood smoke from cooking fires in poorly ventilated conditions may increase the risk of a young child contracting a serious respiratory infection from two to six times (Boezen, *et al.*, 1999).

Adults suffer the ill effects of severe indoor pollution as well. Several studies found strong links between chronic lung diseases in women and exposure to smoke from open cooking stoves, for example, one Colombian study found women exposed to smoke during cooking were more than three times more likely to suffer chronic lung disease. Other studies suggest that this risk increases in response to the years of exposure to smoke. A study in Mexico showed that women who had been exposed to wood smoke for many years faced 75 times more risk of acquiring chronic lung disease than unexposed women about the level of risk that heavy cigarette smokers face (Helleday, *et al.*, 1994). Lung cancer also is associated with high levels of smoke especially coal smoke, which contains a carcinogenic compounds (Ellegard, 1997).

Most studies of coal-smoke exposures have been conducted in China, where residential use of coal is still common. More than 20 studies suggest that women who use coal for cooking and heating over many years are subject to a risk of lung cancer two to six times higher than women who use gas. Rural coal-smoke exposures, which tend to be higher, seem to increase lung cancer risks by a factor of nine or more (Ando, *et al.*, 1996). Exposure to high indoor smoke levels has also been linked with pregnancy-related problems like stillbirths and low birth weight. Indoor air pollution most likely contributes to excess heart disease in developing countries as well. In developed countries, outdoor pollution at levels far below those found in smoky indoor environments has been linked with heart disease (Harrison, 1997).

1.2 Nitrogen dioxide

As mentioned in section 1.1.1 above, the sum of NO and NO_2 is known as NO_x, but the air pollutant species of most interest from the point of view of human health is NO_2. NO_2 is soluble in water, reddish-brown in colour, and also a strong oxidant that reacts in the air to form corrosive nitric acid, as well as toxic organic nitrates. It is an irritant that can lead to the narrowing of airways when high concentrations are experienced. NO_2, along with particles in the air, can often form a reddish brown layer or smog over many urban areas. As NO_2 is formed from the combination of N and O_2 during combustion at high temperatures, therefore, the production of NO_2 is particularly associated with the operation of gas appliances, kerosene, kerosene heaters, and wood burning stoves, as well as the smoking of cigarettes. Additionally, NO_2 from traffic sources is a major pollutant in the atmosphere of urban areas.

NO_2 is an important atmospheric trace gas, not only because of its health effects but also because (i) it absorbs visible solar radiation and contributes to impaired atmospheric visibility, (ii) as an absorber of visible radiation it could have a potential direct role in global climate change if its concentrations were to become high enough, (iii) it is, along with nitric oxide (NO), a chief regulator of the oxidizing capacity of the troposphere by controlling the build-up and fate of radical species, including hydroxyl radicals, and (iv) it plays a critical role in determining O_3 concentrations in the troposphere because the photolysis of NO_2 is the only key initiator of the photochemical formation of O_3, whether in polluted or unpolluted atmospheres (WHO, 2000; USEPA, 1993).

NO_2 is produced as a by-product of the combustion process. NO_2 is both a primary and secondary pollutant. Primary NO_2 is normally present in very small amounts and accounts for about 5% of NO_x emission levels and is emitted directly from most forms of combustion. It is produced from reactions between nitrogen (N) and oxygen (O_2) during combustion processes at high temperatures (DoH, 1993). Secondary NO_2, which is the majority of NO_2, is produced in the atmosphere from reactions that usually take place in two stages. The most important oxidation reaction for NO is that with ozone to produce NO_2 (Buckingham *et al.*, 1997).

$$NO + O_3 \rightarrow NO_2 + O_3. \qquad (1)$$

For this reason, the amount of NO_2 is determined by the availability of O_3. On average, the fraction of NO_x present as NO_2 is 40% in urban areas and can be as high as 90% in rural areas (DoH, 1993). Furthermore, a reverse reaction may take place during daylight where NO_2 is converted back to NO with generation of O_3. The reactions of regenerating NO and O_3 are as follows:

$$NO_2 + hv \rightarrow NO + O^{\cdot} \qquad (2)$$

$$O^{\cdot} + O_2 \rightarrow O_3. \qquad (3)$$

During the day, reactions (1), (2) and (3) lead to establishment of the well-known photostationary state, where the rate of oxidation of NO (equation 1) is balanced by its re-formation by the photolytic dissociation of NO_2 (equation 2)

$$\frac{[NO][O_3]}{NO_2} = K \qquad (4)$$

where the value of K varies from 0 ppb to about 20 ppb at UK latitudes depending on the intensity of UV radiation. At night, the reaction shown in equation 2 does not occur, K = 0, and the oxidation of NO by O_3 proceeds until either the NO or the O_3 is totally depleted.

Another route for the production of NO_2 is the reaction of NO with organic peroxy-radicals (RO_2), which are atmospheric radicals arising from the hydrocarbons in the atmosphere. The reaction is as follows:

$$NO + RO_2 \rightarrow NO_2 + RO. \qquad (5)$$

An essentially non-reversible removal process for NO_2 during the day is its oxidation by hydroxy radicals to form nitric acid with a small amount of the acid subsequently removed by rainfall. The reaction is as follows:

$$NO_2 + OH + M \rightarrow HNO_3 + M \qquad (6)$$

where M is an inert molecule, such as nitrogen, that receives excess energy (AQEG, 2004; USEPA, 1993).

1.2.1 European legislation and national air quality strategy

1.2.1.1 European legislation

The World Health Organisation's recommended air quality guidelines are used as a basis for setting the European Union (EU) standards. WHO first published "Air Quality Guidelines for Europe" in 1987. The recommendations are not mandatory but are accepted as being levels not to be exceeded if healthy air quality is to be maintained. In 1993, WHO began reviewing the guidelines in the light of new scientific data and a Consultation meeting in October 1996 revised guidelines were agreed. Then, the EU has developed legislation to limit our exposure to air pollutants. The first Daughter Directive was implemented in 1999 and set limits for SO_2, NO_2, particles and lead. The EU limit values and Air Quality Strategy Objectives for NO_2 are shown in Table 1.1 below. They are primarily based on health effects. The effects of NO_2 are related to the total exposure to the pollutant over the relevant averaging period, both the 1-hour and annual periods. The hourly objective, is the concentration of NO_2 in the air, averaged over a period of one hour. This is designed to make sure that people are not exposed to high concentrations of NO_2 for short periods of time. High concentrations can arise in episodes, which are associated with particular weather conditions. The annual objective is the concentration of NO_2 in the air averaged over a period of one year. This aims to protect people from being exposed to NO_2 over a long time. The First Air Quality Daughter Directive (1999/30/EC) set limit values for hourly and annual average NO_2 to be achieved throughout the Community by 1 January 2010.

Table 1.1 EU limit values and air quality strategy objectives for NO_2.

Legislation	Hourly (μg/m³) objective	Annual (μg/m³)	Achieve by
EU First Daughter Directive (99/30/EC)	200 μg/m³ with up to 18 exceedences per year	40	2010
Air Quality Strategy (2000)	200 μg/m³ (105 ppb) with up to 18 exceedences per year	40 (21 ppb)	2005

Source: AQEG, 2004. Nitrogen Dioxide in the United Kingdom. p.18.

1.2.1.2 National air quality strategy

As part of the EU, the UK has a statutory duty to comply with the EU legislation. The Government produced a National Air Quality Strategy (NAQS) containing standards and objectives and measures to achieve the objectives. The EU has revised limit values for specific pollutants given in Daughter Directives. As mentioned in section 1.2.1.1, the annual average guideline for NO_2 is 40 μg/m³ and a level of 200 μg/m³ is recommended as NO_2 Air Quality Guidelines for an hourly average guideline value (DETR, 2000). The UK is committed to meeting the objectives, but aims to achieve its objectives 5 years earlier than the EU has set. Therefore, in the UK, there are two air quality objectives for NO_2 in ambient air, the short-term objective of 105 ppb (200μg/m^3) expressed as a maximum one-hour mean, the long-term objective of 21ppb (40μg/m^3) as an annual mean (DETR, 2000). These two air quality objectives are exactly same as the EU limit values (Table 1.1 above) but need to be achieved by 2005.

Local Air Quality Management (LAQM) forms an important part of the Government's strategy to meet both the UK air quality objectives and EU limit values. LAQM requires all local authorities to carry out regular reviews and assessments of air quality in their area (Defra, 2003). NO_2 is one of the eight pollutants [SO_2, NO_2, NO, NH_3, O_3, CO, PM_{10}, benzene, toluene and xylene (BTX)] that a local authority is required to monitor. Therefore, the local authorities became responsible for air pollution control.

1.2.2 Monitoring techniques

There are two major methods for measuring NO_2 concentrations, active samplers and passive samplers. The active sampler or accurate real-time reading instrument permits measurement of short-term variations in NO_2 concentrations and long-term average levels. It requires a power source with pump to deliver the air sampler to a sensor or collector. Analysis of the contaminant concentration is performed subsequent to sample collection, usually in a laboratory. The real-time reading instrument has some disadvantages as follows: (i) it is very expensive, (ii) it has heavy weight, (iii) it needs a source of power such as batteries, (iv) it has nuisance noise, (v) it needs regular maintenance.

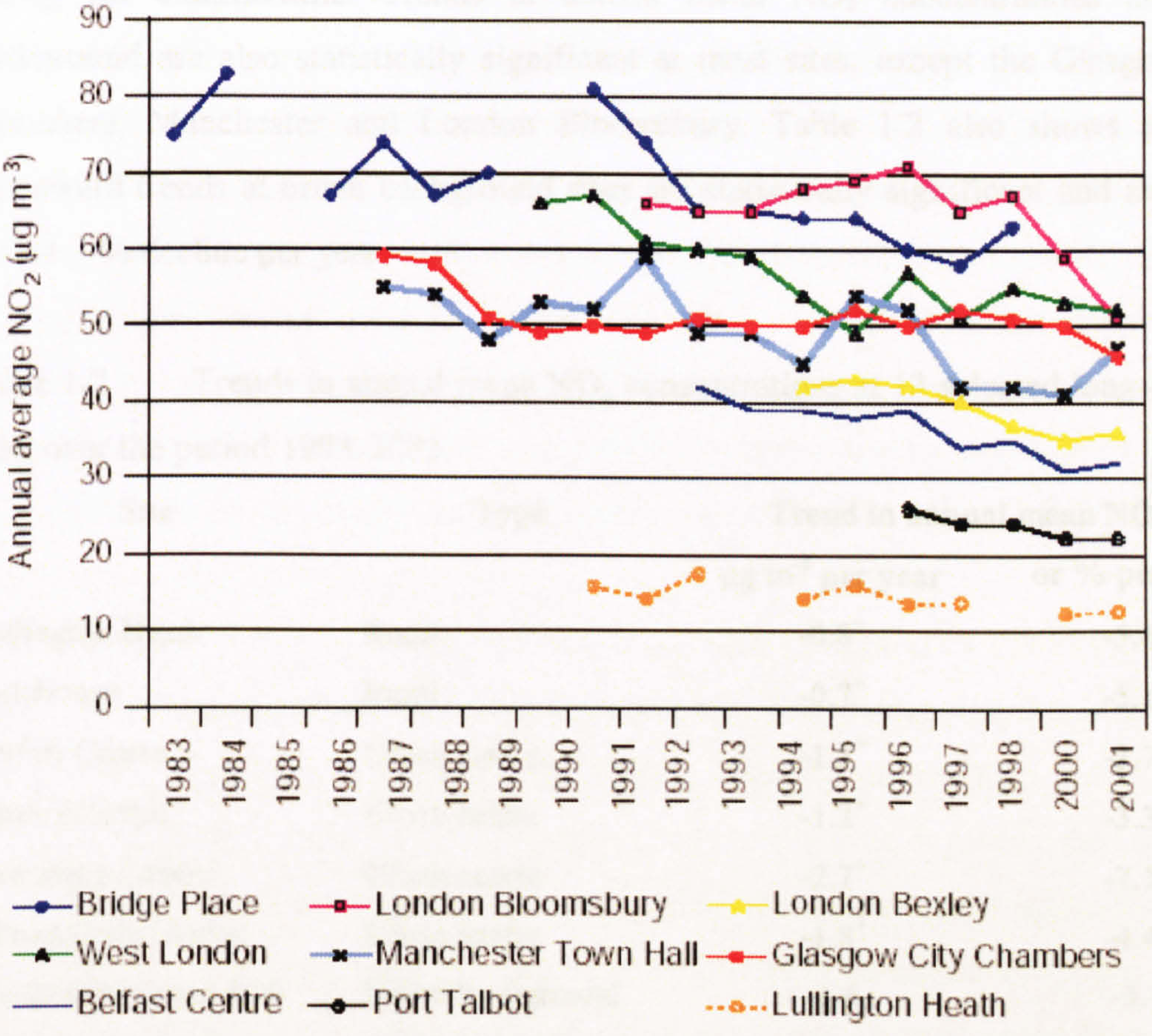
The passive samplers can be grouped into two types: badge and tube. The badge type sampler is characterised by an absorbent of large surface area, and a short diffusion path-length. This type permits a high sampling rate but because the diffusion path-length is short, it is sensitive to error caused by variations in wind speed. The tube type sample usually has a long diffusion path-length and low surface area absorbent. Both badge and tube samplers have been used in industrial hygiene, indoor air, and personal exposure studies. They are focused on atmospheres having high concentrations. Furthermore, they are cheap enough to be used at various locations and large number of sites averaged over a long period of time. Moreover, they can be easily used to obtain detailed spatial information. However, they can only determine mean concentrations, typically over 1-2 weeks. The tubes may be preferred over the badges, based on their robustness and their precision (Van Reeuwijk *et al.*, 1998). More details of the diffusion tube are presented in Chapter 2.

In the UK, local governments are responsible for the monitoring and control of air quality within their area of control as mentioned in section 1.2.1.2. To meet the required monitoring regimes, local authorities have invested in static monitoring equipment. In 1990, the UK Photochemical Oxidants Review Group published a report reviewing all measurements of NO_x in the UK. The group recommended the continued monitoring of NO_x, and pointed out that diffusion tube samplers provided a cost-effective method of determining spatial variation of NO_2 throughout the UK. However, automatic air quality monitoring is expensive to set up, operate and maintain. Historically, this has limited spatial coverage. The simple passive diffusion tube is therefore a useful supplement to automatic monitoring. Then, in 1993 DETR established the UK Nitrogen Dioxide Network, using diffusion tube samplers (Palmes diffusion tubes). The network currently collects data from over 1300 sites operated by more than 300 local authorities (AQEG, 2004). This provides a nation-wide overview of NO_2 concentrations (AEA Technology, 2003). The survey is centrally managed on behalf of the DETR by NETCEN (AQEG, 2004; AEA Technology, 2003; DETR, 2000).

1.2.3 Outdoor sources and trends

NO_2 in ambient air is important both because of exposures that exist there and because of its impacts on indoor air quality. The major sources of NO (which then converts to NO_2 in the atmosphere) are emissions from motor vehicles and the burning of fossil fuels in power plants and for heating (AQEG, 2004). Although NO_2 is mainly a secondary air pollutant it is rapidly formed close to sources of NO, therefore, NO_2 is often used as an indicator of traffic air pollution (Berglund, 1993). NO_2 from motor vehicle exhausts is estimated to represent 50 % of the total NO_x emissions; from the electricity supply industry, about 20 % and from commercial sectors for about 17 % of total NO_x emissions (DETR, 2000).

The latest report of AQEG (2004) stated that over the last 10 years in the UK the annual average concentrations of NO_2 at urban background and urban centre sites have gone down. An assessment of annual mean concentrations at several background and roadside sites in London shows a decrease in NO_2 concentrations in 2001 to 88% of the 1996 values (Figure 1.2).



Urban centre sites: London Bloomsbury, Belfast Centre
Urban background sites: Bridge Place, London Bexley, West London, Manchester Town Hall, Glasgow City Chambers, Port Talbot
Rural site: Lullington Health

Figure 1.2 Annual average NO_2 concentrations at selected urban centre, urban background and rural sites. Source: AQEG, 2004. Nitrogen Dioxide in the United Kingdom. p.207.

The AQEG (2004) also studied sites selected for detailed analysis at the 13 monitoring sites. There are long-running time series of observations, and statistically significant downward trends have been observed in NO_2 concentrations over the 1993-2002 period. Table 1.2 presents the trends in annual mean NO_2 concentrations during the 1993-2002 period, determined using a Mann-Kendell test with linear slopes estimated using Sen's method. The observed trends in NO_2 at the rural sites (Lullington Heath and Ladybower) are highly statistically significant, lying in the range -5.1 to -5.4% per year. It is consistent with the view that in rural areas there is generally enough oxidant to convert all NO to NO_2, particularly at night time and during the summertime. Trends in annual mean NO_2 concentrations at urban background are also statistically significant at most sites, except the Glasgow City Chambers, Manchester and London Bloomsbury. Table 1.2 also shows that the downward trends at urban background sites are statistically significant and average -3.1 ±1.7 % decline per year.

Table 1.2 Trends in annual mean NO_2 concentrations at 13 selected long-running sites over the period 1993-2002.

Site	**Type**	**Trend in annual mean NO_2**	
		$\mu g\ m^{-3}$ per year	**or % per year**
Lullington Heath	Rural	-0.8^+	-5.4^+
Ladybower	Rural	-0.7^+	-5.1^+
Belfast Centre	Urban centre	-1.3^+	-3.7^+
Cardiff Centre	Urban centre	-1.2^+	-3.3^+
Newcastle Centre	Urban centre	-2.7^+	-7.1^+
Birmingham Centre	Urban centre	-1.8^+	-4.4^+
Manchester Town Hall	Urban background	-1.6	-3.4
Walsall Alumwell	Urban background	-1.1^+	-2.5^+
Edinburgh Centre	Urban centre	-0.8^+	-1.8^+
Sheffield Tinsley	Urban industrial	-1.4^+	-2.9^+
Glasgow City Chambers	Urban background	-0.3	-0.6
West London	Urban background	-0.8^+	-1.6^+
London Bloomsbury	Urban centre	-1.9	-3.0

*Note: symbol+ shows those trends that are statistically significant at the 10% level of significance or better.

Source: AQEG, 2004. Nitrogen Dioxide in the United Kingdom. p.203.

The amount of NO_2 attributable to traffic fumes has been difficult to establish and has led to findings that suggest that indoor NO_2 concentration is related to outdoor NO_2 concentration, as long as no significant source of NO_2 emissions is produced indoors as Cotterhill and Kingham (1997) reported for an increase in NO_2 concentration in houses along busy roads.

1.2.4 Indoor sources and trends

Indoor NO_2 comes from emissions from a variety of combustion sources from outdoors and from indoors. The concentration of NO_2 indoors depends on several factors affecting the introduction, dispersion, and removal of NO_2. The factors are as follows: (i) the type, nature and number of sources, (ii) source use characteristics, (iii) building characteristics, (iv) infiltration or ventilation rates, (v) air mixing between and within compartments in an indoor space, (vi) removal rates and potential re-emission or generation by indoor surfaces and chemical transformations, (vii) existence and effectiveness of air contaminant removal systems, and (viii) outdoor concentrations which depend on ventilation and infiltration rates (USEPA, 1993b; Quackenboss *et al.*, 1986).

The major indoor sources of NO_2 have been identified as gas cookers, pilot lights, wood stoves, fireplaces, gas and paraffin/kerosene heaters (Bailie, *et al.*, 1999) and wood burning stoves (Ostro *et al.*, 1994). Cigarette smoke also contributes to indoor levels (Berglund *et al.*, 1993; Samet *et al.*, 1987). NO_2 is often found at higher levels indoors than outdoors, mostly in association with use of gas cookers (Cotterhill and Kingham, 1997). However, lower NO_2 concentrations in homes using gas cookers recorded in summer were found due to the increased ventilation in home (Berglund *et al.*, 1993). Homes with gas cookers have been found to have four to seven times higher mean 24-hr concentrations than homes with electric cookers (Lee *et al.*, 2000; Chao and Law, 2000; Garret *et al.*, 1999; Alm *et al.*, 1998; Levy *et al.*, 1998; Monn *et al.*, 1998; Spengler *et al.*, 1994; Fischer *et al.*, 1986; and Quackenboss *et al.*, 1986). Some studies (Moran *et al.*, 1999; Linaker *et al.*, 1996) have reported that children living in homes using gas cookers have an increased risk of respiratory infections compared to those living in homes with electric cookers. This has been attributed to long-term exposure to raised concentrations of NO_2, although the evidence is not conclusive. Some studies (Braun-Fahrländer *et al.*, 1992; Fischer *et al.*, 1986) have reported that NO_2 concentrations are higher in urban indoor environments compared with those in rural areas. This was attributed to the influence of outdoor levels, and to differences in indoor combustion sources such as gas cookers.

The use of continuous monitoring techniques in homes has led to the detection of short-term peaks in NO_2 levels. A study by Ross (1996), using continuous NO_2 analysers, concluded that gas cookers were the principal source of such peak concentrations in homes. Moreover, Spengler et al (1983) reported that while cooking with a gas range, peak levels in the kitchen may be as high as 400-1000 ppb. As individuals using gas cookers often stay close to the cookers, personal exposures may be even greater than others. Lambert *et al.* (1993) found that NO_2 levels were 21 ppb (39 $\mu g/m^3$) in bedrooms and 34 ppb (63 $\mu g/m^3$) in kitchens from homes with gas cookers in Albuquerque, New Mexico. In comparison, bedroom concentrations in homes using electric stoves averaged just 7 ppb (13 $\mu g/m^3$). On average, normal use of a vented gas cooking range adds 25 ppb (47 $\mu g/m^3$) of NO_2 to the background concentration in a home (Samet *et al.*, 1987). In homes with unvented kerosene space heaters, 1-week average concentrations exceeding 45 ppb (84 $\mu g/m^3$) have been observed (Leaderer *et al.*, 1986). One-week average levels of greater than 50 ppb (47 $\mu g/m^3$) have been reported in homes with unvented gas space heaters (Ryan *et al.*, 1989). An increase in NO_2 concentration in homes along busy roads has also been seen (Cotterhill and Kingham, 1997). The higher concentrations of NO_2 at the roadside have potential health implications for pedestrians and the occupants of adjacent houses. Commuters (in their cars or on public transport) have also been shown to be at risk e.g. commuters on buses have been shown to be exposed to higher levels of NO_2 than a pedestrian at the roadside (Chan and Wu, 1993).

1.2.5 Health effects

NO_2 is associated with adverse effects on human health (DETR, 2000). The Air Quality Objectives refer to NO_2 as the most important oxide in terms of human health (AQEG, 2004; AEA Technology, 2003; DoH, 1993). These health effects include permeation of the respiratory tract which affects lung function and airway responsiveness. NO_2 can also increase the susceptibility to airway infections in exposed groups. The toxicity of NO_2 is likely to be dependent on its oxidative and free radical properties, in addition to its ability to form nitric and nitrous acids in aqueous solution on the moist surfaces of the airspaces (Sandström, 1995). It acts mainly as an irritant, affecting the mucus of the eyes, nose, throat, respiratory tract include mucous membranes of the lung (Spengler *et al.*, 1994). Thus, it causes damage to the cells of the respiratory tract such as mucous membranes of the lung (Spengler *et al.*, 1983). Many studies have shown correlations between exposure to NO_2 and respiratory illness, as well as increased severity of asthma and increased response to inhaled allergens in asthmatics (WHO, 1997b).

Extremely high-dose exposure to NO_2, such as in a building fire, may result in pulmonary edema and diffuse lung injury. Continued exposure to high NO_2 levels can contribute to the development of acute or chronic bronchitis. NO_2 is highly soluble in water, and a large proportion of inhaled NO_2 is removed in the respiratory tract (Lambert *et al.*, 1993). It is thought to combine with water in the lungs to form nitric acid (HNO_3) and may react with lipids and proteins to form nitrite anions and hydrogen ions. NO_2 within the airways is also converted into vapour phase nitrous acid (HONO) via heterogeneous reactions involving water vapour, invoking the formation of free oxygen radicals and lipo-peroxidation (Spicer *et al.*, 1987). Whilst it has been suggested that oxidant injury is the principal mechanism by which NO_2 damages the lung, substantial uncertainty remains (Lambert *et al.*, 1993). The relatively low water solubility of NO_2 results in minimal mucous membrane irritation of the upper airway. The principal site of toxicity is the lower respiratory tract. Frampton *et al.* (1991) suggests that exposure to NO_2 may increase respiratory infections, and adversely affect lung function. In England, Jarvis *et al.* (1996) found that a general population sample of females who reported they used mainly gas for cooking were more likely to report respiratory symptoms in the 12 months prior to the survey. These women were also found to have reduced lung function and increased airway obstruction. No effects were observed amongst males, suggesting women may be more susceptible to NO_2, or are exposed to higher concentrations.

There is evidence that the health effects of NO_2 may be greater amongst certain vulnerable population subgroups, such as children and asthmatics (Raaschou-Nielsen, *et al.*, 1997). In the Harvard Six Cities Study (Hasselblad *et al.*, 1992), involving 10106 children aged 6-10 years old, respiratory track illness in infants was more common with infants from homes with gas cooking. Some meta-analyses suggest that the risk associated with NO_2 exposure was probably only significantly increased for children aged over 2 years old. In Australia, Pilotto *et al.* (1997) reported that NO_2 exposures for 388 children aged 6-11 years were monitored. They found hourly peak levels of 80 ppb (150 $\mu g/m^3$) and above were associated with significant increases in the reporting of sore throats, colds, and absences from school, and they concluded that it was important to consider short-term peak exposures. However, in another study, Samet *et al.* (1993) found no association between personal exposures and symptoms amongst infants, and Brunekreef *et al.* (1990) failed to find an association between NO_2 and the pulmonary function of a sample of children.

Amongst asthmatic women and children, Goldstein *et al.* (1988) examined the relationship between mean 48 hours NO_2 concentrations in the subjects' kitchens, and their spirometric lung function. They found that exposure to NO_2 levels ranging between 300 and 800 ppb (564 and 1504 $\mu g/m^3$) was associated with a reduction in lung capacity of the order of 10%. Salome *et al.* (1996) also found that the experimental exposure of 600 ppb (1128 $\mu g/m^3$) of NO_2 over a period of one hour was associated with a slight increase in airway hyper responsiveness amongst a sample of 20 asthmatics.

Dijkstra *et al.* (1990) reported that the effect of indoor exposure to NO_2 on respiratory health was studied over a 2-year period in Dutch children aged 6-12 years. Lung function was measured at schools, while information on respiratory symptoms was recorded. NO_2 concentrations from homes were measured using Palmes diffusion tubes. Results showed no relationship between exposure to NO_2 in the homes and respiratory symptoms. The development of respiratory symptoms was not associated with indoor exposure to NO_2. However, significant differences were found between the exposure to environmental tobacco smoke in the home and the development of wheezing and between home dampness and the development of coughs.

1.3 Personal Exposure Modelling

1.3.1 Personal exposure

Personal exposure to nitrogen dioxide (NO_2) has been defined as the event when a person comes in contact with NO_2 (Thron, 1996; Ashmore, 1995; Georgopoulos and Lioy, 1994; Sexton and Ryan, 1988; Ott, 1985; Ott, 1982). Thus, the personal exposure directly relates to NO_2 concentrations in microenvironments and to time spent in those microenvironments (EXPOLIS, 1999). Personal exposure could be measured as cross-sectional (between individuals) or longitudinal (within individuals). Personal exposure studied in this thesis is a cross-sectional study.

1.3.2 Modelling of exposure

Modelling to estimate personal exposure to air pollution has been classified as statistical, mathematical and mathematical-stochastic modelling (Ryan, 1991; Sexton and Ryan, 1988). The statistical method involves the statistical determination of the measured exposures in terms of the factors that are assumed to influence these exposures (e.g. regression models). Mathematical modelling involves the application of emission inventories combined with atmospheric dispersion and population activity modelling (e.g. Clench-Aas *et al.*, 1999; Jensen, 1999; and Johansson, 1999). The mathematical-stochastic approach attempts to include a treatment of inherent uncertainties in the models, such as those caused by the turbulent nature of atmospheric flow (e.g. Hänninen *et al.*, 2002, Monte-Carlo simulations). Statistical modelling has been used in this thesis. More details are discussed in Chapter 2.1.

1.4 Aim and objectives

NO_2 is a pollutant that is harmful to humans and a large percentage of the population uses gas as a cooking fuel; it was thus thought appropriate to monitor the NO_2 levels in this study. Lifestyles and activities of people have a great effect on their exposure to air pollutants and on their health. The target populations in this thesis are office workers, due to large numbers of workers who may have similar exposure pattern, and their exposures are most affected by urban traffic planning (EXPOLIS, 1999). It focuses on 21-60 year old individuals, to explore the relative importance of home and work environments, and to assess any variations in the exposure patterns. Houses with gas cookers and electric cookers were chosen as gas cookers are the main indoor sources of NO_2 and houses with electric cookers could acts as control.

The aim of this thesis was to investigate the relationships between NO_2 concentrations measured on the person (referred to as personal exposure) and the concentrations measured in different microenvironments used by office workers in Hertfordshire with the aid of activity data. The project objectives were as follows:

1. to assess and improve Palmes diffusion tube preparation and analysis method for NO_2.

2. to sample and measure indoor and outdoor weekly average NO_2 concentrations and personal exposure to NO_2 of office workers in Hertfordshire.
3. to compare the weekly average NO_2 concentrations in different seasons such as winter and summer.
4. to compare and relate the personal exposure to concentrations of NO_2 in microenvironments and time spent in each microenvironment.
5. to test the performance of an empirical time weighted exposure model based on microenvironmental concentrations with personal exposure measurements and activity data.

1.5 Thesis structure

In this Chapter, the background to air pollution is briefly reviewed, then focussed on NO_2: its main sources, monitoring and control legislation and also its health effects. Following this introductory chapter, Chapter 2 comprises four sections: the first, second and third are concerned with assessment of personal exposure, NO_2, and Palmes diffusion tube sampler for personal exposure to NO_2, respectively. The fourth section is concerned with examples of case studies. In Chapter 3, the development of the Palmes diffusion tubes preparation procedure is indicated and described. The monitoring campaigns carried out over a 7 day period for autumn, winter and summer in chosen indoor locations (houses: bedroom, living room and kitchen, offices and cars) and outdoors (front door of the houses) including sampling methodology, study areas, population, monitoring strategy, sitting protocol for the diffusion tubes and questionnaire design are described in Chapter 4. The results and discussion of the campaigns including the simulation of personal exposure using a spreadsheet model, based on the measured NO_2 concentrations in microenvironments and the individual time spent in each microenvironment are presented in Chapter 5. Finally, conclusions, new contributions and future work are summarised in Chapter 6.

Chapter 2

Measurement of personal exposure to nitrogen dioxide using Palmes diffusion tubes

In this chapter, methods for measuring personal exposure to NO_2 are reviewed. The chapter then reviews the Palmes diffusion tube sampler for personal NO_2 exposure measurement; its theoretical basis; chemistry of absorption of NO_2 by Triethanolamine; advantages and disadvantages of the diffusion sampling; accuracy and detection limits; health effects, and examples of case studies. Finally the chapter discusses the modelling of exposure. It should be noted that both sets of units for concentration are used, ppb and $\mu g/m^3$. The conversion factor between these units is shown in chapter 3. For the purpose of discussion, ppb values can be converted to $\mu g/m^3$ by multiplying by a factor of 2.

2.1 Personal exposure monitoring methods for measuring personal exposure to NO_2

Many studies have been suggested that measurement of personal exposure to air pollutants including NO_2 could be measured directly as direct method (Monn, 2001; EXPOLIS, 1999; Thron, 1996; Ashmore, 1995; Sexton and Ryan, 1988; Ott, 1985; and Ott, 1982). It could be grouped into two methods: personal exposure monitoring and biological monitoring (Sexton and Ryan, 1988; Ott, 1985; and Ott, 1982). The biological monitoring is involved with using some type of body material (e.g. urine, blood) in which the concentration of a pollutant is determined. It is more a relevant measurement than ambient concentrations for defining populations at risk or for conducting health effects research. This method is also especially useful, if highly selective and specific markers of exposure are available, (Ryan and Lambert, 1991).

The personal exposure monitoring has been grouped into two types of monitors, integrating personal passive sampling devices (PSD) and continuously recording personal exposure monitors (PEM). These devices have been used for direct measurement of personal exposure as well as measurement of air pollutant concentrations in representative microenvironments (MEs). Individuals carry or wear a device during that person's normal daily activity as she/he moves from one microenvironment (ME) to another. The monitor measures the concentrations of NO_2 around the individual's breathing zone area. During the monitoring period, the participant should record the locations visited and the activities. Even though the continuous monitoring devices continue to be developed for use in personal sampling studies, one disadvantage of this method (Table 2.1) is cost of the instrument and subsequent analysis (EXPOLIS, 1999; Ross, 1996). There are a number of passive samplers that can provide time-integrated measurements of personal exposure although integrated samplers only provide information on total personal exposure and not the contribution from different microenvironments. Nevertheless, it is suitable for a large group personal exposure study (EXPOLIS, 1999).

Table 2.1 Advantages and disadvantages of the methods of personal exposure monitoring to NO_2

Methods of personal exposure monitoring to NO_2	**Advantages**	**Disadvantages**
Continuously recording personal exposure monitors	-Most accurate means of NO_2 exposure assessment -Determines the NO_2 exposure of individual participants	-Can be expensive -Limited continuous sampling only one or a few measurements -Not easily suited to estimate the personal NO_2 exposure of populations, or large groups
Integrating personal passive sampling devices	-Low cost -Suitable for large sample size -Less disruption to the volunteers	-Need more periods of continuous monitoring -Indoor microenvironments are not well understood

Active sampling

Active sampling involves monitors that draw air through a pump into the sampler to allow analysis over shorter periods giving data of higher temporal resolution. The active sampling has the disadvantage of being expensive and the need for a pump and battery power can limits its use for routine or maintenance-free applications.

Passive sampling

In contrast, passive sampling is low cost per analysis and does not requires a power source or the need for detailed maintenance. The disadvantage is that as it requires as long as 7 days to register accurate results. This method can be considered in two broad categories: the badge and the tube. The passive tube relies on molecular diffusion of NO_2 through an acrylic tube of known length and cross-sectional area to a reactive surface or absorbent meshes where the NO_2 molecule is captured by chemical reaction forming a nitrite (Palmes *et al.*, 1976, Gair *et al.*, 1991). After exposure, the duration of which can range from several hours to days (depending on the concentrations being measured), the reactive surface is analysed and the integrated loading of the reaction product is used to infer the average pollutant concentration.

Another passive monitor, the badge, relies on a filter to control the sampling rate rather than an air column inside the tube (Loth and Ashmore, 1994). One example is the Yanagisawa badge which has a detection limit of 124 $\mu g/m^3$ and used for exposure periods of 24 hours (Yanagisawa and Nishimura, 1982). Later, badge monitors were developed with a lower exposure detection limit of 84.6 $\mu g/m^3$ and have been used to measure indoor NO_2 levels (Pilotto *et al.*, 1997). A study by Van Reeuwijk *et al.* (1998) compared measurement of NO_2 between Palmes diffusion tubes and Badge samplers. Two-week average NO_2 levels were measured in Amsterdam, Huddersfield and Prague at 80 sites in each study area. The average NO_2 concentrations measured by both methods did not differ significantly. Moreover, the authors concluded that both methods were suitable for determining real variation in small area. They can provide reliable information about variation in NO_2 concentrations within urban or rural areas on a small spatial scale. However, the tubes were preferred over the badges, based on their robustness and their precision. The badge has not yet proved to be effective in outdoor locations where weather conditions affect the diffusion rate, although it is capable of detecting average exposure concentrations over much shorter periods of time. Consequently, the tube is generally preferred over the badge, based on its robustness and its accuracy (Van Reeuwijk *et al.*, 1998).

2.2 Palmes diffusion tube sampler for personal NO_2 exposure measurement

The diffusion tube sampler was first developed for measuring indoor occupational exposure, by Palmes *et al.* in 1976. It was originally designed to be attached to the clothing of miners. The original Palmes diffusion tube sampler consisted of an acrylic tube 7.1 cm in length and 0.71 cm^2 cross-sectional area, three stainless steel meshes, and two1.2x1.2 cm polyethylene cap (Palmes *et al.*, 1976). The tubes were tested for the effect of wind velocity and direction and Atkins *et al.* (1978) has shown that high wind speeds may cause an effect. They suggested that the wind speed should not be higher than 4.5 m s^{-1} because it could increase in average uptake with increased velocity. After that the tubes were developed and Atkins *et al.* (1986) used diffusion tube samplers for measurement concentrations of NO_2 in homes that use gas and electricity, and later evaluated them for outdoor use in urban environments. Since then, diffusion tube samplers have been evaluated and used for outdoor measurements of nitrogen dioxide in a number of studies including Campbell *et al.* (1994), Shooter (1993), Bower *et al.* (1991a, 1991b), Gair *et al.* (1991), and Campbell (1988).

2.2.1. Theoretical bases of diffusion tubes

The development and use of the passive diffusion tube originated in the field of occupational exposure monitoring (Palmes *et al.*, 1976). This sampling technique was further developed and tested (Atkins *et al.*, 1986), and is now widely used for ambient air quality monitoring (AQEG, 2004).

The diffusion tube sampler operates on the principle of molecular diffusion, with molecules of a gas diffusing from a region of high concentration (open end of the sampler) to a region of low concentration (absorbent end of the sampler). The movement of molecules of gas (1) through gas (2) is described by Fick's law, which states that the flux is proportional to the concentration gradient:

$$F = -D_{12}\frac{dC}{dz} \qquad (1)$$

where: F = the diffusive flux of gas (1) through gas (2) across unit area in the z direction (mol cm^{-2} s^{-1}),

C = the concentration of gas (1) in gas (2) (mol cm^{-3}),

z = the length of the diffusion path (cm),

D_{12} = the constant of proportionality – the molecular diffusion constant of gas (1) in gas (2), with dimensions of length^2 time^{-1} (cm^2 s^{-1}).

For a tube of area a (m^2) and length l (m) then Q (moles), the quantity of gas transferred along the tube in t seconds, is given by:

$$Q = \frac{D_{12}(C_1 - C_0)at}{l} \qquad (2)$$

where: C_0 and C_1 are the gas concentrations at either end of the tube.

In a diffusion tube, the concentration of gas (1) is maintained at zero (by an efficient absorbent) at one end of the tube (i.e. C_0 = zero) and the concentration C_1 is the average concentration of the gas (1) at the open end of the tube over the period of exposure. Therefore:

$$C = \frac{Ql}{D_{12}at} \qquad (3)$$

where: Q = the quantity of the gas absorbed over the period of exposure

a = the cross sectional area of the tube (πr^2)

t = the time of exposure

l = the length of the tube

by integration of equation (2), the quantity of gas transferred (Q moles) in t seconds for a cylinder of radius r is given by Equation 4 and 5

$$Q = F(\pi r^2)t \text{ mol} \qquad (4)$$

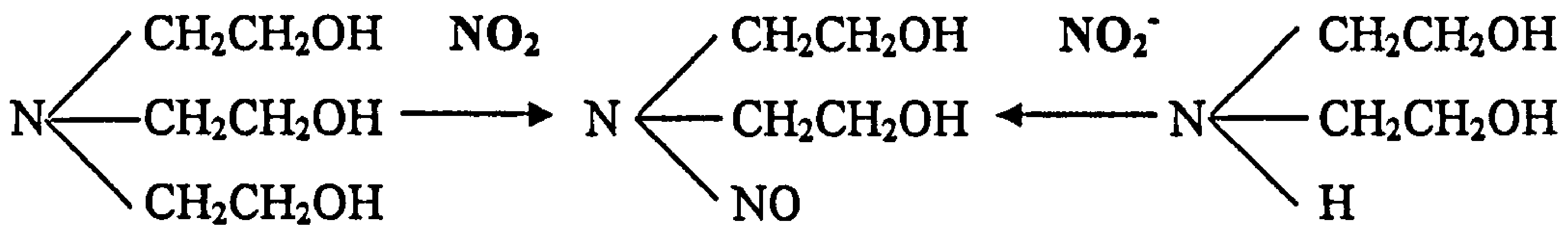
For the gas monitored, the diffusion coefficient must be determined or obtained from the literature (AEA Technology, 2003). The area and length of the tube are determined by measurement. For the collection of NO_2 with diffusion tubes with a tube length of 7.1 cm and an internal radius of 0.55 cm, the number of moles of NO_2 collected is given by:

$$Q = \frac{(0.154)c(0.95)t}{7.1} mol \qquad (5)$$

2.2.2 Analysis and chemistry of absorption of NO_2 by TEA

Analysis is accomplished by extracting the meshes in solution and analysing the extract for nitrite ion (NO_2^-) using a spectrophotometer at 540 nm (Palmes *et al.*, 1976). The spectrometer is calibrated against standard nitrite solutions, to allow the total NO_2 as nitrite, collected by the tube, to be determined. This analysis method is suitable for dosages between 1 and 30 ppm/h. Later, an improvement in sensitivity from 0.03 ppm/h to 0.3 ppm/h was achieved by analysing the NO_2^- using ion chromatography with a concentrator column (Miller, 1984). The colorimetric analysis is calibrated by dilution of gravimetrically prepared nitrite solutions. However, the spectrophotometer is still a more popular method than ion chromatography as it is cheaper and is readily available in most analytical laboratories.

The chemistry of the absorption of NO_2 by Triethanolamine (TEA) and its conversion to nitrite ion (NO_2^-) was clarified by Aoyama and Yashiro (1983). They have provided convincing evidence that nitrosodiethanolamine (NDELA) is the product of the reaction between NO_2 and triethanolamine. It was also shown that an identical product was produced by the reaction between NO_2^- and Diethanolamine (DEA).



$$N(CH_2CH_2OH)_3 \xrightarrow{NO_2} N(CH_2CH_2OH)_2NO \xleftarrow{NO_2^-} N(CH_2CH_2OH)_2H \qquad (6)$$

Triethanolamine (TEA) Nitrosodiethanolamine (NDELA) Diethanolamine (DEA)

Nitrosodiethanolamine is easily hydrolysed to form nitrite.

$$R_2N - NO + H_2O \xrightarrow{H_3PO_4} R_2NH + HNO_2 \qquad (7)$$

This generally involves the addition of a solution of sulphanilamide in orthophosphoric acid and naphthyl ethylene diamine dihydrochloride (NEDA) solution, to form an azo dye. A diazonium salt is formed with the N-1-naphthylethylene-diamine dihydrochloride (NEDA) to form a purple azo dye. The colour-formation process is called the diazotisation of the sulphanilamide by nitrite.

2.2.3 Advantages and disadvantages of Palmes diffusion tube sampler

The advantages of the Palmes diffusion tube sampler are as follow: low cost, lightweight, simple deployment, requires minimal maintenance, no power supply, needs only short preparation time, and ease of use. These factors makes it suitable for field studies and for wide-scale environmental monitoring. (Atkins et al., 1978 and Shooter, 1993). The tube takes advantage of the small area-to-length ratio to minimise the influence from turbulence in the front of the tube (Royset, 1998). Moreover, the tube is an integrating device best suited to long-term measurements (Shooter, 1993).

Table 2.2 Summary of advantages and disadvantages of the Palmes diffusion tube

Advantages	**Disadvantages**
- low cost, - lightweight, - simple application, - maintenance not required, - power supply not required, - short time for preparation, - suitable for use in large-scale surveys	- give only average concentrations, can not provide peak concentrations

2.2.4 Accuracy and detection limit

Shooter (1993) reported on the evaluation of diffusion tubes by comparing with three other NO_2 measurement techniques; conventional chemiluminescence, differential Optical Absorption Spectroscopy, and the European Monitoring and Evaluation Program network standard method TGS-ANSA. The diffusion samplers agreed within 15% in this comparison over a concentration range of 1 to 12 ppb NO_2. The author observed that simultaneous exposure of 20 samplers gave a percentage standard deviation of approximately 10%, and reuse of the tubes did not affect performance. Moreover, the author suggested that the detection limit for spectrophotometric method suggested is 10 ppb nitrite, equivalent to an average NO_2 concentration of 0.2 ppb during a one-week exposure. Miller (1988), using ion chromatography, also suggested a similar detection limit as spectrophotometric method reported by Shooter (1993). Moreover, Heal *et al.* (1999b) reported that Palmes diffusion tubes were found to be reasonably accurate in indoor measurement during short-term (2 and 3 days).

2.2.5 Examples of case studies

2.2.5.1 Personal exposure

Studies of personal exposure to NO_2 as a function of outdoor and indoor concentrations, and time-activity patterns has been reported by different authors. Dockery *et al.* (1981) reported that in June 1979, personal exposure to NO_2 indoor and outdoor NO_2 concentrations were measured using Palmes diffusion tubes for 23 family members from 9 houses in Topeka, Kansas. Results showed that NO_2 concentrations were two times higher in houses with gas cookers than in houses with electric cookers and the outdoor concentrations. A linear model explained 77% of the variance in observed NO_2 exposure.

Quackenboss *et al.* (1982) reported that personal exposure to NO_2 and time spent in various microenvironments were measured for 66 family members from 19 houses in the Portage area, Wisconsin, during March 1981. Palmes diffusion tubes were used to measure NO_2 in kitchen, bedroom and outside and also were worn by individuals. The individuals from houses with gas cookers had significantly higher average NO_2 exposure than those from houses with electric cookers. Personal exposures were more closely related to bedroom levels than to kitchen or outdoor concentrations.

Leaderer *et al.* (1986) studied the association between acute respiratory illness and the use of unvented kerosene space heaters in 333 residences in the New Haven, Connecticut from September 1982 to April 1983. Personal exposures were measured, for a 2-week period, to SO_2, formaldehyde and NO_2 in kitchen, living room, bedroom and outside. Then, average NO_2 and SO_2 values for each house were calculated by summing the values measured in each location in the house and dividing by the total number of samples. The results showed that residences with one kerosene heater and no gas stove had NO_2 levels 4-5 times higher than the levels in residences without NO_2 sources. Indoor NO_2 levels from houses without NO_2 sources were lower than outdoor levels. Total personal NO_2 exposure levels were found to be 90% of the house average NO_2 levels for the individuals. Moreover, total personal NO_2 exposure were not found to be related to outdoors levels of NO_2 measured at each residence ($r = 0.14$, $p > 0.5$).

Harlos et al. (1987) reported on personal exposure to NO_2 of infants and outdoor and indoor NO_2 levels (bedroom, living room and kitchen) measured using Palmes diffusion tubes during January to March 1985. Infants spent 65%, 32% and 5% of their time in bedroom, living room and kitchen, respectively. Results showed that personal NO_2 levels could be predicted by using average room NO_2 concentrations and a time-weighted average. Bedroom concentrations alone could be used as an alternative predictor, suitable for use in large-scale surveys.

Houthuijs *et al.* (1990) reported that continuous and categorical variables for estimation of exposure to NO_2 were measured twice over a 2-year period, once in January 1985 and once in January 1987, in 1269 children aged 6-12 years in the south east of the Netherlands. Personal exposure and weekly average NO_2 concentrations were measured using Palmes diffusion tubes. Measurements were also conducted in bedroom, living room, and kitchen and at schools. The repeatability of the measurement of both methods was excellent.

Sega and Fugas (1991) reported that personal exposure to NO_2 of 15 working women in Zagreb, Yugoslavia was estimated using 3 different approaches; i) direct measurement, ii) calculation of weighted average exposure using data on time spent and concentrations measured at bedroom, living room, kitchen, in office, outside houses and workplace, iii) the same calculation but instead of actual concentrations, using concentrations measured in other houses. Average NO_2 concentrations were measured using passive badge samplers for 2-week periods. Results showed ii) method gave better agreement than iii) method.

In the report by Quackenboss *et al.* (1991), personal exposure to NO_2 of 400 children aged 6-15 years in Tucson, Arizona were estimated, using average indoor NO_2 concentrations (in kitchen, living room and bedroom measured by Palmes diffusion tubes for 2-week periods) and total time spent in microenvironments during May 1986 to November 1988. Results showed that NO_2 concentrations inside houses with gas cookers were 2 times higher than those with electric cookers, especially in kitchens. Indoor/outdoor ratio in houses without major NO_2 sources was 0.84 in summer, 0.57 in spring and fall, and 0.41 in winter. Personal exposure of children from houses without major NO_2 sources was not significantly different between seasons, while personal exposure of children from houses with NO_2 sources was found to be higher in winter than in summer.

Chan and Wu (1993) reported on exposure to NO_2 of bus commuters and pedestrians in Hong Kong, measured using active continuous samplers during July to August 1990. Results showed that average NO_2 exposure of bus commuters was 0.077 μL/L for trips lasting between 20 and 45 min., while hourly average NO_2 exposure of pedestrians to NO_2 was 0.051 μL/L. NO_2 concentrations in buses were higher than roadsides. Moreover, data from fixed stations were found give an unreliable representation of exposure levels.

In the study by Linaker *et al.* (1996), 1-week NO_2 samples were obtained between January and March, 1994 by Palmes diffusion tube for 46 children, 9-11 years old, studying in two schools in Southampton, UK. Both schools used gas-fired central heating. The personal samplers were supplemented with household measurements made in the kitchen and living room, and school measurements made in classroom and playground, and time spent in various microenvironments and information of household characteristics. The personal exposures to NO_2 averaged over 7 days ranged from 11 to 257 μg/m^3 (6 to 137 ppb). Exposures correlated with concentrations of NO_2 recorded in the home, but the relation was far from exact. Factors associated with increased personal exposure included the use of gas appliances in the home, living with one or more smokers, and travel to school by means other than a car. However, together these variables only explained a small part of the variation in personal exposures. They suggested that these findings reinforce the need for personal monitoring of exposure in studies investigating potential health effects of NO_2 in children. They also suggested that the technique for passive monitoring of NO_2 is well established and reliable.

Lovova *et al.* (1997) reported that personal exposure to NO_2 of 20 children aged 10-12 years in Bulgaria were measured while indoors (kitchen and living room) and outdoors NO_2 concentrations were collected using Palmes diffusion tubes. High NO_2 concentrations were found in kitchens with gas cooker. The highest personal exposure to NO_2 was recorded in a child, whose parents both were smokers, living in a house with gas cooker in city centre.

Alm *et al.* (1998) obtained data for 1-week NO_2 samples collected during 13 weeks in winter and spring period in 1991 by Palmes diffusion tubes for 246 pre-school children, 3-6 year old, at 8 day-care centres in suburban and downtown areas in Helsinki, Finland. The personal samplers were supplemented with measurements made outside and inside each day-care centre, and information on household characteristics. The Palmes diffusion tubes were found to be applicable for NO_2 exposure measurements of pre-school children, but rather high sampler losses could be expected. The geometric mean of personal NO_2 exposure concentrations in the 13 week period was 26.5 $\mu g/m^3$ in the downtown and 17.5 $\mu g/m^3$ in the suburban area. Most of the weekly NO_2 exposures of pre-school children were between 10 and 50 $\mu g/m^3$. The weekly personal NO_2 exposures correlated rather poorly with the fixed site ambient air NO_2 levels ($R^2 = 0.88$ and 0.86). They reported that in downtown the winter exposures were lower than the spring exposures. The concentrations of NO_2 measured inside or outside day-care centres by Palmes diffusion tubes explained the variations in the personal NO_2 exposure much better than the concentrations measured at the fixed air quality monitoring sites. They both explained the variation of exposures much better during the spring than during the winter.

Monn *et al.* (1998) reported that 1-week NO_2 samples were obtained between December 1993 and December 1994 by Palmes diffusion tubes for over 500 volunteers living in eight areas in Switzerland: four urban/suburban areas (Geneva, Basle, Lugano, Aarau), two rural areas (Wald, Payerne), and two alpine areas (Montana, Davos) of Switzerland. The personal samplers were supplemented with household measurements made outside and inside the bedroom of each house, information on cooking methods, home ventilation, smoking, occupational exposure and household characteristics with respect to traffic density. Average NO_2 personal level was 27 μg m^{-3} between the average outdoor (31 μg m^{-3}) and indoor concentrations (21 μg m^{-3}). Correlations between indoor concentrations and personal concentrations were higher than between outdoor concentrations and personal concentrations.

Linaker *et al.* (2000), studied personal exposure to NO_2 for 114 children, aged 7-12 years, in Southampton, UK. Data were obtained between October and December 1994 using Palmes diffusion tube for 7-day periods while outdoor NO_2 concentrations were collected by a monitoring network station located in the city centre. A subgroup (56 children) was carried out again during September to December 1995. Results showed average personal exposures to NO_2 ranged from 0.7 to 496 μg/m^3. Daily outdoor NO_2 concentrations ranged from 4.3 to 29.8 μg/m^3. There was no evidence of seasonal variation in outdoor NO_2 concentrations and no significant correlation was found between personal exposures to NO_2 and outdoor concentrations.

In Italy, personal exposure to NO_2 of 23 school children (11 asthmatics and 12 non-asthmatics) was investigated (Panella *et al.*, 2000). Palmes diffusion tubes were used to measure NO_2 concentrations in the kitchen, bedroom and outside the childrens' houses. The results showed a significant difference between average personal exposure to NO_2 of asthmatic children and non-asthmatic children. The average personal exposure to NO_2 of asthmatic children was 39.0 μg/m^3, which was higher than the average personal exposure to NO_2 of 12 non-asthmatic children, 47.3 μg/m^3. Average outdoor and indoor NO_2 concentrations of asthmatic children's houses were higher than those non-asthmatic children's houses (Panella *et al.*, 2000).

In Hong Kong, personal exposure to NO_2 of 60 adults (aged 22-45 years) was studied by Chao and Law, 2000). A subgroup, 12 volunteers, was investigated for concentrations of NO_2 inside (kitchen, living room and bedroom) and outside their houses using Palmes diffusion tubes. The results showed that average personal exposure to NO_2 of 60 adults was 46.0 μg/m^3, which was close to average personal exposure to NO_2 of 12 adults, 47.3 μg/m^3. Average indoor NO_2 concentrations from 12 houses was 55.2 μg/m^3 while average outdoor NO_2 concentrations was 71.8 μg/m^3 (Chao and Law, 2000).

The EXPOLIS study (Kousa *et al.*, 2001) reported that personal, residential indoor, outdoor and workplace levels of NO_2 were measured for 262 urban adults (25-

55 years in Basel, Switzerland; Helsinki, Finland and Prague, Czech Republic, using passive samplers for 48 h sampling periods during 1996-1997. The average residential outdoor and indoor NO_2 levels were lowest in Helsinki (24±12 and 18±11 $\mu g/m^3$, respectively), highest in Prague (61±20 and 43±23 $\mu g/m^3$), with Basel in between (36±13 and 27±13 $\mu g/m^3$). Average workplace NO_2 levels were highest in Basel (36±24 $\mu g/m^3$), lowest in Helsinki (27±15 $\mu g/m^3$ with Prague in between (30±18 $\mu g/m^3$). A time-weighted microenvironmental exposure model explained 74% of the personal exposure variation in all centres and, on average, 88% of the exposure. Regression models based on ambient fixed site NO_2 concentration, found to be poor predictors for personal exposure variation, explaining only 11-19% of personal exposure variation.

Personal exposure to NO_2 as a function of indoor concentrations, was studied by Remijn *et al.*, 1985; Fischer *et al.*, 1986; and Noy *et al.*, 1986.

Remijn *et al.* (1985) reported that indoor NO_2 concentrations were measured in 163 houses in 1982. Personal exposure to NO_2 was calculated from the measured levels and the activity pattern (ranged from 11-139 $\mu g/m^3$), while historic exposure was estimated using regression models of NO_2 on house characteristics. Results showed that estimation of historic exposure to indoor NO_2, on the basis of house characteristics only, was too inaccurate for use in epidemiological studies. Actual measurement of NO_2 is unavoidable for exposure assessment in health effect studies of indoor exposure to NO_2.

Fischer *et al.* (1986) reported that personal exposure to NO_2 and indoor NO_2 concentrations (kitchen, living room and bedroom) were measured for 612 houses in two areas in the Netherlands during winter 1982 and 1983 using Palmes diffusion tubes. Time-weighted averages were calculated using NO_2 concentrations and time spent in microenvironments. Results found that personal exposure was only different between the two areas in the group with the lowest indoor NO_2 concentrations. Gas cooker was found as the most important factor for indoor NO_2 concentrations.

Noy *et al.* (1986) reported that 1-week personal exposure to NO_2 and indoor NO_2 concentrations (bedroom, living room and kitchen) were measured in 37 housewives living in houses with unvented gas appliances in Wageningen, the Netherlands, using Palmes diffusion tubes, while time spent in various microenvironments were recorded during January/February, 1984. Relationships between personal exposure and indoor concentrations were investigated using bivariate regression and multiple regression techniques. The NO_2 peak concentrations were high, especially in the kitchens where up to 2034 $\mu g/m^3$ was found. Indoor NO_2 concentrations were found to be highly related to personal exposure. Moreover, time-activity data reported that the volunteers spent only 5% of the time outdoors. The largest part of the time was spent in kitchen, living room, and bedroom. Noy et al. (1986) concluded that personal NO_2 exposure could be well explained by indoor NO_2 measurements. A combination of indoor concentrations in the kitchen, living room and bedroom explained personal exposure better than separate concentrations.

The study on personal exposure to NO_2 as a function of season was studied by Quackenboss *et al.*, 1986; Noy *et al.*, 1990; and Mukala *et al.*, 1996.

In the study by Quackenboss *et al.* (1986), 1-week NO_2 samples were obtained during both summer and winter of 1981-1982 by Palmes diffusion tube for 324 volunteers living in 82 homes in the rural area of Portage, WI. The personal samplers were supplemented with household measurements made outside and in kitchen and bedroom, time spent in various microenvironments and information of household characteristics. Average NO_2 personal exposures were weakly correlated to outdoor NO_2 concentrations in the winter and moderately correlated in the summer. Outdoor concentrations were lower than personal exposures for individuals in homes with gas cooking ranges and higher than personal exposures for individuals in homes with electric stoves. Personal exposures were closely related to indoor averages for households with gas stoves and with electric stoves. Moreover, time-activity diary results showed that the volunteers spent more than 65% of their time at home, 15% was spent outdoors in the summer and 5% in the winter. They had spent approximately 4% of their time in motor vehicles, up to 15% at work or school, and approximately 8% in other indoors.

Noy *et al.*, 1990 reported that in April, October and December1984, 1-week personal exposure to NO_2 was studied in 128 housewives and children (4-6 years old) in Veenendaal, the Netherlands. Personal exposure, indoor NO_2 concentrations (kitchen, living room, and bedroom) and peak exposures were measured using Palmes diffusion tubes, while time spent in various microenvironments were recorded. Three different exposures were calculated i) using NO_2 concentrations from kitchen, living room, bedroom and outdoors and time that each individual spent in microenvironments, ii) using the population mean instead of individual time, iii) the arithmetic average of kitchen, living room and bedroom concentration were used, while the time spent in the microenvironment was not used. Results showed all three different exposure estimates were closed with measured personal exposure. High peak NO_2 concentrations, up to 2000 μg/m^3 were found in kitchens. A gas fired water heater and a gas stove in the kitchen were found to be the most important factors in determining personal concentration levels. Time-activity diary results showed that volunteers spent most of their time in the living room and bedroom. However, the mothers and children spent a maximum of 13% and 7% of their time in locations not covered by the monitoring. This indicates that the assumptions made about the NO_2 concentrations of the locations do not have a large influence on the estimated weekly average exposure. Noy *et al.*, 1990 suggested that personal exposure to NO_2 depends on the amount of time spent in different locations, and the NO_2 concentrations encountered in the locations. Moreover, time weighting was of minor importance for estimating exposure in these populations of housewives and young children.

Mukala *et al.* (1996) reported on personal exposure to NO_2 of 172 preschool children aged 3-6 years at day-care centres in central and suburban area of Helsinki, Finland who were studied for 7 weeks during winter season and for 8 weeks during spring season in 1991. Information on households and on respiratory symptoms were recorded. There were significantly more days with stuffed nose (26% vs. 20%) and cough (18% vs. 15%) in the central area than the suburban area. The median of personally measured seasonal NO_2 exposure was 21 μg/m^3. Seasonal median NO_2 exposure was significantly higher in the central area (27.4 μg/m^3) than in the suburban area (18.2 μg/m^3).

2.2.5.2 Outdoor NO_2 concentrations

A National Network of NO_2 diffusion tube samplers has been operated at over 1200 sites in the UK for over 5 years (DETR, 2000). UK outdoor NO_2 concentrations have been reported by Campbell, 1988; Hewitt, 1991; Campbell *et al.*, 1994; Atkin and Lee, 1995; Ashenden and Edge, 1995; Oduyemi and Davidson, 1998; Hargreaves *et al.*, 2000; and Stevenson *et al.*, 2001.

Campbell (1988) reported on NO_2 concentrations at rural sites, measured using Palmes diffusion tubes, during February to July 1987. The calculated annual mean NO_2 concentrations varied from 1 μg/m^3 in Northern Ireland to 7 μg/m^3 in East

Anglia. The NO_2 concentrations during winter were higher than concentrations in summer.

In Hewitt's (1991) report, NO_2 concentrations were measured between 22 January 1989 to 21 January 1990 by Palmes diffusion tube for 49 sites in Lancaster. The highest annual mean of NO_2, 63 $\mu g/m^3$ with a range of 12-222 $\mu g/m^3$, was found at sample sites on a main road in the city centre. The annual mean concentration on an adjacent main road was 58 $\mu g/m^3$ with a range of 5-107 $\mu g/m^3$. The annual mean concentrations at the suburban sites: main road, residential street and city pedestrian precinct were 38 $\mu g/m^3$, 30 $\mu g/m^3$ and 30 $\mu g/m^3$ respectively.

A survey of NO_2 levels in 363 urban sites across was reported by Campbell *et al.* (1994). NO_2 concentrations were measured by Palmes diffusion tube for one-week sampling period between July to December 1991. The average NO_2 levels varied from 10 ppb at urban sites in north eastern Scotland to a traffic-light-controlled junction in inner London.

A survey of NO_2 levels in 57 rural sites across was reported by Atkin and Lee (1995). NO_2 concentrations were measured by Palmes diffusion tube for 2-week sampling period between winter and summer, June 1987-May 1990. The maximum NO_2 level was found at Rothamsted site, in the southeast of England with average of 23.1 ppb and 25.2 ppb, for April-September 1987 and October 1987-March 1988, respectively.

A 1-year survey of NO_2 concentrations in rural Wales was carried out by Ashenden and Edge (1995). NO_2 levels were measured by Palmes diffusion tube for 2-week sampling period, from 23 sites. The highest levels for most sites were recorded during the winter months, November 1991-February 1992 probably related to a greater use of fossil fuels for heating buildings. However, the high levels of NO_2 in May and June for several sites in North Wales, and in July and August for a site on Mount Snowdon were found probably related to increased traffic associated with tourism.

Oduyemi and Davidson (1998) presented data from a diffusion tube survey run between January 1995 and June 1997 in Dundee city centre. Average NO_2 concentrations ranged from 26.4-61.3 $\mu g/m^3$ at the Seagate site, 27.5-68.6 $\mu g/m^3$ at the Marketgait siteand 24.1-44.0 $\mu g/m^3$ at the Commercial Street site.

Hargreaves *et al.* (2000) reported that in September 1993, Palmes diffusion tubes were set up to measure NO_2 concentrations at Rothamsted Experimental Station as a part of the UK Environmental Change Network. Concentrations recorded between September 1993 and April 1997 were found to be high in winter and low in summer.

Stevenson *et al.* (2001) presented NO_2 results for the first 5-years (1993-1997) of passive diffusion tubes NO_2 monitoring in the UK National Air Quality Network for the National Nitrogen Dioxide Survey. The network has shown that highest NO_2 concentrations recorded in London and urban areas of Yorkshire and Humberside and the East and West Midlands of the UK, though a significant decrease was found at urban background locations in 1997. Overall, average NO_2 concentrations during 1997 were 23 ppb at kerbside locations and 13 ppb at urban background locations.

Studies of outdoor NO_2 levels in many areas of Europe have been reported by, e.g. Gerboles and Amantini, 1993; Bernard *et al.*, 1997; Perkauskas and Mikelinskiene, 1998; and Glasius *et al.*, 1999.

Gerboles and Amantini (1993) reported that Palmes diffusion tubes were used for collecting NO_2 by the Central Laboratory of Air Pollution of Environment Institute at the JRC Ispra, Italy. They found that the most important parameters governing the processes of diffusion were humidity, face velocity and various species, especially from inorganic nitrites, that interfere with NO_2 during the trapping process in the sampler. Humidity did not have a relevant effect on the process of diffusion. However losses in efficiency of the absorbant used to trap NO_2 was reported with decreasing relative humidity. Face velocity was also a major factor in the process. If too low a face velocity (< 0.15 m/s was observed) diffusion tubes will underestimate the NO_2 concentrations. High face velocity overestimates NO_2 levels as transport of NO_2 into the diffusion tubes was due not only to diffusion but also to convection. Gerboles and Amanati (1993) noted that change in atmospheric pressure did not disturb diffusion whilst change of temperature intervenes for less than 0.2% per °K.

Bernard *et al.* (1997) reported on background NO_2 concentrations in Montpellier, France, measured using Palmes diffusion tubes, in 1995. The highest mean NO_2 concentration was found from a site that was close by the city centre.

NO_2 concentrations in Vilnius, capital city of Lithunia, during 1995-1996 were measured using Palmes diffusion tubes (Perkauskas and Mikelinskiene 1998). The authors reported that NO_2 concentration was strongly related to traffic. The NO_2

concentrations were found to be high at crossroads, ranging from 52-82 μg/m^3 and low at background-suburban sites, ranging from 9-16 μg/m^3.

Glasius *et al.* (1999) reported that in 1996, NO_2 concentrations from 57 sites on Funen Island, Denmark were measured using Palmes diffusion tubes. Results showed low average NO_2 concentrations (5 ppb), and ranged from 2-20 ppb.

2.2.5.3 Indoor NO_2 concentrations

The study of indoor NO_2 levels mainly in houses with gas and electric cookers from many areas including the UK have been published e.g. by Melia *et al.*, 1978; Lambert *et al.*, 1993; and Yoon *et al.*, 1996. All studies reported that average NO_2 concentration in houses with gas cookers was greater than those with electric cookers.

In similar suburban areas of south west London, UK, NO_2 concentrations in 4 kitchens, 2 with gas cookers and 2 with electric cookers, were measured using Palmes diffusion tubes for 96 h (Melia *et al.*, 1978). The average hourly concentration of NO_2 in houses with gas cookers was 72.3 ppb, which was more than 7 times greater than those houses with electric cookers (9.5 ppb).

Lambert *et al.*, 1993 reported that during 1988 to 1991 indoor NO_2 concentrations in homes of 1205 infants in Albuquerque, New Mexico were measured using Palmes diffusion tubes for 2 weeks while time spent in each microenvironment was recorded. Results showed average NO_2 in the bedroom, living room and kitchen, from houses with gas cookers, was 21 ppb, 29 ppb and 34 ppb, respectively. Average NO_2 in the bedroom from houses with electric cookers was 7 ppb during winter. On average, infants spent approximately 12.3 hours, 7.3 hours, 35 minutes and 3.8 hours per day in bedroom, living room, kitchen and outdoors. Then, estimated by measurements in bedrooms, comparisons were made with time-weighted average concentrations based on time-activity data and simultaneous NO_2 measurements in bedroom, living room and kitchen. Results for 1937 two-week intervals from 587 infants, showed that 90% of time-weighted exposure estimates were in agreement with estimates based on the bedroom concentrations. The agreement of the time-weighted NO_2 exposure estimates with the bedroom concentrations is attributed to limited cooker use, small room-to-room differences in NO_2 concentrations, and the relatively large proportion of time that infants spent in their bedrooms.

Yoon *et al.* (1996) reported that NO_2 concentrations in 19 ice skating rinks in Boston, USA, were measured using Palmes diffusion tubes for four 7-day periods (once a month) in winter 1994 (November 1994 to February 1995). Levels of NO_2 depended on the type of fuels used (propane>gasoline>electric) and the ventilation in the ice rink building.

2.2.5.4 Indoors and outdoors concentrations

The study of indoor and outdoor NO_2 levels from many areas, including the UK, were reported by Spengler *et al.*, 1983; Parkhurst *et al.*, 1988; Farrow and Preece, 1994; Cotterill and Kingham, 1997; and Cyrys *et al.*, 2000. Overall, they agreed that average NO_2 concentrations inside houses with gas cookers or NO_2 sources were higher than outside while NO_2 concentrations inside houses without such NO_2 sources were lower than outdoors.

Spengler *et al.* (1983) reported that Palmes diffusion tubes were used for measuring NO_2 concentrations inside and outside 137 houses in rural areas of Portage, WI for 1 year. Annual mean ambient NO_2 concentrations were 10-15 $\mu g/m^3$. Average NO_2 concentrations inside bedrooms and kitchens in houses with gas cookers were 30 and 50 $\mu g/m^3$, which were higher than outdoor concentrations. In contrast, average NO_2 concentrations inside bedrooms and kitchens in houses with electric cookers were lower than outdoor concentrations.

NO_2 concentrations from inside and outside 235 homes in Chattanooga, Tennessee during January – March 1987 were measured using Palmes diffusion tubes Parkhurst *et al.* (1988). Mean outdoor NO_2 concentrations ranged from 16-26 ppb (average 21 ppb) while mean indoor NO_2 concentrations ranged from 17-129 ppb (average 84 ppb). Average NO_2 concentrations in houses with gas stoves was 96 ppb, which was higher than those houses with electric cookers (17 ppb). Average NO_2 concentration in houses with electric cookers was 0.8 of the outdoor concentrations while average NO_2 concentration in houses with gas cookers ranged from 2.6-5.8 times the outdoor concentrations.

Farrow and Preece (1994) reported that Palmes diffusion tubes were used for measured NO_2 concentrations inside infants' bedrooms (aged 4-6 months) and outside houses for a 2 week period in Avon, UK during November 1992. Mean indoor NO_2 level was 7.2 ppb while mean outdoor was 14.3 ppb. The ratio of outdoor:indoor NO_2

levels was 2:1. Houses with gas cookers had indoor NO_2 levels 1.8 times greater than those with electric cookers.

In the study by Cotterill and Kingham (1997), indoor and outdoor NO_2 levels were measured using Palmes diffusion tubes in 40 houses in Huddersfield, UK. Half of the houses were located close to a busy main road and other houses were located on residential roads set back and parallel to the main road. These subsets were split so half of the houses had gas cookers and other houses had electric cookers. Then, the subsets were split again so that half had double-glazing and half had single-glazing windows. Monitoring was carried out over three 2-week periods between November and December 1994. The results showed that while gas cookers had a significant effect on indoor levels of NO_2, window type and proximity to a main road have little effect. There was no statistically significant variation (p-value = 0.811) between sampling periods. The living rooms had the second highest inside levels of NO_2 with a mean of 25 $\mu g.m^{-3}$. As was the case with the kitchen measurements, there was large variation in levels with a range of 4 to 118 $\mu g.m^{-3}$ (standard deviation (SD) = 16). Again there was no significant variation (p- value = 0.478) between sampling periods. The bedrooms had the lowest levels of NO_2 with a mean of 18 $\mu g/m^{-3}$. The variation between homes was also less with a smaller range of levels: 5 to 52 $\mu g/m^{-3}$ (SD = 8). As with the other inside measurement, there was no significant variation between periods. (p-value = 0.897). The results showed that mean levels of NO_2 in houses with gas cookers were greater than levels in houses with electric cookers. The difference was greatest for the kitchen, although it was also noticeably different for levels in the living room and bedroom. The presence or absence of cooker hoods did not affect levels for either homes with gas or electric cookers. The mean outside concentration of NO_2 for the main road site was 43 $\mu g/m^{-3}$ and the mean for the side road site was 37 $\mu g/m^{-3}$. Analysis of variance suggested there was a significant difference between two sites (p-value < 0.001). There was no difference in indoor levels of NO_2 due to proximity to the main road.

Ross and Wilde (1999) reported that indoor (kitchen) NO_2 concentrations of 73 houses with gas cookers in south east of England during summer and winter 1998 were measured using Palmes diffusion tubes and Scintrex LMA-3 continuous analyses while outdoor NO_2 concentration also measured by the Palmes tubes. Average indoor NO_2 levels were greater than outside. The authors found approximately 67% of the houses had NO_2 levels that exceeded the proposed WHO one hour time-averaged guideline value.

Cyrys *et al.* (2000) measured indoor (living room and bedroom) and outdoor concentrations of NO_2 for 201 houses in Hamburg and 204 houses in Erankfurt, Germany using Palmes diffusion tubes for one week during June 1995 and November 1996. Indoor NO_2 levels in winter were lower than in summer. The ratio between indoor and outdoor concentrations was higher in summer (0.5) than in winter (0.8). Use of gas for cooking and smoking in the living room were associated with an increase in indoor NO_2 levels, while type of heating system did not influence indoor NO_2 levels.

2.2.5.5 Comparison of NO_2 measurement between the Palmes diffusion tube sampler and other methods

Numerous studies (such as Atkins *et al.*, 1986; Boleij *et al.*, 1986; Wilson *et al.*, 1987; Campbell, 1988; Moschandreas *et al.*, 1990; Gerboles and Amantini, 1993; Bernard *et al.*, 1997; Glasius *et al.*, 1999; Heal *et al.*, 2000; Bush *et al.*, 2001) have reported measurement of NO_2 comparison between Palmes diffusion tubes and real-time continuous techniques such as chemiluminescence monitors or Scintrex LMA-3 continuous NO_2 analyser (Ross, 1996; Ross and Wilde, 1999) and passive badge samplers (Van Reeuwijk *et al.*, 1998). Overall, Palmes diffusion tube was generally accepted for measuring NO_2 both from personal exposure and indoors and outdoors.

Atkins *et al.* (1986) observed a significant difference for NO_2 concentrations measured during validation trials in the field. They noted that no significant change in the ratio between the diffusion tubes and chemiluminescence monitor was detectable over the range for average weekly wind speeds between 1.0 and 4.5 m s^{-1}. Any difference was too small to be detected by this approach and was contained within the limits of precision quoted earlier. The comparison between Palmes diffusion tubes and a chemiluminescence monitor for Harwell data was performed over a period of more than one year during which average weekly temperatures at the site are likely to have ranged between <5°C and >20°C; no bias dependence on temperature was evident in the data.

Boleij *et al.* (1986) studied NO_2 levels in the kitchen, living room, bedroom and outside 9 houses in Netherlands using Palmes diffusion tubes and a Bendix chemiluminescence monitor for 10 sampling periods of 3-12 days. The coefficients of variation between the Palmes diffusion tube and the chemiluminescence monitor measurement was 14%. For outdoors, results from the Palmes diffusion tubes were overestimates when compared with results from the chemiluminescence monitor. For indoors, the ratio between the Palmes diffusion tubes and the chemiluminescence monitor was on average 1.33, 0.88 and 0.85 for the kitchens, the living room and the bedroom, respectively.

Reasonable agreement between Palmes tubes and chemiluminecence method was reported by Wilson *et al.* (1987). Palmes diffusion tubes were located at 20 air monitoring sites in the Los Angeles Basin for a year. A strong correlation between Palmes tubes and chemiluminescence monitor was observed. The monitor explained 83% of the variability in the NO_2 concentrations as measured by the Palmes tube with a regression slope of 0.9. In another study, Campbell (1988) reported that Palmes diffusion tubes were used at a rural air monitoring site in the UK showed no significant difference when compared to the chemiluminescence method. A comparison was conducted by Gerboles and Amantini (1993) between Palmes tubes and a chemiluminescence monitor, measuring NO_2 in ambient air during December 1990 to December 1992 managed by the Central Laboratory of Air Pollution of the Environment Institute at the JRC Ispra. The correlation of both techniques was acceptable (r=0.93 and r=0.94 respectively). Change of pressure did not disturb diffusion while change of temperature intervened for less than 2% by °K. Moreover, humidity did not affect the process of diffusion.

Moschandreas *et al.* (1990) concluded that low temperature in the range 251-283°K resulted in underestimation of NO_2 because of possible irregular behaviour of TEA below its freezing point of 294°K. The effect of other trace species has been investigated by Atkins *et al.* (1986). The author concluded that no interference in British conditions is caused by the presence of peroxyacetyl nitrate (PAN) or nitrous acid (HONO), which can both lead to NO_2^- being present in a complex with TEA. A similar conclusion was reached by Gair *et al.* (1991). Hisham and Grosjean (1990) however, noted that PAH can cause interference when quantifying NO_2 by a TEA diffusion tube. Healey *et al.* (1994) also presented a significant overestimation of NO_2 by passive diffusion samplers in their comparative trials, which they attributed to chemical interferences from PAN, other nitrogen containing species, and oxidation of NO by O_3 in the absorbent.

Bernard *et al.* (1997) reported that in 1995, NO_2 levels in Montpellier, France were measured using Palmes diffusion tube and automatic chemiluminescence analysers. A satisfactory reproducibility and a good precision of the Palmes diffusion tubes was found. The validation by comparison with the chemiluminescence analysers showed that the tube samplers performed adequately for measurement of the NO_2 range under environmental conditions. The average NO_2 measured by the tubes were well correlated with the hourly-mean NO_2 assessed by the continuous analysers.

Glasius *et al.* (1999) reported that in 1996, NO_2 concentrations from 57 sites on Funen Island, Denmark were measured using Palmes diffusion tubes and automatic chemiluminescence analysers. The average NO_2 measured by the tubes were correlated with the hourly-mean NO_2 assessed by the continuous analysers. Less than 10% overestimation of NO_2 concentrations as measured by the Palmes tubes was found.

Heal *et al.* (2000) presented information that NO_2 measurements using Palmes diffusion tubes over 22 months in Cambridge, UK was between 11-16% overestimation compared with chemiluminescence analyses; Bush et al. (2001) reported that average NO_2 concentrations calculated from Palmes diffusion tubes at 17 urban background monitoring sites in the UK were found within 10% of chemiluminescence measurement data. Moreover, highly significant correlations were found between both methods.

In a report by Ross (1996), a comparison between Palmes tubes and Scintrex LMA-3 continuous analysers measuring NO_2 from 12 houses in the South of England was presented. There was a good correlation of measured average levels of NO_2 between the two methods and also good correlation between the 7-day average recorded by the diffusion tubes and the maximum 1-hour averages recorded by the continuous monitoring.

2.3 Personal exposure modelling

As presented in section 1.3 (Chapter 1), the personal exposure modelling has been developed to predict the personal exposure to air pollution. Personal exposure to nitrogen dioxide (NO_2) has been defined as contact of an individual to the NO_2 concentrations in microenvironments over time period. Therefore the personal exposure modelling has used the concept of personal integrated exposure over time period t (t_0, t_1) for an individual i in microenvironment j (Ott, 1982) for what is known as time weighted average microenvironment exposure modelling. Detailed records of where and how long individuals spend their time are required (Abbey *et al.*, 1993). Studies such as Ashmore (1995) have suggested that the time budget data over long period of time and indoor microenvironments are not well understood. In addition, Lambert et al. (1993) recommended that more extensive periods of continuous monitoring are needed in order to reduce the effects of misclassification of exposure.

Ambient NO_2 concentrations can be computed by dispersion models or collected from fixed-site air quality monitoring stations. Calculating personal exposure to NO_2 needs to take into account the spatial and temporal fluctuations in NO_2 concentration, in addition to variations in activities of an individual (Ashmore, 1995). To evaluate the spatial distributions of exposures, air pollution concentrations can be combined with the population statistics e.g. Brauer *et al.*, (2001). Some studies have utilised additional time-microenvironment data (Clench-Aas *et al.*, 1999; Jensen, 1999) or divided the entire population into day and night populations according to statistics on homes and workplaces (Johansson *et al.*, 1999).

As indoor air pollution has been known to have a big impact on personal exposure as high proportion of time (over 80%) is spent in indoor microenvironments (Samet and Utell, 1990), some studies have linked personal exposure modelling with indoor concentration for more accurate estimation of personal exposure. In some studies (De Haan *et al.*, 2001; Jensen, 1999; Kousa *et al.*, 2002), the indoor concentrations are evaluated by multiplying the outdoor concentrations by a constant. However, in studies such as Dimitroupoulou *et al.* (2001), the indoor concentrations have been estimated by an indoor model evaluating NO_2 exposure and Kulmala *et al.* (1999) have developed an indoor model for particles. A weakness of these types of models is the difficulty in obtaining exact building-specific input parameters e.g. ventilation rate, indoor volume, indoor total surface area, penetration coefficient.

2.3.1 Regression modelling

In a study by Kousa *et al.* (2001), a log-linear multiple regression modelling has been used to estimate personal exposures to NO_2. The equation is presented as following:

$$\ln(E_i) = \sum \alpha_{ij} C_{ij} + \ln(O_i) \qquad (8)$$

where

E_i = the measured personal NO_2 exposure for individual *i*,

C_{ij} = the indicator variable for j^{th} characteristic for individual *i*,

α_{ij} = the calculated regression coefficient for j^{th} individual characteristic,

O_i = the measured residential outdoor or ambient fixed site concentration for individual *i*.

2.3.2 Time-weighted average microenvironmental exposure modelling (TWME)

People spend different of their time in different locations depending on the population sub group and their activities but most of the time is spent indoors such as in homes, followed by few other indoor locations (EXPOLIS, 1999). Most adults spend large amount of time at work (EXPOLIS, 1999) and school children in schools (Alm *et al.*, 2000; 1998; and 1994). These locations are called microenvironments (MEs) and the concentrations in the microenvironments are assumed to be constant and homogeneous (Ott, 1982). Exposure model for calculating the average exposure levels based on these microenvironments is called time-weighted average microenvironmental exposure modelling. The time-weighted average microenvironmental exposure model is based on average NO_2 concentrations from various microenvironments (e.g. kitchen, living room, bedroom, office, street, restaurant, public house, car, etc.) and the lengths of time spent in each of those microenvironments. The model equation is expressed as following (Sexton and Ryan, 1988; USEPA, 1993):

$$E_i = \sum_{j}^{J} C_j t_{ij} \tag{9}$$

where

E_i is the total time-weighted average NO_2 exposure for person (*i*) over the specified time period across the visited microenvironments (*J*),

C_j is the NO_2 concentration (ppb) in microenvironment *j* for sampling time period,

t_{ij} is the aggregate time that person *i* spends in microenvironment *j*.

J is the total number of microenvironments that the person i moves through during the specified time period such as indoors at home, indoors at work, indoors in other locations, in transit, and outdoors.

The model output (E_i) is calculated as the sum of partial exposures in each microenvironment. The partial exposures are calculated by multiplying the NO_2 concentration (C) in each microenvironment by the fraction of time (t) spent there. The NO_2 concentrations can be measured from those microenvironments, or could be calculated or computed from indoor concentrations modelling or outdoor dispersion modelling (Sexton and Ryan, 1988). Several assumptions are implicit in the application of Equation (9). The assumptions are presented as following: (i) The concentration C_j in microenvironment j is assumed to be constant during the time t_{ij}. However this is not always true as indoor NO_2 concentrations will vary during the 14 to 16 hr/day that most people spend at home as the NO_2 concentrations depending on emission rates and air exchanges over this time period; (ii) The concentration C_j within the microenvironment j and the time t_{ij} that the person i spends there are assumed to be independent events, though, this assumption is not generally valid. A person who is sensitive to tobacco smoke and noxious odours is likely to avoid microenvironments where concentrations of these pollutants are elevated; (iii) The number of microenvironments necessary to characterise the personal exposure to NO_2 is assumed to be small and defined. However, there is no agreement on how many microenvironments are required.

2.3.3 Probabilistic modelling

Probabilistic modelling uses the same equations as the corresponding deterministic modelling that describe the relationships of the input variables. A probabilistic model is run using distributions of the input variables instead of point values describing specific individuals. Hypothetical non-existing individuals are created by randomly sampling input variable values from the corresponding distributions in each iteration in the model run. Hundreds or thousands of iterations are used to create the estimated distribution of the output variables. The probability distributions of the input variables can be defined in the model using alternative techniques. Values from literature or other study sites could be applied into the modelling. Known mathematical probability density functions, like normal, or in many cases with concentration data, lognormal, could be used, or empirical distributions could be applied using a variety of techniques, including empirical cumulative distribution, or bootstrap sampling from original empirical data sets.

Advantages of the parametric probability density functions are no requires of observed data for each variable and easily adjusted for alternative or modified scenarios. Assessment of the goodness-of-fit (GOF) of the parametric distribution against observed data should be conducted using graphical comparisons, statistical tests and other numerical comparison methods.

2.3.4 Modelling of indoor concentrations

Some studies in the USA have successfully used mass-balance equations based on techniques in probabilistic modelling (Burke *et al.*, 2001; Yeh and Small, 2002). Modelling of indoor concentrations using the mass-balance equation to estimate indoor concentrations requires knowledge on the air exchange, penetration and removal rates of the pollutants (Wilson *et al.*, 2000). However, those data are not currently available for cities in the UK and Europe (FUMAPEX, 2004), and the usability of the data would be limited in the future due to the ways the inhabitants affect these parameters significantly e.g. when the windows are kept open the air exchange and penetration rates are altered. An alternative way called infiltration method uses effective infiltration factors to model indoor concentrations from ambient pollution (C_a). The equation is as follows (FUMAPEX, 2004):

$$C = F_{\inf} \times C_a + \sum_{i=1}^{n} C_{Si} \qquad (10)$$

where

C = indoor concentrations

F_{inf} = effective infiltration factors

C_a = ambient pollution

C_{Si} = indoor concentration

These factors or their probability density distributions could be determined from population-based samples of suitable indoor and ambient concentration data and with the additional concentrations caused by indoor sources.

Chapter 3

Development of the Palmes Diffusion Tubes Preparation Procedure

This chapter describes the experimental investigations undertaken to develop and where possible improve methods for preparing Palmes diffusion tubes for NO_2 applications. In terms of reproducibility of NO_2 concentrations, a key aspect was how to control the coating process for the tube meshes. The chapter provides details of analytical procedures once the diffusion tubes had been exposed. It also demonstrates the reliability of the new modified procedure of using a fixed quantity of triethanolamine (TEA) to coat the wire mesh.

3.1 Palmes diffusion tube preparation and analysis method for NO_2 measurement

As stated in Chapter 2 passive Palmes Diffusion tubes are now routinely used for measuring NO_2 concentrations in the UK. It is important to note that there are four different TEA/solvent preparation methods currently used in the UK which are based on 50% TEA in acetone, 50% TEA in water, and 20% TEA in water, with a few laboratories using 10% TEA in water (AQEG, 2004). There are also two different preparation methods in which grids or meshes are coated in advance of tube assembly by dipping into TEA/solvent mixtures or the TEA/solvent is pipetted onto grids or meshes after the tubes have been assembled.

Campbell et al., 1994 reported that an average bias of diffusion tube prepared with 50% TEA in acetone was +26% variation from site to site around the UK for monthly exposures. Bush et al., (2001) also found that an average bias of diffusion tube prepared with 50% TEA in acetone (prepared and analysed by Harwell Laboratory) was +8% for monthly exposure. In Edinburgh, Heal et al. (1999) reported that an average over estimation of diffusion tube prepared with 50% TEA in acetone (prepared and analysed by their own Laboratory) was +1%. However, Laxen and Wilson (2000) found that the diffusion tubes (from 23 local authorities around the UK) can give both under and over estimate concentrations by up to ±30% or more. They suggested that the most significant factor affecting tube performance is the laboratory preparing and analysing the tubes and the reasons for the differences between the laboratories were currently not understood. Various studies have examined whether preparation method affects performance but no consistent pattern has emerged (AQEG, 2004).

The Palmes diffusion tubes used in the research for this thesis were made from inert plastic, acrylic tube approximately 71mm long and 11mm internal diameter. Each tube was machined to an outside diameter of 13-13.6 mm for a distance of 7 cm from each end, allowing the tube to be fitted with polyethylene caps (Figure 3.1). Two reactive meshes coated with triethanolamine (TEA) are secured and sealed at one end of the acrylic tube by a colour plastic cap. Another side of the tube is sealed with a colourless plastic cap (AEA Technology, 2003; Campbell, 1988). A sample is collected by removing the clear plastic cap, placing the Palmes diffusion tube in the location with the open end facing down, sampling for the appropriate period, recording the time, recapping the tube, and returning the tube to the laboratory for analysis.

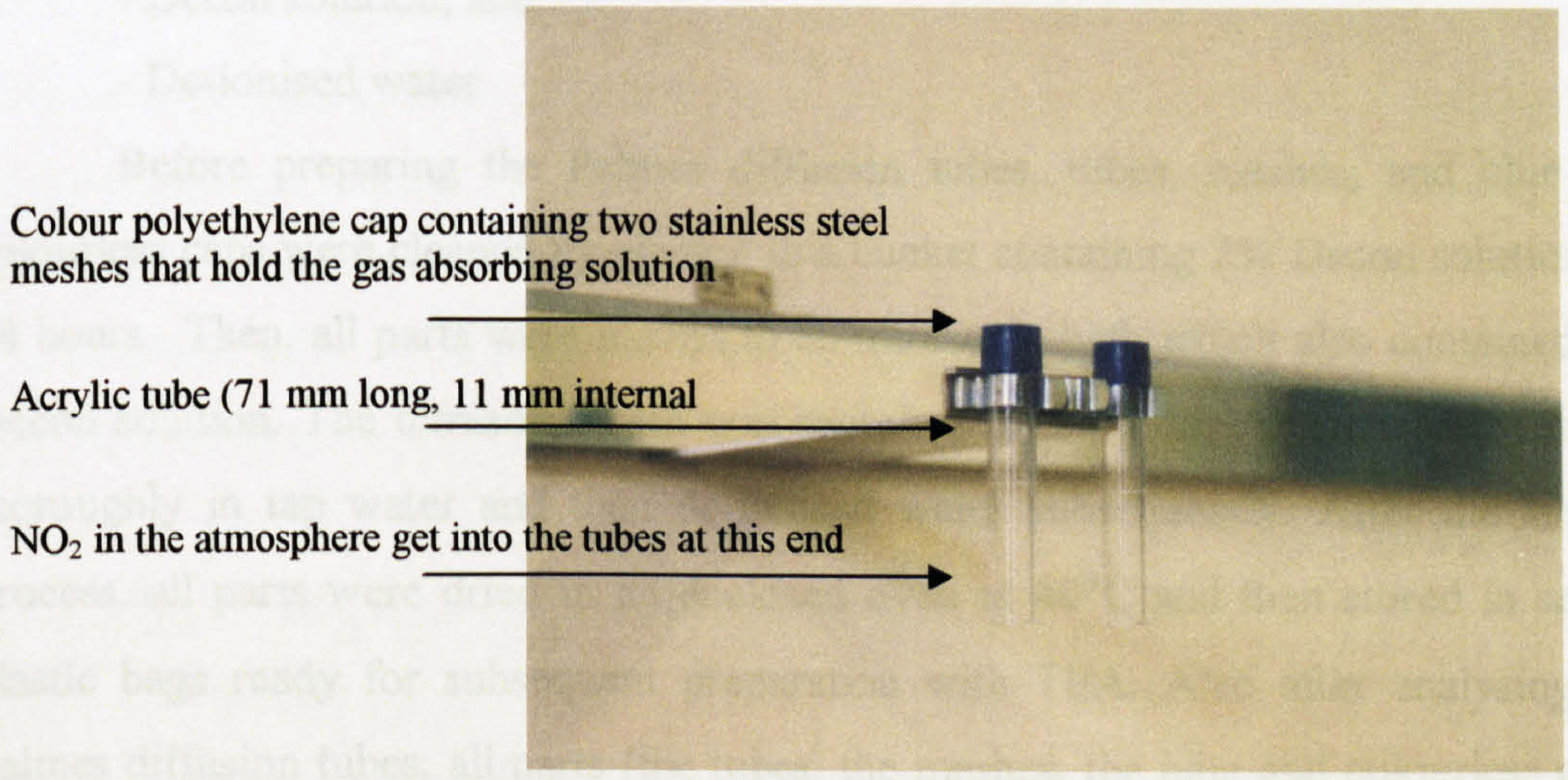


Figure 3.1 Palmes diffusion tube.

In this thesis, the 50% TEA in acetone was used, one of triethanolamine (TEA)/solvent preparation methods as mentioned in first paragraph above. Also since there are two different ways to coat the meshes: dipping into the solvent mixture (stated as the original method in this thesis) or the mixture is pipetted onto meshes (stated as the modified method in this thesis), some experiments were run. Objectives of these experiments were as follows:

1. to check the reproducibility of the preparation procedure for the Palmes diffusion tubes.
2. to check the preparation method of the Palmes diffusion tube by using a micropipette to control the quantity of TEA:acetone solution.
3. to compare data from two different preparation methods of the Palmes diffusion tube. TEA:acetone solution, 60 µl of the mixture solution controlled by micropipette, was the first method. TEA:brij-35 solution, prepared by Gradko International Ltd where each mesh was dipped in the mixture, was the second method.
4. to participate in a preliminary campaign in urban, semi-urban and rural areas (in collaboration with BRE).

3.1.1 Cleaning method

Chemicals

For cleaning the Palmes diffusion tubes and the components, these were:

- Decon solution, and
- De-ionised water

Before preparing the Palmes diffusion tubes, tubes, meshes, and blue and colourless caps were cleaned by placing in a bucket containing 2% Decon solution for 24 hours. Then, all parts were moved to an ultrasonic bath which also contained 2% Decon solution. The ultrasonic bath was switched on for 1 hr. All parts were rinsed thoroughly in tap water and then de-ionised water subsequently. After the rinsing process, all parts were dried in an enclosed oven at 40°C and then stored in sealed plastic bags ready for subsequent preparation with TEA. Also after analysing the Palmes diffusion tubes, all parts (the tubes, the meshes, the blue and colourless caps) were re-used. Hence, they were cleaned, rinsed, dried and stored as described above. After all these processes were completed, they were ready for the next coating.

3.1.2 Palmes diffusion tube preparation

Chemicals

Analytical grade chemicals were used for preparing the Palmes diffusion tubes, these were:

- Acetone, and
- Triethanolamine (TEA)

3.1.2.1 Original method

Acetone and triethanolamine (TEA) were mixed in equal volumes in a beaker. The beaker was placed on an electromagnetic stirrer and then each mesh was dipped in the mixture of acetone and triethanolamine (TEA) until fully coated. Two coated meshes were placed on a blue cap and left for 10-15 minutes to allow the acetone to evaporate. The tube body was then pushed completely into the blue cap and sealed using a clear cap. The prepared tubes were sealed in sealed plastic bags and stored in a refrigerator at 4°C for subsequent analysis.

3.1.2.2 Modified method

Acetone and triethanolamine (TEA) were mixed in equal volumes in a beaker. Two meshes were placed on each of a blue cap. 60 µl of the mixture solution was dropped onto the meshes and left for 10-15 minutes to allow the acetone to evaporate. The tube body was pushed completely into the blue cap and sealed using a clear cap. The prepared tubes were sealed in sealed plastic bags and stored in a refrigerator at 4°C for subsequent analysis.

3.1.3 Palmes diffusion tube analysis method

Chemicals

Analytical grade chemicals were used for analysing Palmes diffusion tubes, these were:

- De-ionised water
- N-1-naphthylethylene-diamine dihydrochloride (NEDA)
- Orthophosphoric acid
- Sodium nitrite
- Sulphanilamide

3.1.3.1 Preparation of NEDA reagent

300 ml of de-ionised water was put into a 1-litre volumetric flask and then 25 ml of orthophosphoric acid (H_3PO_4) and 10 g of sulphanilamide were added. Then de-ionised water was added to make up 1 litre solution. The mixture was transferred to a 1-litre conical flask. 0.07 g of N-1-naphthylethylene-diamine dihydrochloride (NEDA) was dissolved in 50 ml of de-ionised water. The NEDA solution was immediately added into the mixture. The solution was stored in a refrigerator at 4°C to avoid degradation/decomposition.

3.1.3.2 Preparation of stock nitrite solution

In order to prepare 100 ml stock solution with 1 mg/ml concentration the following amount of $NaNO_2$ was used. (Molecular weight of Na is 23, molecular weight of NO_2 is 46, therefore, total of $NaNO_2$ is 69.)

$$100 \times \frac{69}{46} = 150mg$$

150mg of $NaNO_2$ was put into a 100 ml volumetric flask and then made up to 100 ml with de-ionised water. Normally, the stock solution can be stored for 6 months. However, to maintain the quality of the data the stock solution was freshly mixed every time before analysing the tubes.

3.1.3.3 Calibration of the PU 8720 UV/VIS scanning spectrophotometer

In order to measure the nitrite, the Spectrophotometer has to be calibrated. Eight standard solutions were prepared from the stock solution as follows and transferred into the volumetric flask. Various amounts of stock solution were diluted with de-ionised water and made up to 100ml as listed in Table 3.1.

Nine test tubes were lined up into a test tube rack. 2 ml of de-ionised water placed in a first tube as a blank. 2 ml of each calibration standard was put into the rest of the test tubes and then 2 ml of NEDA reagent was added to each test tube. The test tubes were left to stand for 30 minutes to allow the solution built up the colour. The spectrophotometer was set to 540 nanometres of wavelength. The spectrophotometer was set (absorbance) to zero using the first test tube. Then the absorbances of the calibration standards were measured using the spectrophotometer. The zero standard was re-measured to ensure there was no drift. A typical calibration graph is shown in

Figure 3.2. It shows the high degree of linearity between the absorbance and the nitrite concentrations.

Table 3.1 Various amounts of stock solution and their concentrations

Stock solution*	**Total concentration**
5 μl	0.05 μg NO_2 ml^{-1}
10 μl	0.1 μg NO_2 ml^{-1}
20 μl	0.2 μg NO_2 ml^{-1}
30 μl	0.3 μg NO_2 ml^{-1}
40 μl	0.4 μg NO_2 ml^{-1}
50 μl	0.5 μg NO_2 ml^{-1}
100 μl	1.0 μg NO_2 ml^{-1}
200 μl	2.0 μg NO_2 ml^{-1}

*Note: the stock solutions were made up to 100ml with de-ionised water.

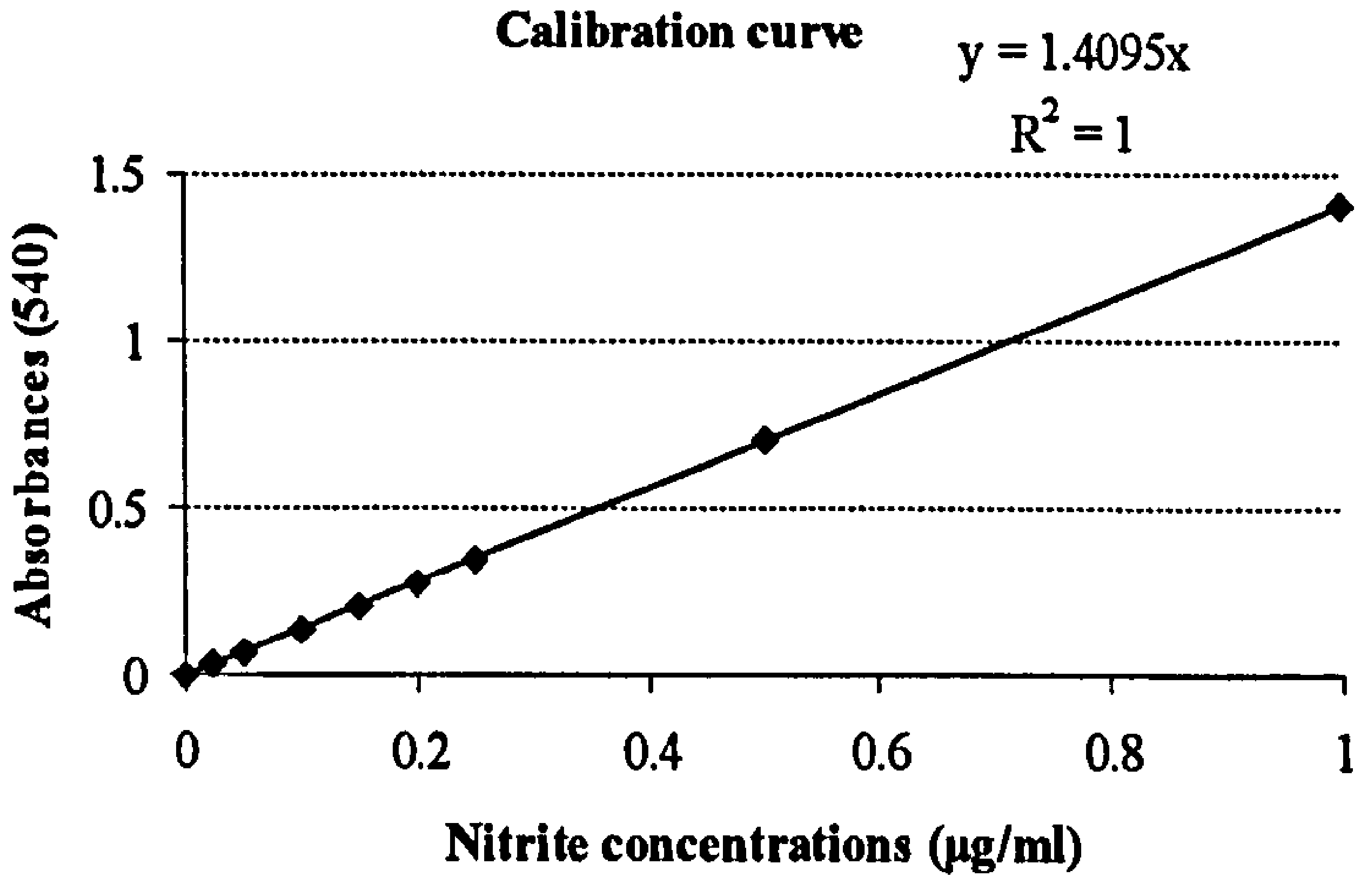


Figure 3.2 An example of the calibration curve standard.

3.1.3.4 Tubes analysis

The calibration curve was set up at the start of the analytical run. Palmes diffusion tubes were lined up in number order in the test tube rack, the blue cap at the top and the clear cap at the bottom. The clear cap was removed from each tube and then 2 ml of de-ionised water was added in each tube. After that, the clear cap was replaced. The Palmes diffusion tubes were shaken to mix. Then, they were left to stand for 30 minutes. 2 ml of NEDA reagent was added to each tube. The Palmes diffusion tubes were swirled gently to mix and allowed to stand for a further 30 minutes to allow the mixed solution developed the colour. Then, two cuvettes were used in every analysis. First cuvette was used for setting zero using de-ionised water: reagent blank from the first test tube. The de-ionised water: reagent blank was checked to ensure for reading zero before and after each batch of samples. Another cuvette was used for analysing the liquid from each tube. The cuvette was washed with 2% Decon solution, rinsed with de-ionised water and dried with tissue paper before analysing the next sample. The absorbance of each sample was measured using the spectrophotometer. The concentration of the sample was calculated in the form of $\mu g\ NO_2\ ml^{-1}$.

3.1.3.5 Calculation of NO_2 Concentrations

The tube identification number, exposure time, and concentration of NO_2 were entered onto the computer database to calculate the concentration of airborne NO_2 in $\mu g\ NO_2\ ml^{-1}$. The following formula was used.

$$NO_2\ (\mu g\ m^{-3}) = \frac{q(\mu g)\ c(hours.m^{-3})}{t\ (hours)}$$

where $q = \mu g\ NO_2\ ml^{-1} \times 2$ (2 is from 2 ml of solution),

$$c = \frac{Z}{AD_{NO_2}}.$$

where Z = length of tube (0.071 m),

A = internal area of tube ($0.00009503\ m^2$),

D = diffusion coefficient ($0.0000154\ m^2\ s^{-1}$),

$$c = \frac{0.071\ m}{0.00009503\ m^2 \times 0.0000154\ m^2\ s^{-1}}.$$

$$c = \frac{48515096.39}{m^3\ s^{-1}}. \quad \text{or} \quad = \frac{48515096.39\ s}{m^3}.$$

Then, seconds (s) were changed to hours, divided by 3600.

(3600 seconds = 1 hour)

$$\text{Thus, } c = \frac{13476.4\ hours}{m^3}.$$

In Europe, NO_2 concentrations have been set in $\mu g.m^{-3}$ unit (AQEG, 2004). In the UK, the NO_2 concentrations have historically been reported in unit of ppb. Recently, $\mu g.m^{-3}$ unit started reporting. The conversion factors from $\mu g.m^{-3}$ to ppb and ppb to $\mu g.m^{-3}$ are needed. Table 3.2 lists the conversion factors for NO_2 from $\mu g.m^{-3}$ to ppb and ppb to $\mu g.m^{-3}$. Using procedure that details are shown below (Kiely 1997).

Table 3.2 The conversion factors for NO_2 concentration from $\mu g.m^{-3}$ to ppb and ppb to $\mu g.m^{-3}$

Seasons	**Temp (°K)***	**Temp (°C)**	**$\mu g.m^{-3}$ to ppb**	**ppb to $\mu g.m^{-3}$**
winter	276.9	3.3	0.494134	2.023744
spring	282.3	9.3	0.503770	1.985033
summer	290.8	17.8	0.518938	1.927011
autumn	284.6	11.6	0.507874	1.968991
annual	283.0	10.0	0.505019	1.980123
	282.6	9.6	0.504305	1.982926

Note: °C = °K - 273

Source: Kiely G. 1997.

One mole of an ideal gas at standard temperature (0°C) and pressure (101.325 kPa) occupies 22.4 litres (Kiely, 1997).

$$[\mathrm{conc}]\ \mathrm{ppmv}\ \frac{m^3}{m^3} = \frac{L}{L} = \frac{[\mathrm{conc}]\ g/m^3}{(\mathrm{mol\ wt})\ g/mol} \times (V_{ideal} = 22.4)\frac{L}{mol} \times 10^{-3}$$

where, ppmv = parts per million by volume

and ppmm = parts per million by mass = [conc] g/m^3

If concentration of NO_2 is 400 $\mu g\ m^{-3}$,

mol wt of NO_2 = 14+2x16 = 46 g/mol

Therefore,

$$V_{NO_2} = \frac{400 \times 10^{-6}\ g/m^3}{46\ g/mol} \times 22.4 \times 10^{-3}\ m^3/mol$$

$$= 195 \times 10^{-9}\ g/g$$

$$= 195\ \mathrm{ppb}$$

3.2 Procedure of the Experiments

Palmes diffusion tubes were prepared and analysed at the Atmospheric Sciences Research Group (ASRG) laboratory in the University of Hertfordshire. To determine whether satisfactory results could be achieved, the reproducibility of the preparation and analysis methods was investigated. These studies set out to determine whether the Palmes diffusion tubes methodology could be successfully applied at the University of Hertfordshire.

3.2.1 Reproducibility of Preparation Procedure

Aim of these experiments was to check the reproducibility of the original preparation procedure for the Palmes diffusion tubes. All diffusion tubes were prepared by the original method (explained in 3.1.2.1). The tubes were located in each of the following sites: in the middle of two kitchens with gas cookers and one back ground outdoor site for five 7-day periods (six diffusion tubes/location/period). Temperature in the kitchens and cooking times were recorded every day. Temperature from the back ground site was also recorded twice every workday. Later, the experiment was repeated (thirty tubes/location/period) for two 10-day periods.

Experiment 1.1 Reproducibility of the original preparation procedure (1)

Ninety Palmes diffusion tubes were prepared by using the original method, six diffusion tubes were held vertically with the cap uppermost and the open end facing downward in the middle of two kitchens with gas cookers and at a background outdoor site, for five 7-day periods (6 tubes x 3 areas x 5 periods = 90 tubes).

Overall average NO_2 concentrations from all sites in each period of experiments are shown in Table 3.3. Most NO_2 concentrations from all three sites gave high standard deviation and high range, which means the data spread out from the mean value. It had been expected that the NO_2 concentrations would have been more consistent and closer to the mean value than was the case in the results. These anomalous results might have been due to the meshes in each diffusion tube receiving an unequal coating with the TEA solution. However, it must be noted that this conclusion was only tentative due to the low number of samples analysed. Therefore, larger sample size was required to confirm this finding (experiment 1.2).

Table 3.3 Mean, minimum, maximum and standard deviation value of NO_2 concentrations from all three sites over five 7-day periods

Periods	**Kitchen A**		**Kitchen B**		**Outdoors**	
	Mean (ppb) (Min-Max)	**Stdev.**	**Mean (ppb) (Min-Max)**	**Stdev.**	**Mean (ppb) (Min-Max)**	**Stdev.**
1	12.2 (10.1-16.2)	2.1	10.8 (7.5-13.5)	2.1	17.9 (15.9-21.0)	2.3
2	13.6 (12.7-16.6)	1.7	11.9 (10.5-12.9)	0.9	14.9 (13.8-16.3)	0.9
3	11.0 (10.1-12.4)	1.1	9.1 (7.1-10.5)	1.2	10.0 (9.7-10.3)	0.2
4	11.8 (11.4-12.2)	0.4	-*	-	11.8 (10.7-12.7)	0.8
5	10.8 (9.8-12.5)	1.1	8.7 (7.0-9.8)	1.0	10.1 (9.1-10.9)	0.7

*Note: data missing as all tubes (mixed with solution) were left in the laboratory over 45 min. due to fire alarm in the building, therefore, the colour were all gone from the tubes.

Experiment 1.2 Reproducibility of the original preparation procedure (2)

For statistical reasons the larger the sample size used the more certain one can be that the results reflect the population. To ensure confidence in the results at least thirty samples are needed in order to characterise the population (Walpole, Myers and Myers, 1998). Therefore, one hundred and eighty tubes were prepared. Thirty tubes were located in each of the following sites: in the middle of two kitchens with gas cooker and one background outdoor site. The tubes were exposed for two 10-day periods.

Temperature and total cooking time data of two 10-day periods were recorded in Kitchens A and B. In Kitchen A, the average temperatures for the two periods were 21.50 and 18.55°C. The total cooking times were 1 hr and 35 min. (95 min.) and 2 hr and 45 min. (165 min.), respectively. In Kitchen B, the average temperatures were 20.65 and 21.44°C. The total cooking time was 5 hr (300 min.) and 3 hr and 20 min. (200 min.), respectively. Outdoor temperature was also recorded twice every workday during two 10-day periods, the average temperature was 19.99°C and 20.04°C, respectively. The average concentration of NO_2 is presented in the Figures 3.3a, 3.3b and 3.3c.

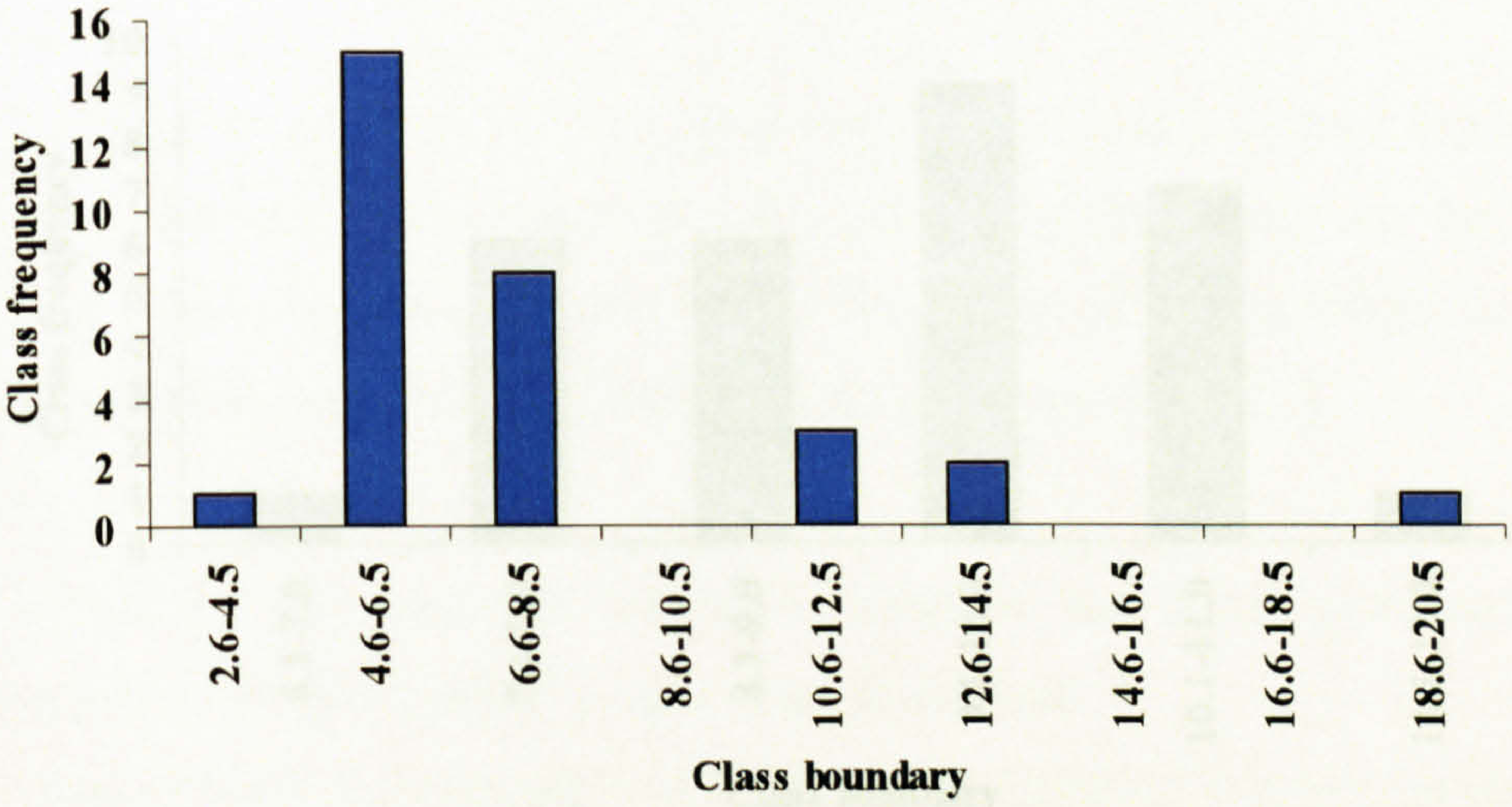


Fig.3.3a Histogram of average NO_2 concentrations from kitchen A with a gas cooker, obtained using the original preparation procedure

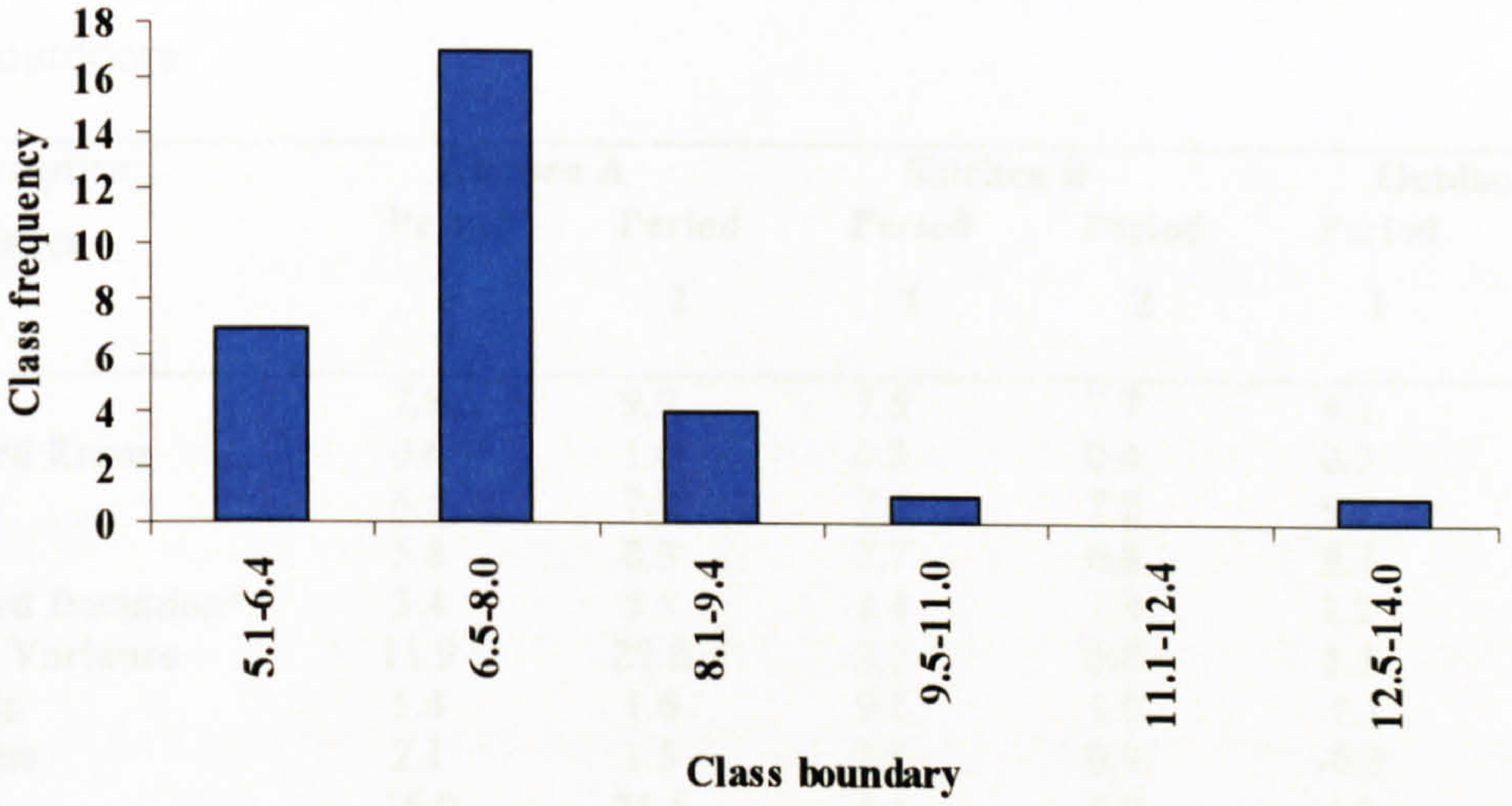


Fig.3.3b Histogram of average NO_2 concentrations from kitchen B with a gas cooker, obtained using the original preparation procedure

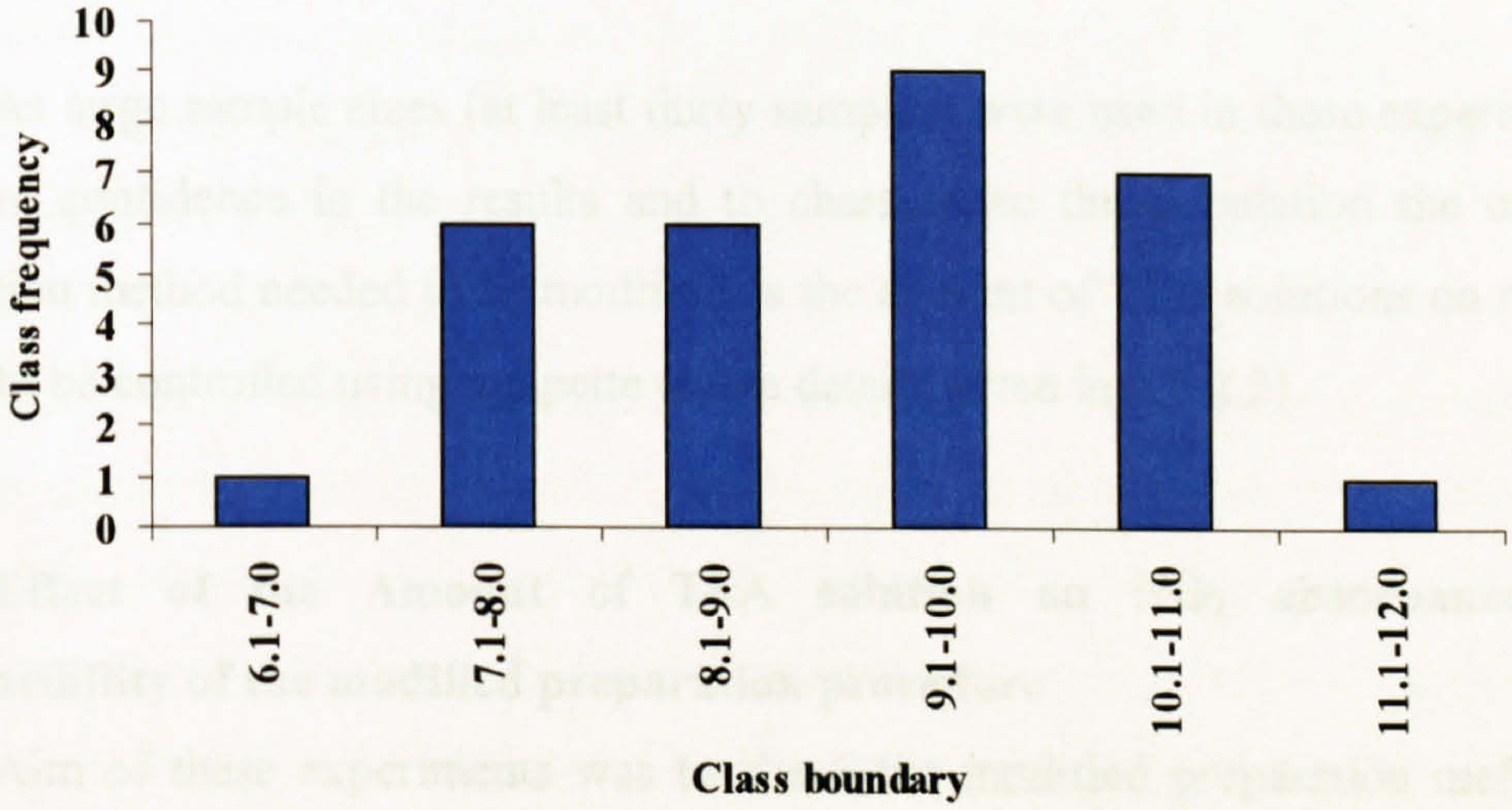


Fig.3.3c Histogram of average NO_2 concentrations from a background outdoors site, obtained using the original preparation procedure

Descriptive statistics of NO_2 concentrations from both kitchens (A and B) and a background outdoor site (Table 3.4) show a high standard deviation and the differences between minimum value and maximum value were high, which means the data spread from the average value was probably due to the meshes in each diffusion tube receiving unequal coating with the TEA solution.

Table 3.4 Descriptive statistics of NO_2 concentrations from Kitchen A, Kitchen B and outdoors

Descriptive statistics	Kitchen A		Kitchen B		Outdoors	
	Period 1	Period 2	Period 1	Period 2	Period 1	Period 2
Mean*	7.8	9.9	7.5	7.7	9.1	11.4
Standard Error	0.6	1.0	0.3	0.4	0.2	0.3
Median	6.5	7.9	7.4	7.2	9.3	11.4
Mode	5.8	8.3	7.7	6.8	9.7	12.8
Standard Deviation*	3.4	5.5	1.4	1.9	1.2	1.5
Sample Variance	11.9	29.8	2.1	3.8	1.5	2.3
Kurtosis	5.4	1.6	9.8	1.0	-1.1	-0.5
Skewness	2.1	1.5	2.5	0.9	-0.3	0.1
Range	16.0	21.5	8.1	8.9	4.2	6.1
Minimum*	4.5	4.3	5.3	4.5	6.9	8.8
Maximum*	20.5	25.8	13.4	13.4	11.1	14.9
Sum	233.2	295.7	224.3	230.6	272.1	342.6
Count	30	30	30	30	30	30
Confidence Level (95.0%)	1.3	2.0	0.5	0.7	0.5	0.6

As large sample sizes (at least thirty samples) were used in these experiments, to ensure confidence in the results and to characterise the population the original preparation method needed to be modified as the amount of TEA solutions on meshes needed to be controlled using a pipette (more details given in 3.1.2.2).

3.2.2 Effect of the Amount of TEA solution on NO_2 absorbance and reproducibility of the modified preparation procedure

Aim of these experiments was to check the modified preparation method of the Palmes diffusion tube by using a micropipette to control the quantity of TEA:acetone solution. It was decided that the amount of the TEA on the mesh had to be controlled. Unlike for the original method a fixed amount of TEA was measured using a micropipette to control the amount of TEA solution. In this modified method, a known quantity of the solution was dropped onto the meshes whereas in the original method the meshes had been dipped into the solution.

Experiment 2 Comparison of the Original and Modified Methods for Coating the Mesh

The diffusion tubes were prepared using both original and modified methods. The amount of TEA solution used during the modified preparation procedure was varied and the amount of NO_2 absorbance was tested. For the modified method, the quantity of TEA solution was varied starting with 40 µl (the minimum quantity required to coat the meshes fully) and then adding 5 µl each time until the quantity was up to 90 µl, at which level the solution started leaking from the meshes. The quantity of solution was varied between 40ul to 90ul in 5µl amounts. Five tubes with each of these amounts were prepared and placed at a roadside (A1M) site in Hatfield for a 7-day period. The total number of tubes was 5 tubes x 11 different TEA solution amounts + 5 tubes with original dipped method, giving 60 tubes.

The average NO_2 concentrations from the roadside (A1M) site, from tubes with all the different quantities of TEA solution (modified method) and dipped method are shown in Figure 3.4. Results showed that the original dipped method gave highest standard deviation (1.8) when compared with the modified method (ranged from 0.3 to 1.2).

Table 3.5a shows the descriptive statistics of NO_2 concentrations from diffusion tubes using modified and original preparation methods, in which the overall average NO_2 concentration from all the different quantities of TEA solution was 22.3 ppb, minimum and maximum NO_2 concentrations were 20.1 and 24.5 ppb, with a standard deviation of 0.9. Using the ANOVA test (Table 3.5b), the overall data were not significantly different (p value = 0.05), which means that any amount of TEA solution between 40 to 90 µl could be used for coating the meshes, because it gave similar steady values of the concentration of NO_2. The lowest standard deviation value was 0.1 for the amount of TEA solution of 50 and 60 µl.

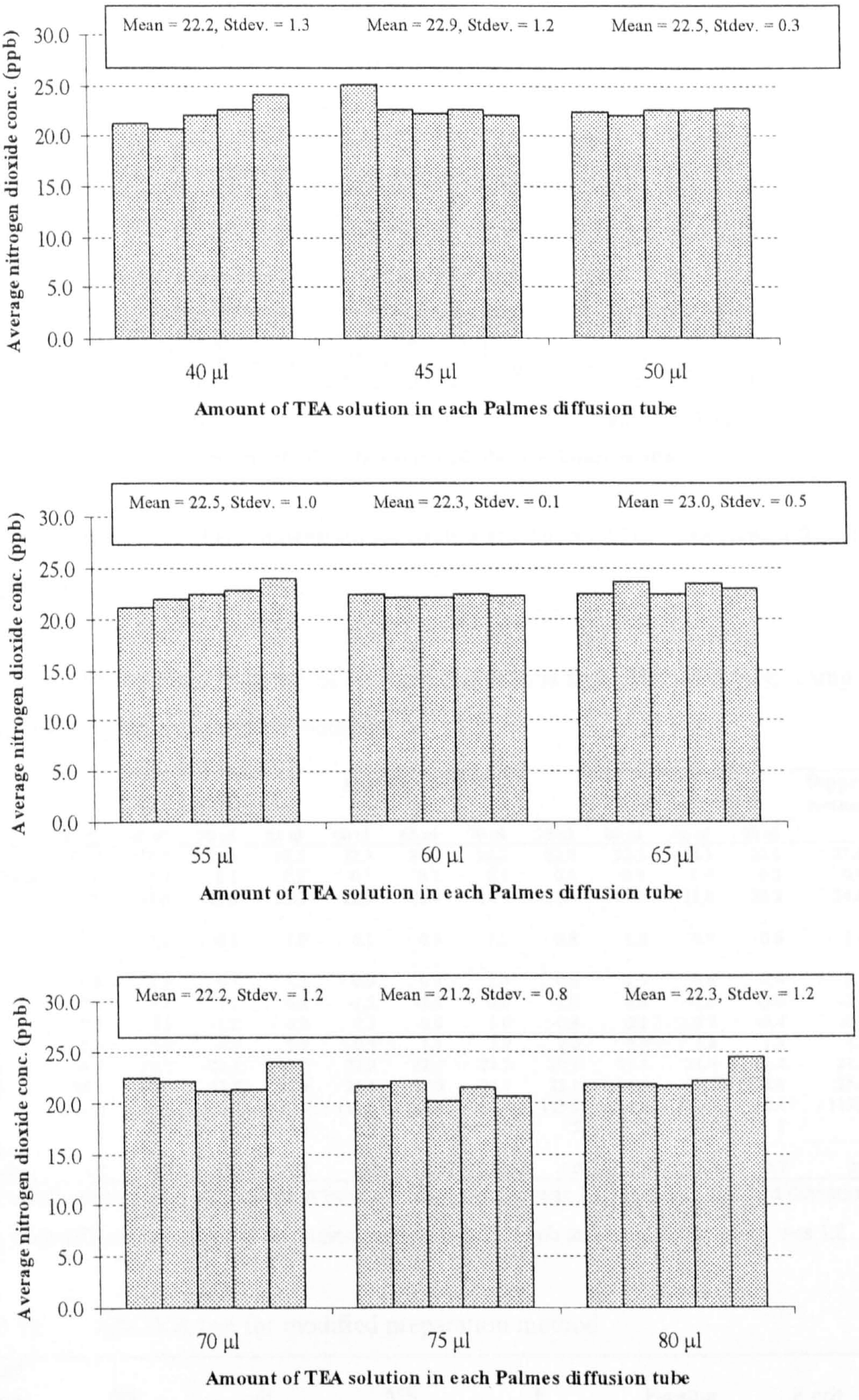


Figure 3.4 Average NO_2 concentrations from a roadside (A1M) site over a 7-day period.

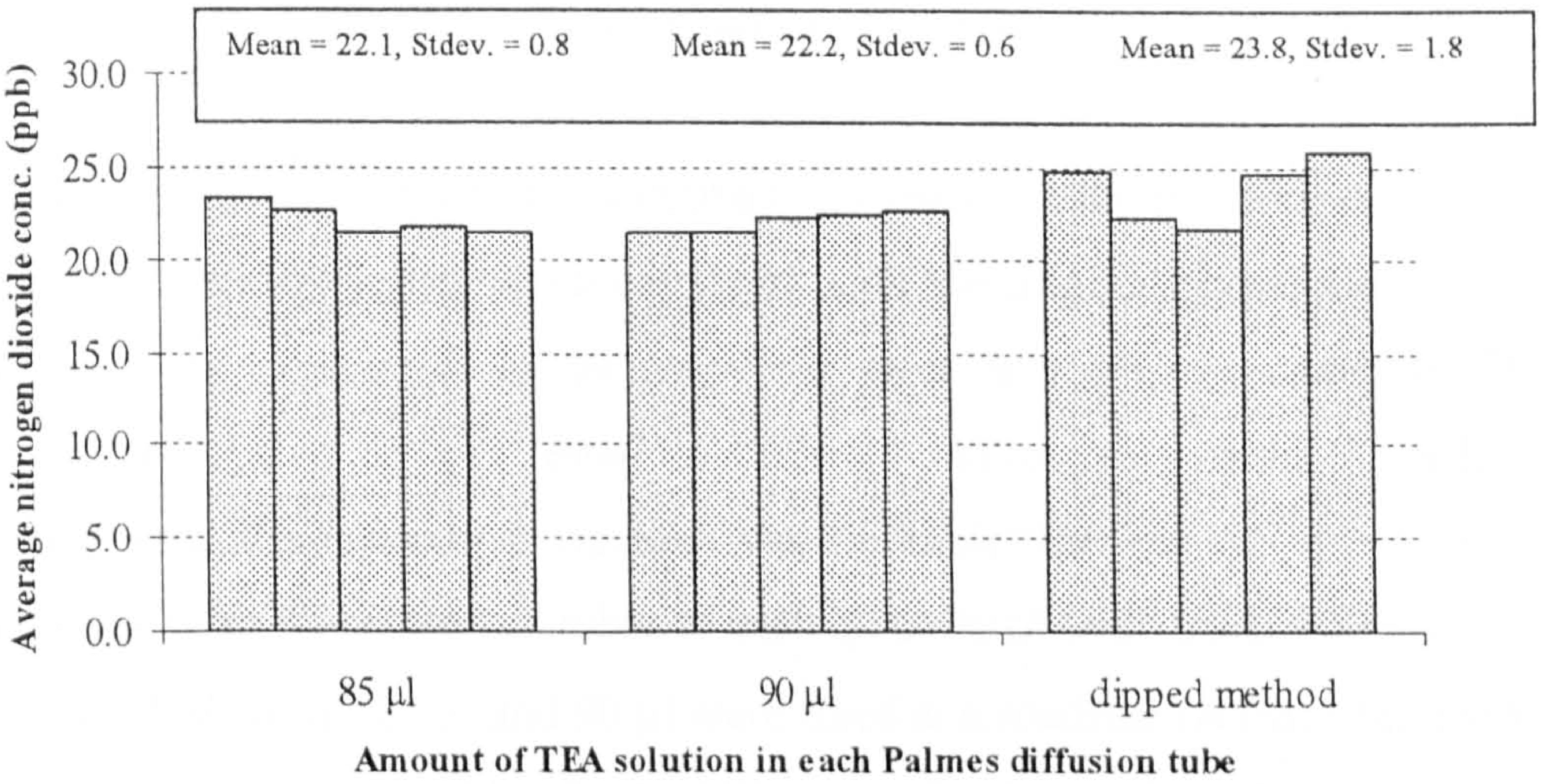


Figure 3.4 Average NO_2 concentrations from a roadside (A1M) site over a 7-day period (cont.).

Table 3.5a Descriptive statistics of NO_2 concentrations from diffusion tubes using modified and original preparation methods

	Modified method (μl)											Dipped method
	40 ul	**45 ul**	**50 ul**	**55 ul**	**60 ul**	**65 ul**	**70 ul**	**75 ul**	**80 ul**	**85 ul**	**90 ul**	
Mean	22.2	22.9	22.5	22.5	22.3	23.0	22.2	21.2	22.3	22.1	22.1	23.8
Standard Error	0.6	0.5	0.1	0.5	0.1	0.2	0.5	0.3	0.5	0.4	0.3	0.8
Median	22.1	22.5	22.6	22.5	22.3	23.0	22.2	21.4	21.8	21.8	22.3	24.6
Standard Deviation	1.3	1.2	0.3	1.0	0.1	0.5	1.2	0.8	1.2	0.8	0.6	1.8
Sample Variance	1.8	1.5	0.1	1.1	0.0	0.3	1.4	0.6	1.5	0.6	0.4	3.1
Kurtosis	0.0	4.4	1.1	0.2	-1.5	-2.9	0.6	-1.0	4.6	-1.6	-3.0	-2.4
Skewness	0.8	2.1	-1.3	0.2	0.5	0.0	1.0	-0.4	2.1	0.7	-0.4	-0.4
Range	3.3	3.0	0.7	2.8	0.3	1.1	2.9	2.0	2.9	1.8	1.3	4.1
Minimum	20.8	22.1	22.1	21.2	22.2	22.4	21.2	20.1	21.6	21.4	21.4	21.6
Maximum	24.1	25.1	22.8	23.9	22.5	23.6	24.0	22.1	24.5	23.2	22.6	25.8
Sum	110.8	114.6	112.5	112.4	111.6	114.8	111.2	105.9	111.7	110.6	110.4	119.1
Count	5	5	5	5	5	5	5	5	5	5	5	5
Confidence Level (95.0%)	1.6	1.5	0.3	1.3	0.2	0.7	1.4	1.0	1.5	1.0	0.7	2.2

Notes: Overall average NO_2 concentration from modified method was 22.3 ppb and standard deviation was 0.9, while NO_2 concentration from original method was 23.8 ppb and standard deviation was 1.8.

Table 3.5b ANOVA test for modified preparation method

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	21.99814	11	1.999831	1.965928	0.053643	1.994579
Within Groups	48.82778	48	1.017245			
Total	70.82591	59				

Experiment 3.1 Modified Methods for Coating the Mesh (1)

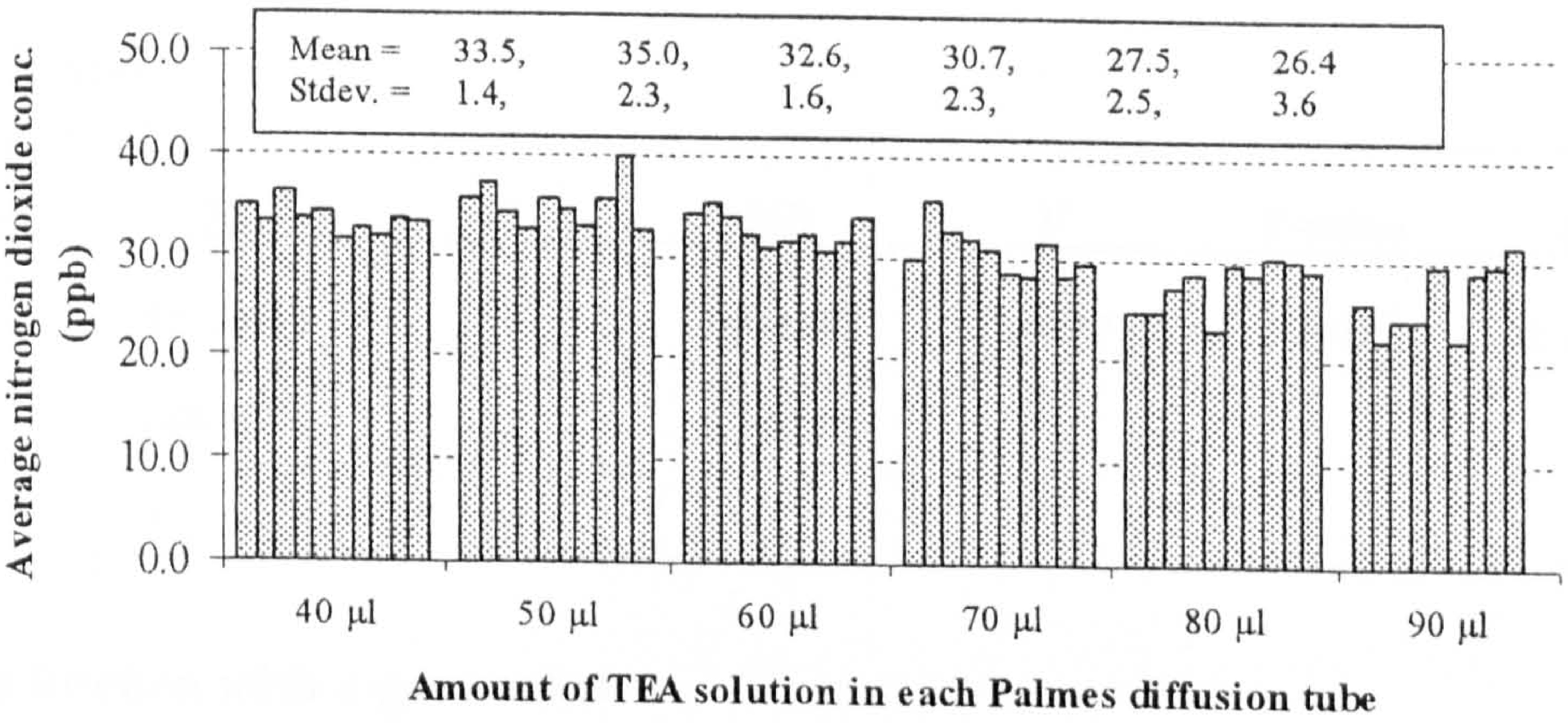
Even though the result from experiment 2 shows that the modified preparation method gave the steady values when compared with the original preparation method the reproducibility experiment to determine the most appropriate quantity of TEA solution was continued. It was tested in different microenvironments in order to demonstrate that this modified method was suitable for use in a variety of microenvironments. Therefore, ten tubes of each quantity of solution as follows:
40 µl, 50 µl, 60 µl, 70 µl, 80 µl and 90 µl were fixed at a roadside (A1M) site, inside a kitchen with a gas cooker and inside the UH gas boiler house for a 7-day period; in total one hundred and eighty tubes. Average NO_2 concentrations from the three different sites (the roadside, kitchen with a gas cooker and the UH gas boiler house) are shown in Figure 3.5. This time, the lowest standard deviation was 1.4 for the amount of TEA solution of 40 µl.

The data from indoors (the kitchen and the boiler house) and outdoors (the roadside) were not found to be significantly different from results obtained, using the ANOVA test (p value = 0.0001), (Table 3.6) which means that any amount of TEA solution between 40 to 90 µl could be used for coating the meshes because it gave similar steady values of the concentration of NO_2, although the standard deviation value of outdoor NO_2 concentration was higher than indoors.

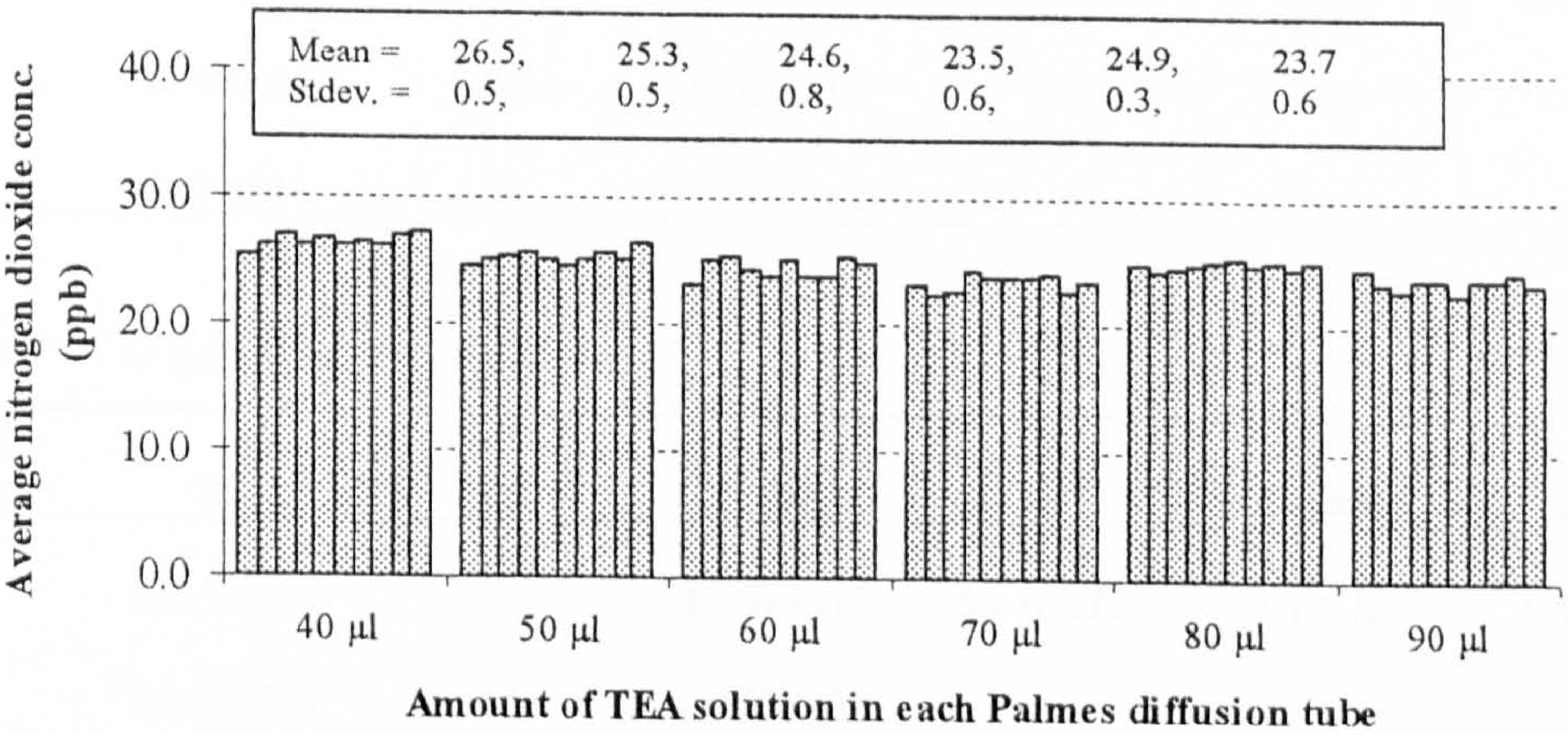
Experiment 3.2 Modified Methods for Coating the Mesh (2)

Another experiment was carried out to test the amount of TEA solution used. Sixty Palmes diffusion tubes with 40 µl, 50 µl, 60 µl, 70 µl, 80 µl and 90 µl of solution were tested inside a kitchen with a gas cooker for a 6-day period. The average NO_2 concentrations are shown in Figure 3.6. The results showed all acceptable standard deviations. Good values were obtained using all amounts, but the lowest standard deviation value was obtained when using 60 µl.

Roadside (A1M) site



Inside a kitchen with a gas cooker



Inside the UH gas boiler house

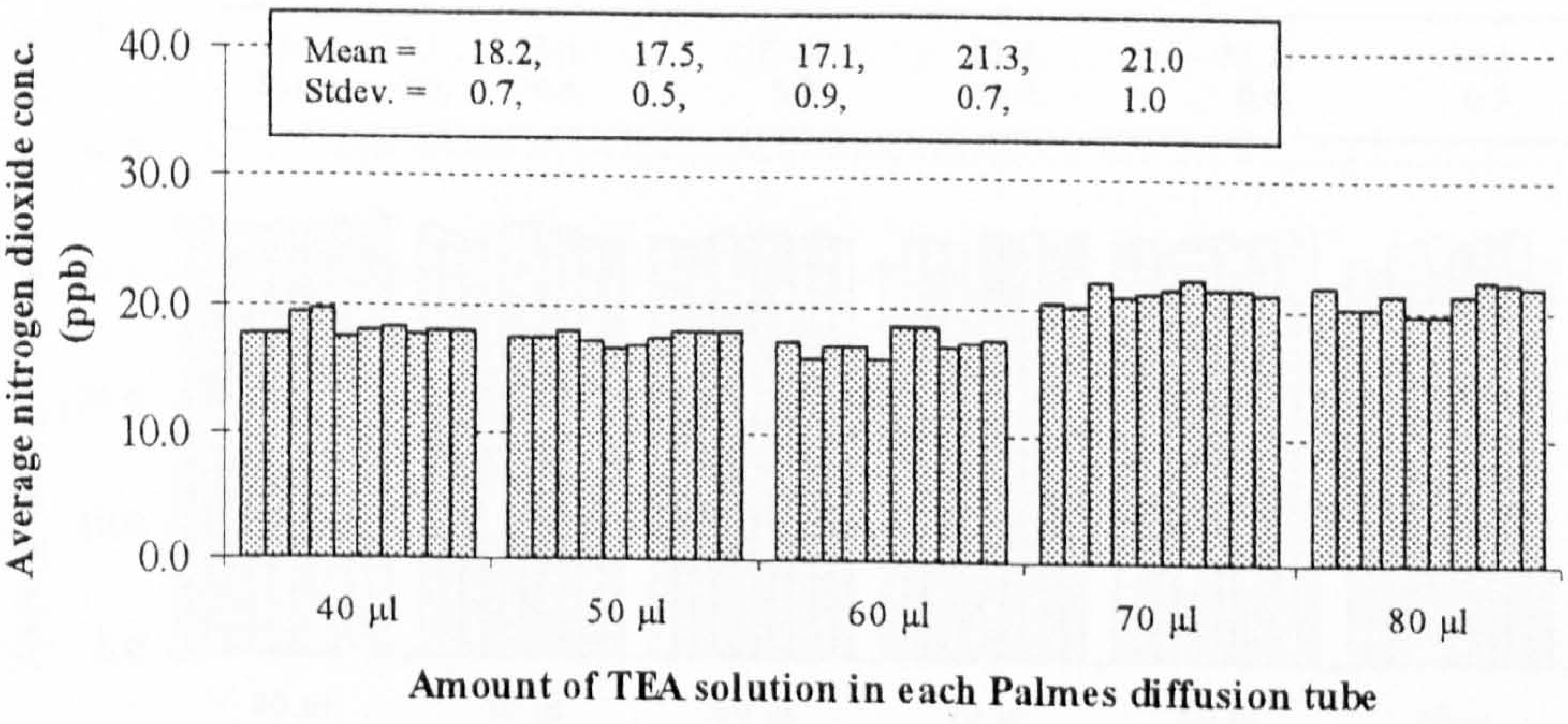


Figure 3.5 Average NO_2 concentrations from a roadside, a kitchen with a gas cooker and the UH gas boiler house sites over a 7-day period.

Table 3.6 ANOVA test for NO_2 data on concentrations from roadside site, in kitchen and gas boiler house.

Roadside site

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	557.4441	5	111.4888	20.47173	$2.54E^{-11}$	2.389442
Within Groups	288.6374	53	5.44599			
Total	846.0815	58				

Inside a kitchen with a gas cooker

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	60.76467	5	12.15293	36.56593	$3.6E^{-18}$	2.386066
Within Groups	17.94726	54	0.332357			
Total	78.71194	59				

Inside the UH gas boiler house

Source of Variation	SS	df	MS	F	P-value	F crit
Between Groups	156.05349	4	39.013372	65.802759	$3.191E^{-18}$	2.5787372
Within Groups	26.679759	45	0.5928835			
Total	182.73325	49				

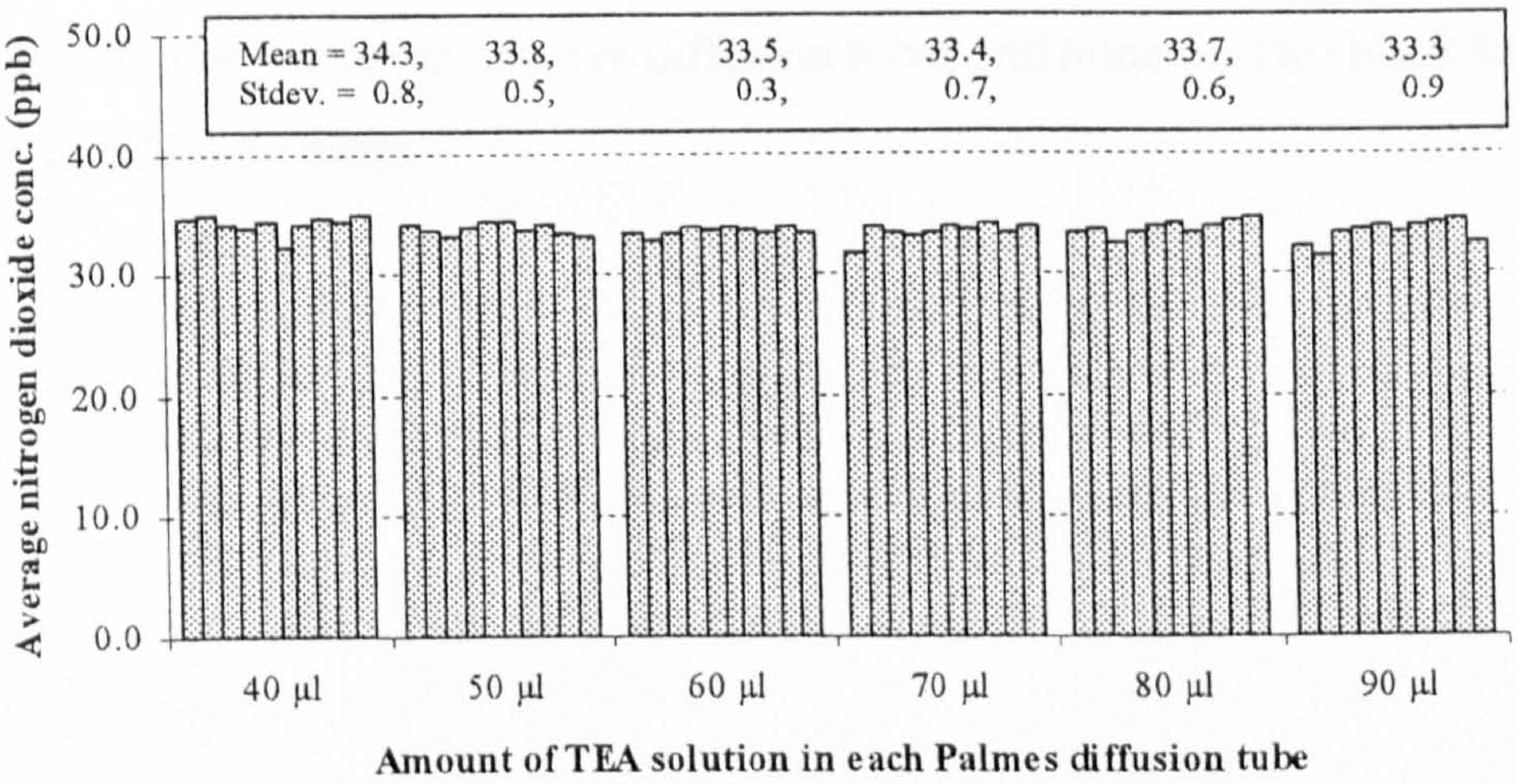


Figure 3.6 Average NO_2 concentrations from a kitchen with a gas cooker over a 6-day period.

Experiment 4.1 **Confirmation of Modified Methods for Coating the Mesh (1)**

Results from experiment 3.2 showed that the amount of 60 µl gave the lowest standard deviation value. Therefore, reproducibility of the amount of 60 µl with a larger sample size was tested in this experiment.

Eighty diffusion tubes were prepared using a micropipette that measured 60 µl of TEA solution for coating the meshes. All Palmes tubes were fixed in the UH gas boiler house for a 7-day period. Results are shown in Figure 3.7. The minimum and maximum NO_2 concentration were 17.1 and 20.2 ppb (average value was 18.5 ppb), and the standard deviation was 0.8. The large sample size was used in this experiment, so, the results should accurately reflect the population. The amount of 60 µl TEA solution was accepted to be used for coating the meshes in each diffusion tube. From now on, the amount of 60 µl has been using for the modified preparation method in this research project.

Experiment 4.2 **Confirmation of Modified Methods for Coating the Mesh (2)**

Although the overall data gave very good accuracy throughout all the experiments, in order to verify further the accuracy of the diffusion tube analyses additional analytical tests were carried out by doping the meshes within the diffusion tubes with known amounts of nitrite (NO_2^-). The absorbance obtained from these tubes should be predictable and correspond to the same concentration on a calibration curve. A known amount of nitrite solution, 40 µg NO_2^- (or 60 µg $NaNO_2$) would be doped onto meshes within ten passive diffusion tubes and none for two blank tubes: in total twelve diffusion tubes.

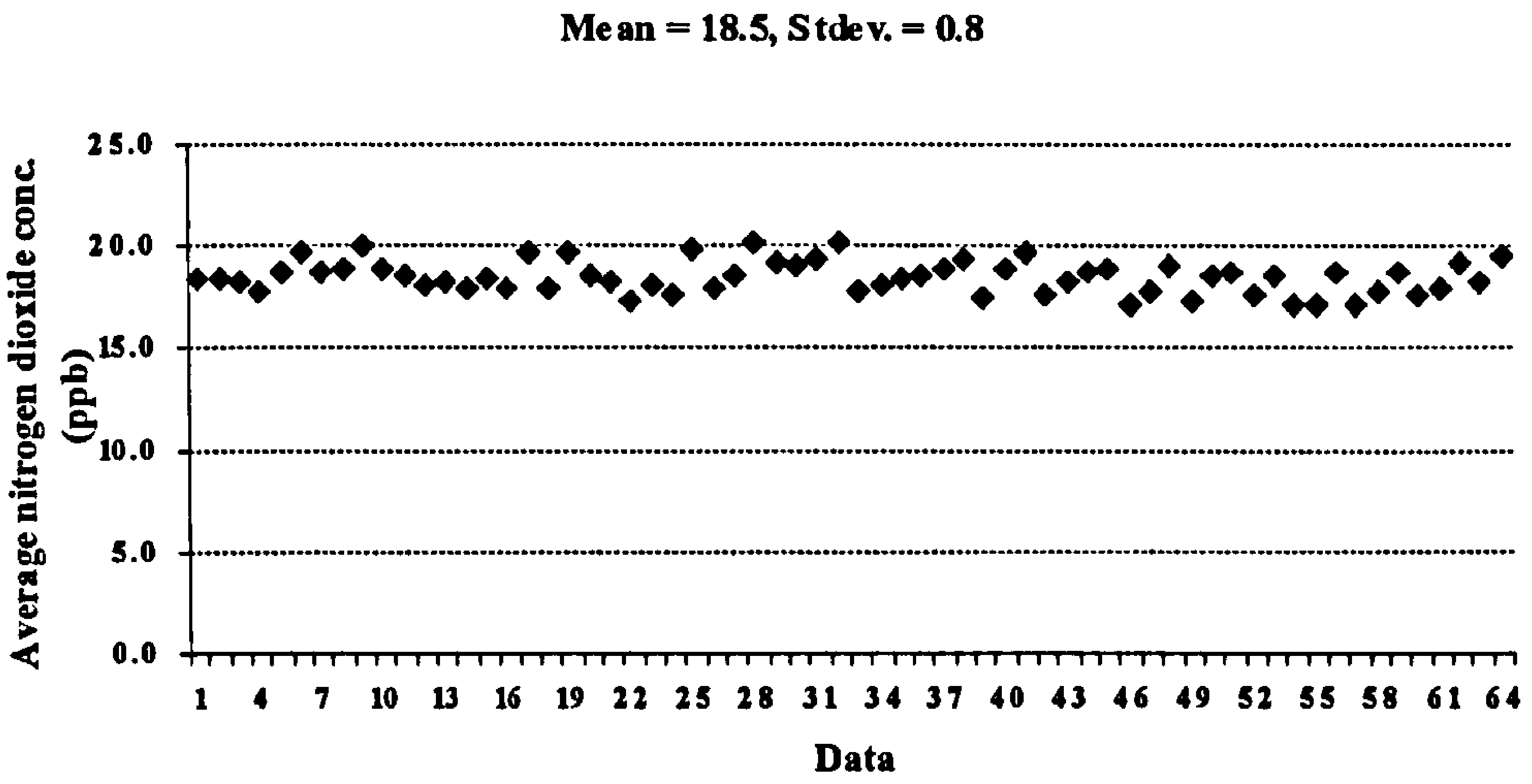


Figure 3.7 Average NO_2 concentrations from inside the UH gas boiler house, using the amount of 60 µl TEA solution. Notes: data from tube 65-80 were missing

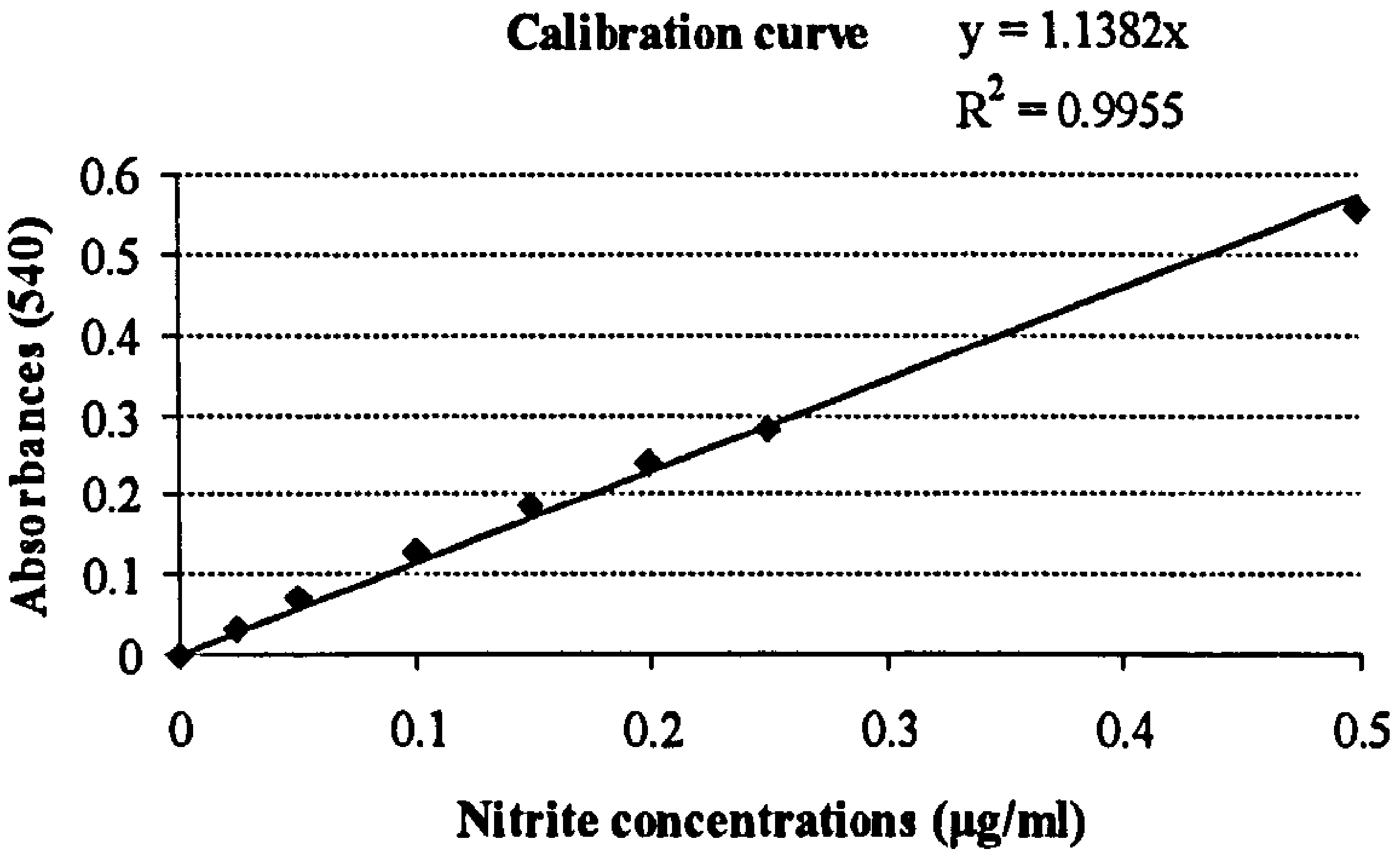


Figure 3.8a Calibration curve for calculating the results (nitrite)

The calibration curve is shown in Figure 3.8a. The equation of the calibration curve below was Y = 1.1382X. The calculation method used was as follows:

60 µg $NaNO_2$ = 40 µg NO_2^-

16 mg $NaNO_2$/L = 0.016g/L (or 0.0016g/100ml or 0.004g/250ml)

This solution = 0.56 µg NO_2^- /ml

Thus, 60µl of the solution = 0.6336 µg NO_2^-

60 µl + 4 ml (2 ml water + 2 ml NEDA solution)

Therefore, 0.6336 divided by 4 = 0.1584 µg NO_2^-

Equation of the calibration curve was Y = 1.1382X

That means, X = Y/1.1382

When Y = 0.189, then, X = 0.189/1.1382

Therefore, X = 0.166052 µg NO_2

The absorbance result for the nitrite is shown in Figure 3.8b. The average of absorbance was 0.189, which is only 14% greater than the calculated value for X, 0.166 and the standard deviation also gave a low value of 0.002. It was accepted that the amount of 60 µl TEA solution could be used to coat the meshes in each diffusion tube.

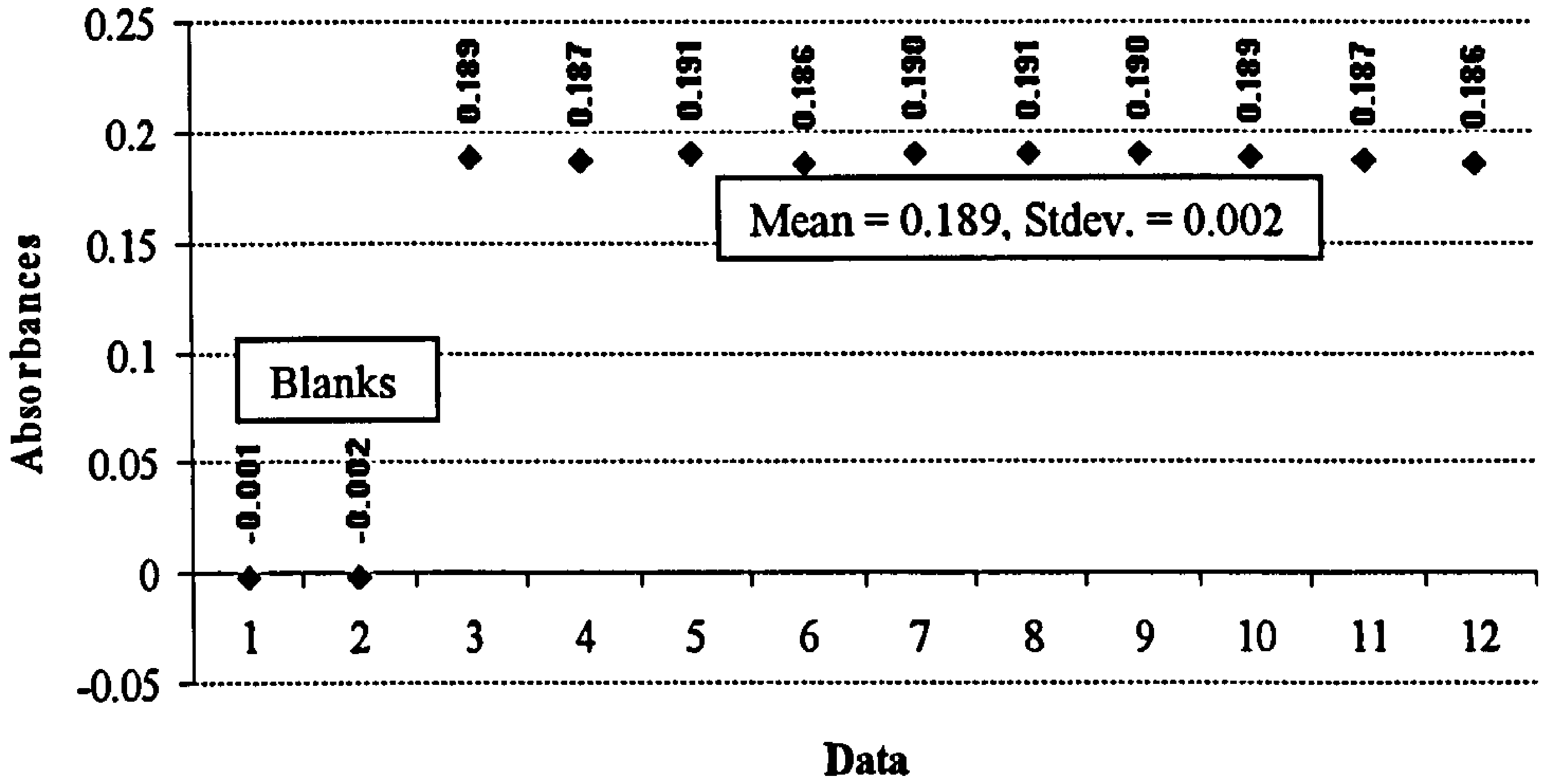


Figure 3.8b Absorbance data for nitrite.

<u>Experiment 4.3</u> Comparison with known NO_2 concentrations

This experiment was conducted to compare the procedure with known concentrations of NO_2. The experimental was set up by BRE staff in a BRE laboratory. Chamber A (a NO_2 permeation chamber) and Chamber B (a known NO_2 chamber) were connected together by a rubber tube. A NO_2 permeation tube was put into Chamber A with a flow rate of 700 ml per min. Four diffusion tubes were prepared by dropping 60 µl TEA: acetone solution onto meshes. These were placed into Chamber B and left in this Chamber for 3 days. The other four tubes were kept in a fridge as lab blank tubes.

The calculation method used was as follows:

$$NO_2 \text{ Emission rate (ppm)} = \frac{\text{Ko x ng/min.}}{F}$$

:where, F is diffusion flow in cc/min at S.T.P. (F = 700 ml/min.)

Emission rate of the NO_2 permeation tube = 1440 ng/min, Ko = 0.487

$$\text{Thus, } NO_2 \text{ emission rate (ppm)} = \frac{0.487x1440}{700}$$

$$= 1.001829 \text{ ppm}$$

$$= 1.001829x1000 \text{ ppb}$$

$$= 1001 \text{ ppb}$$

The average NO_2 concentration from the chamber, given in Figure 3.9, was found to show a high level of accuracy throughout the analysis runs. The result, 916.8 ppb, was only around 8 % lower than the calculated NO_2 emission rate, 1001 ppb. Therefore, this experiment further confirmed that the amount of 60 µl TEA solution was suitable for NO_2 analysis.

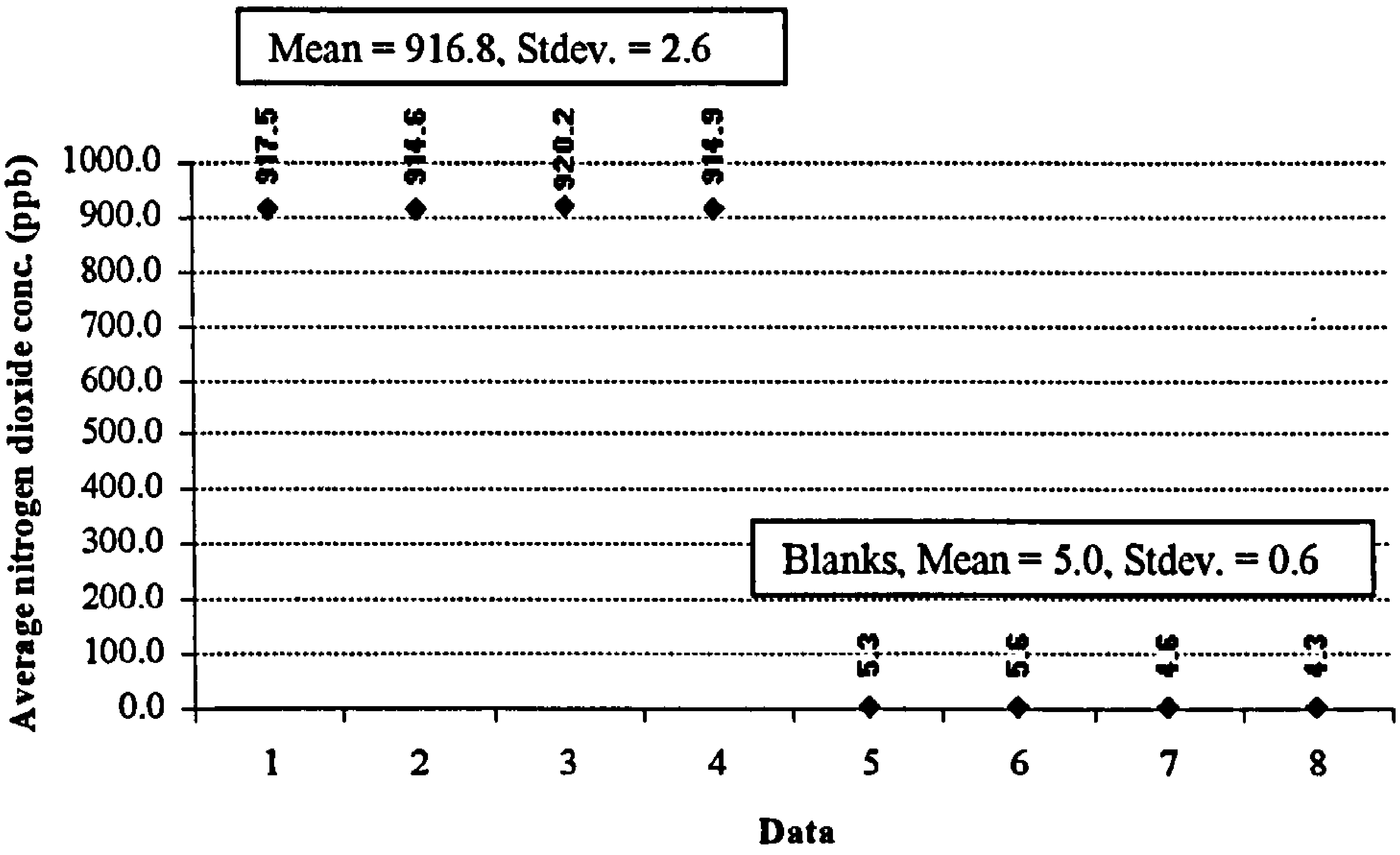


Figure 3.9 Nitrogen dioxide concentrations from a known NO_2 chamber.

Experiment 5.1 Long exposure period

The diffusion tubes were then tested over a long exposure period to ensure that they would give reliable results when used for lengthy periods of time. Fifty tubes (forty tubes plus ten blank tubes) were fixed next to a roadside (A1M) site and another fifty tubes (same as above) were sited on the roof of a building as a background site, one hundred tubes in total. Every week, five tubes from both sites were analysed. The results are shown in Figure 3.10. Relationship between average NO_2 concentrations from both sites was found. The standard deviation values over the entire ten 7-day periods from both sites were low. The results showed that the concentrations are falling with exposure time, therefore, it would be possible to use the diffusion tubes for measuring NO_2 concentrations for one week or two weeks.

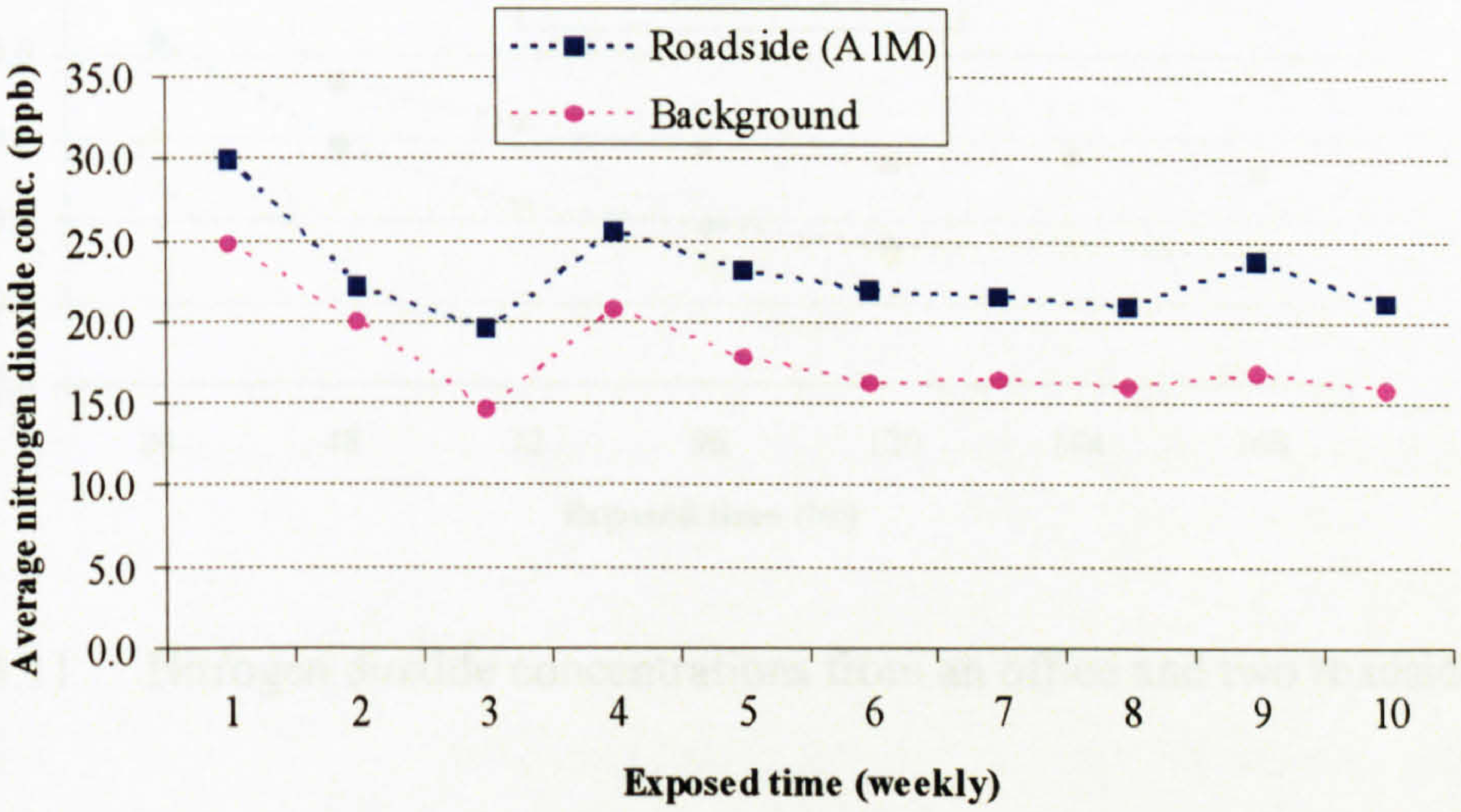


Figure 3.10 Average nitrogen dioxide concentration from roadside and background sites over ten 7-day periods.

Experiment 5.2 Short exposure period

The diffusion tubes were also tested over a short exposure period to ensure that they would give reliable results when used for short periods of time. Ninety eight diffusion tubes were prepared, twenty eight tubes were located in an office and a roadside site (Roadside site A) (fourteen tubes were placed at each site). Furthermore, seventy diffusion tubes were positioned at another roadside site (Roadside site B). Every day, two tubes from the office and Roadside A and ten tubes from Roadside B were analysed until all tubes were gone. Results are shown in Figure 3.11. The exposed times that gave the low standard deviation values for the office site (without NO_2 source) were from 48 hr to 168 hr, but not 24 hr. However, the exposed times that gave the low standard deviation values for the roadside sites (with NO_2 source) were from 144 hr and 168 hr. Therefore, 168 hr (7 days) has been accepted as a suitable measure-time for measuring NO_2 concentrations in this study (personal exposure to NO_2) as it covered a full range of activity patterns over both weekdays and weekends and covered both indoor and outdoor sites.

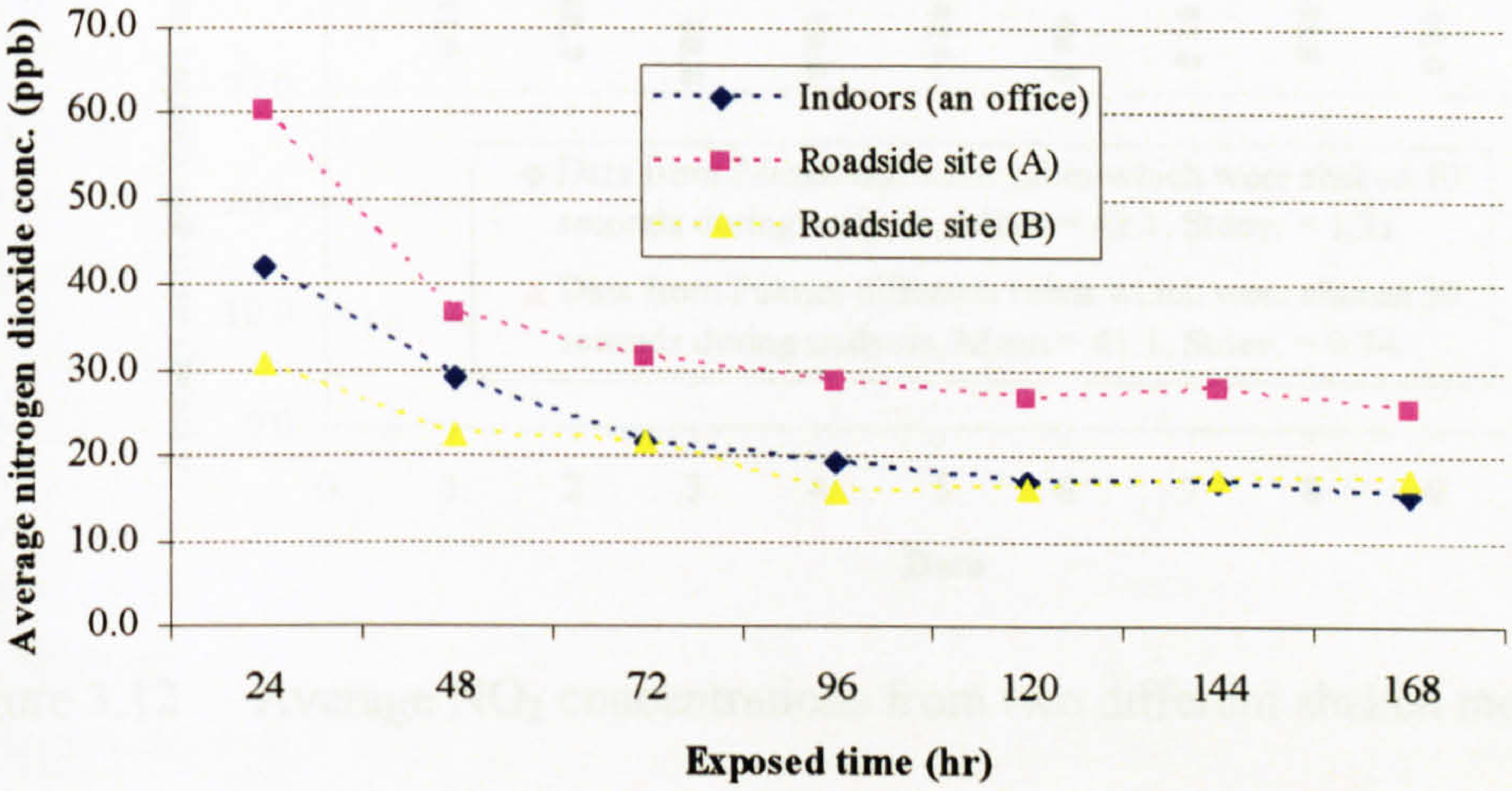


Figure 3.11 Nitrogen dioxide concentrations from an office and two roadside sites.

Experiment 6 Shaken diffusion tubes method

After consultation AEA Technology, UK advised that the diffusion tubes should be frequently shaken during the analysis period to help the solution to mix and develop the colour well. An experiment was carried out to test the validity of this advice. One set of diffusion tubes was gently shaken once (for 10 seconds) during the analysis time. The second set was gently shaken three times (around 30 seconds) during the analysis time. Results are shown in Figure 3.12.

F-test was used for checking variances of data from both methods. Then, t-test was used for comparing mean value of both methods (table 3.7 and 3.8). No significant difference between both average NO_2 concentrations was found (p-value = 0.05), which means that the average NO_2 concentration of both methods were not different. The result was found that the standard deviation from the diffusion tubes which were shaken for 30 seconds was lower (0.74) than the value obtained when the tubes were shaken for 10 seconds (1.31). The method of shaking the tubes for 30 seconds, was then incorporated into the analysis method for the Palmes diffusion tubes.

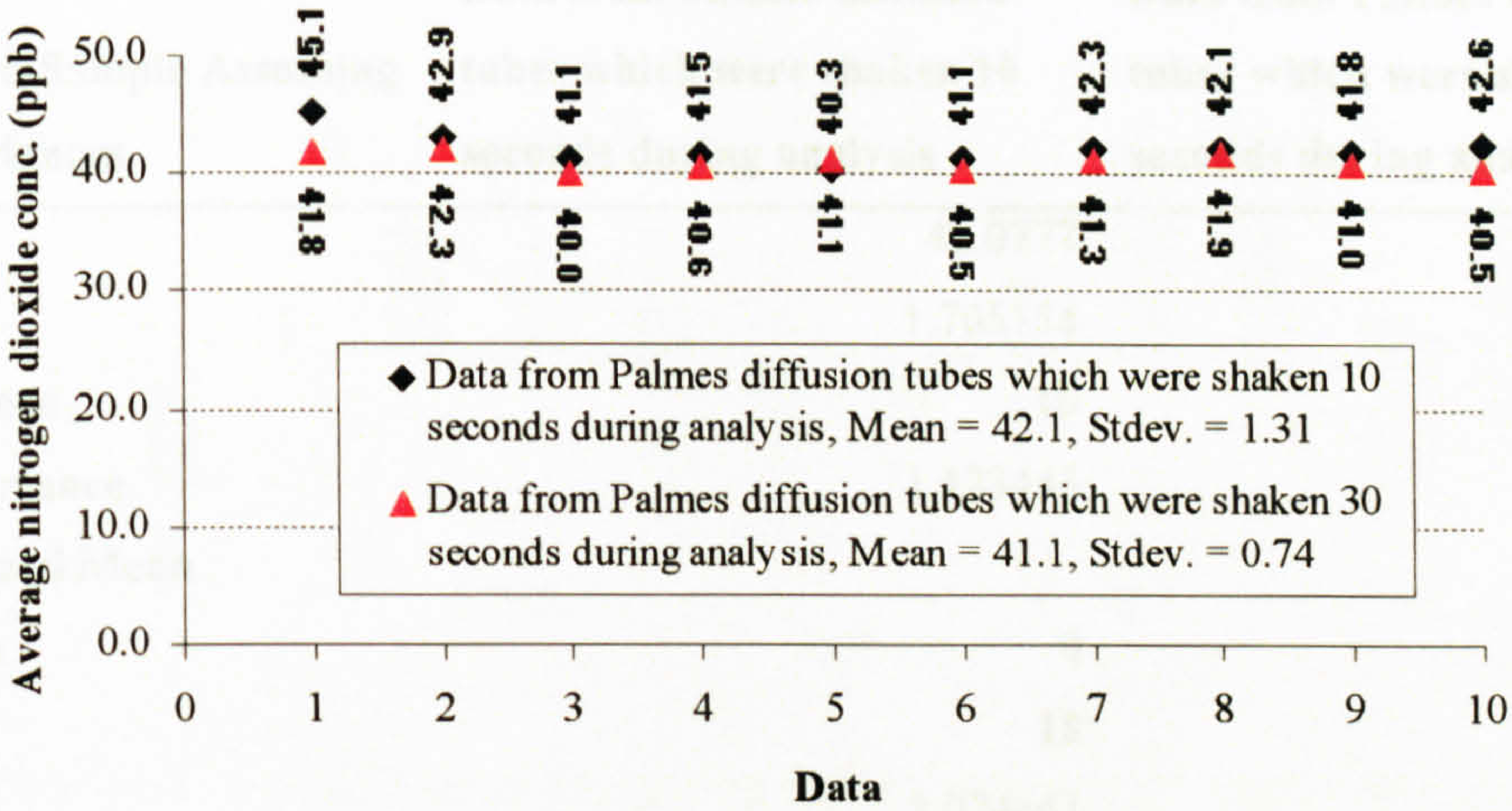


Figure 3.12 Average NO_2 concentrations from two different shaken methods.

Table 3.7 Results of F-test

F-Test Two-Sample for Variances	Data from Palmes diffusion tubes which were shaken 10 seconds during analysis	Data from Palmes diffusion tubes which were shaken 30 seconds during analysis
Mean	42.0777	41.09458
Variance	1.705154	0.541736
Observations	10	10
Df	9	9
F	3.147577	
P(F<=f) one-tail	0.051398	
F Critical one-tail	3.178897	

Experiment 7 Cleaning method

An experiment was then carried out to check that the cleaning method used for the Palmes diffusion tubes removed all nitrite and TEA:acetone solution from the meshes. All parts of ten diffusion tubes were cleaned and dried to remove any coating solution from the meshes. These were then located in a kitchen with gas cooker for a week. The results, shown in Figure 3.13a and 3.13b, confirmed that the cleaning method could clean most of nitrite from the Palmes diffusion tubes. Therefore, the cleaning method was acceptable and continued in this project.

Table 3.8 Results of t-test

t-Test: Two-Sample Assuming Equal Variances	Data from Palmes diffusion tubes which were shaken 10 seconds during analysis	Data from Palmes diffusion tubes which were shaken 30 seconds during analysis
Mean	42.0777	41.09458
Variance	1.705154	0.541736
Observations	10	10
Pooled Variance	1.123445	
Hypothesized Mean Difference	0	
df	18	
t Stat	2.074041	
P(T<=t) one-tail	0.026349	
t Critical one-tail	1.734063	
P(T<=t) two-tail	0.052697	
t Critical two-tail	2.100924	

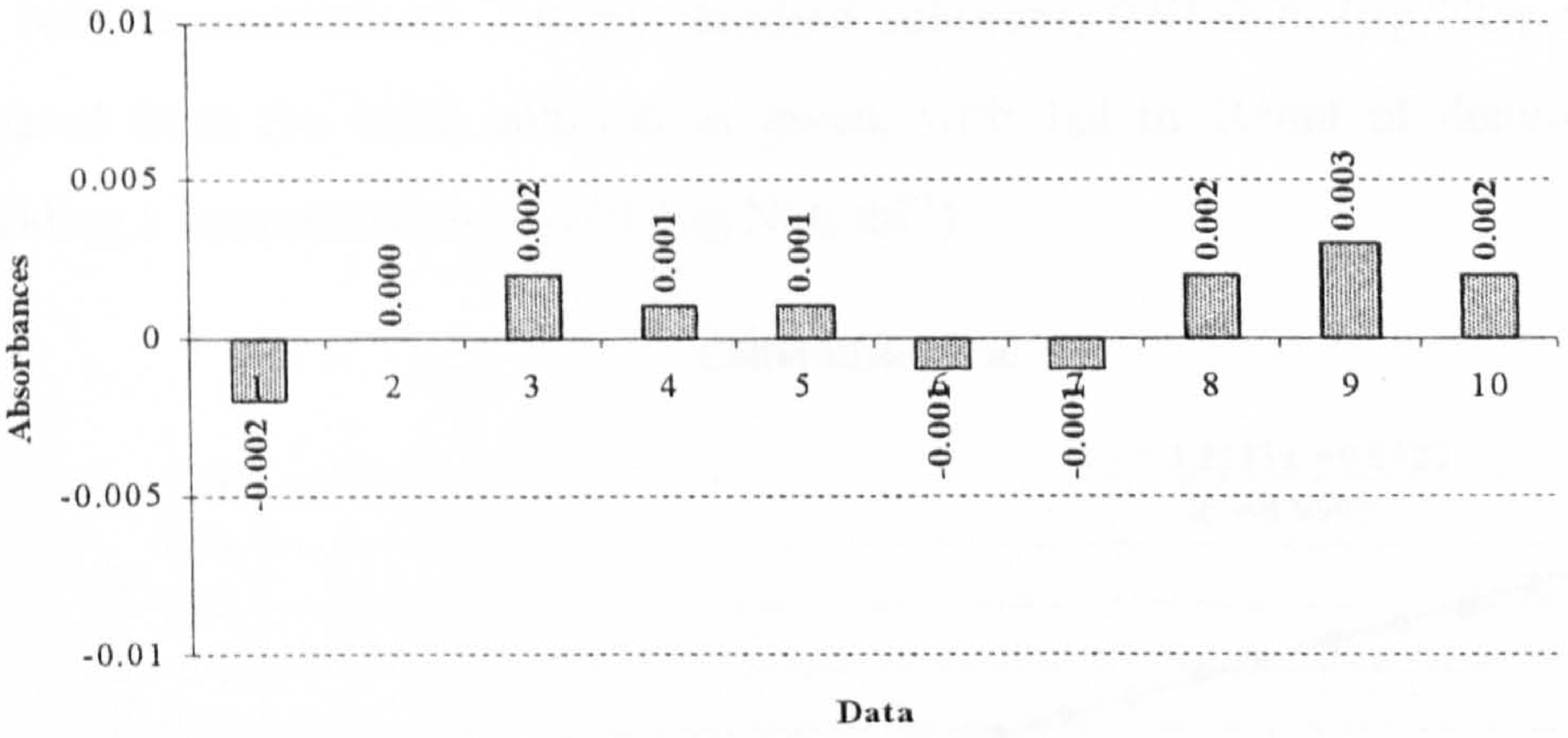


Figure 3.13a Absorbance data for nitrite from the cleaned Palmes diffusion tubes.

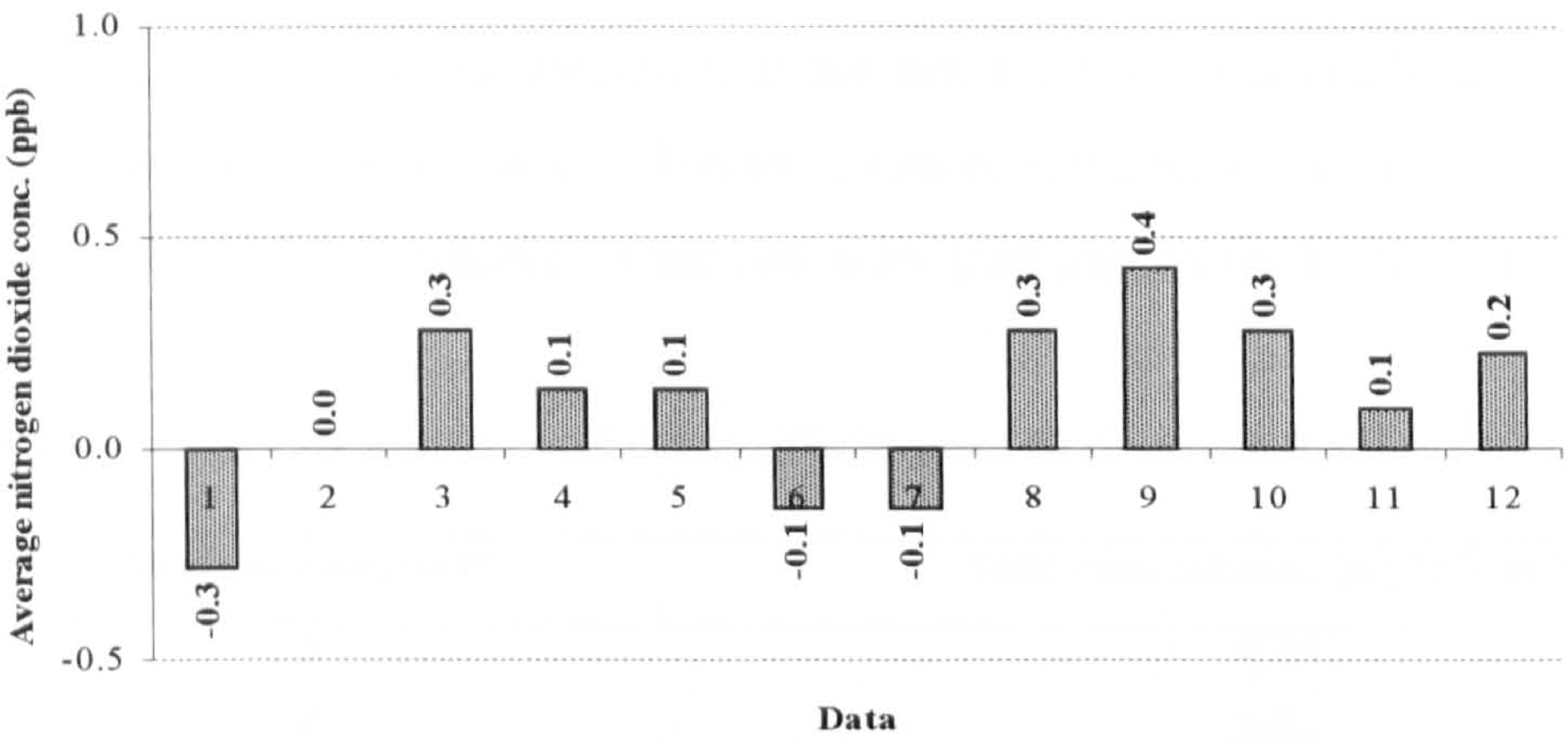


Figure 3.13b Average NO_2 concentrations from the cleaned Palmes diffusion tubes.

Experiment 8.1 Calibration curves with low concentrations of standard solutions

In previous experiments, the concentrations of NO_2 have sometimes been found to be very low but these calculations were carried out using high calibration curves (Section 3.1.3.3). Thus, a new low calibration curve was used for calculating low NO_2 concentrations. Twenty standard solutions, 0.01-0.20 (μg NO_2 ml^{-1} were prepared from the stock solution as given, with 1μl in 100ml of deionised water providing a concentration of 0.01 (μg NO_2 ml^{-1}).

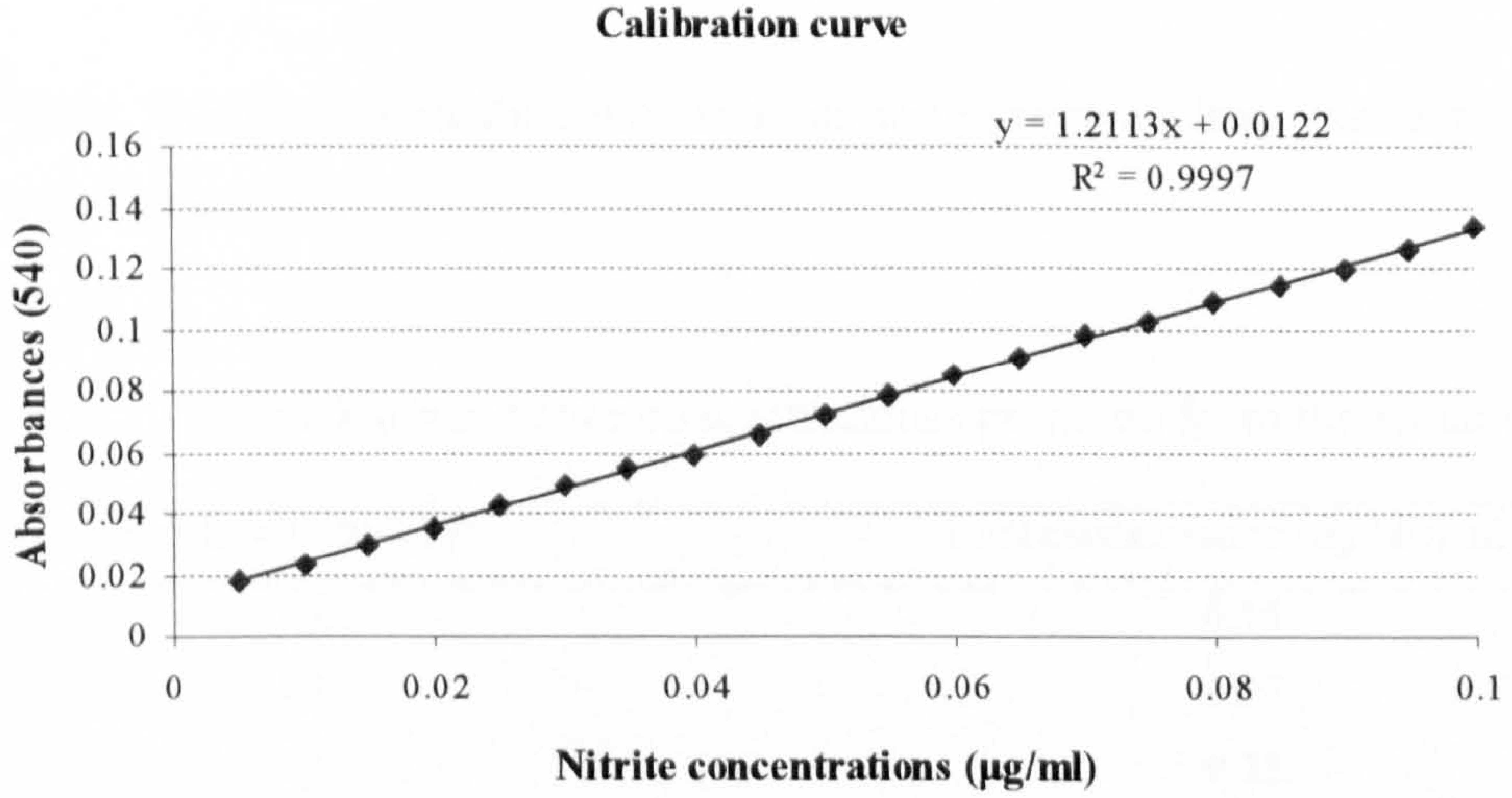


Figure 3.14 Calibration curve for low NO_2 concentrations

The calibration curve Figure 3.14. shows R^2 (0.9997) of the curve was found very close to 1.

Experiment 8.2 Calibration curves tested with known nitrite concentrations

In this experiment, to confirm that the low calibration could be accepted for calculating low NO_2 concentrations, known nitrite concentrations were tested with the low calibration. Thirteen standard solutions were prepared from the stock solution as given in Table 3.9.

Table 3.9 Various amounts of stock solution and their concentrations

Stock solution (μl)*	Total concentration (μg NO_2 ml^{-1})
5	0.05
6	0.06
7	0.07
8	0.08
9	0.09
10	0.10
20	0.20
30	0.30
40	0.40
50	0.50
100	1.00
150	1.50
200	2.00

Note: made up to 100 ml with de-ionised water

Then, five known nitrite concentrations were prepared from the stock solution as given in Table 3.10.

Table 3.10 Various known nitrite concentrations (prepared from the stock solution)

Stock solution (μl)*	Total concentration (μg NO_2 ml^{-1})
15	0.15
25	0.25
35	0.35
45	0.45
155	1.55

Note: made up to 100 ml with de-ionised water

The calibration curve was plotted (Figure 3.15) and shows the R^2 of the curve was 0.9989. The known nitrite solutions were analysed and shown in Figure 3.16 All the nitrite concentrations showed very good values which also fell within the range of the calibration curve in Figure 3.15. Moreover, R^2 of the curve was 0.9993. Therefore, the low calibration curve was acceptable for calculating low NO_2 concentrations.

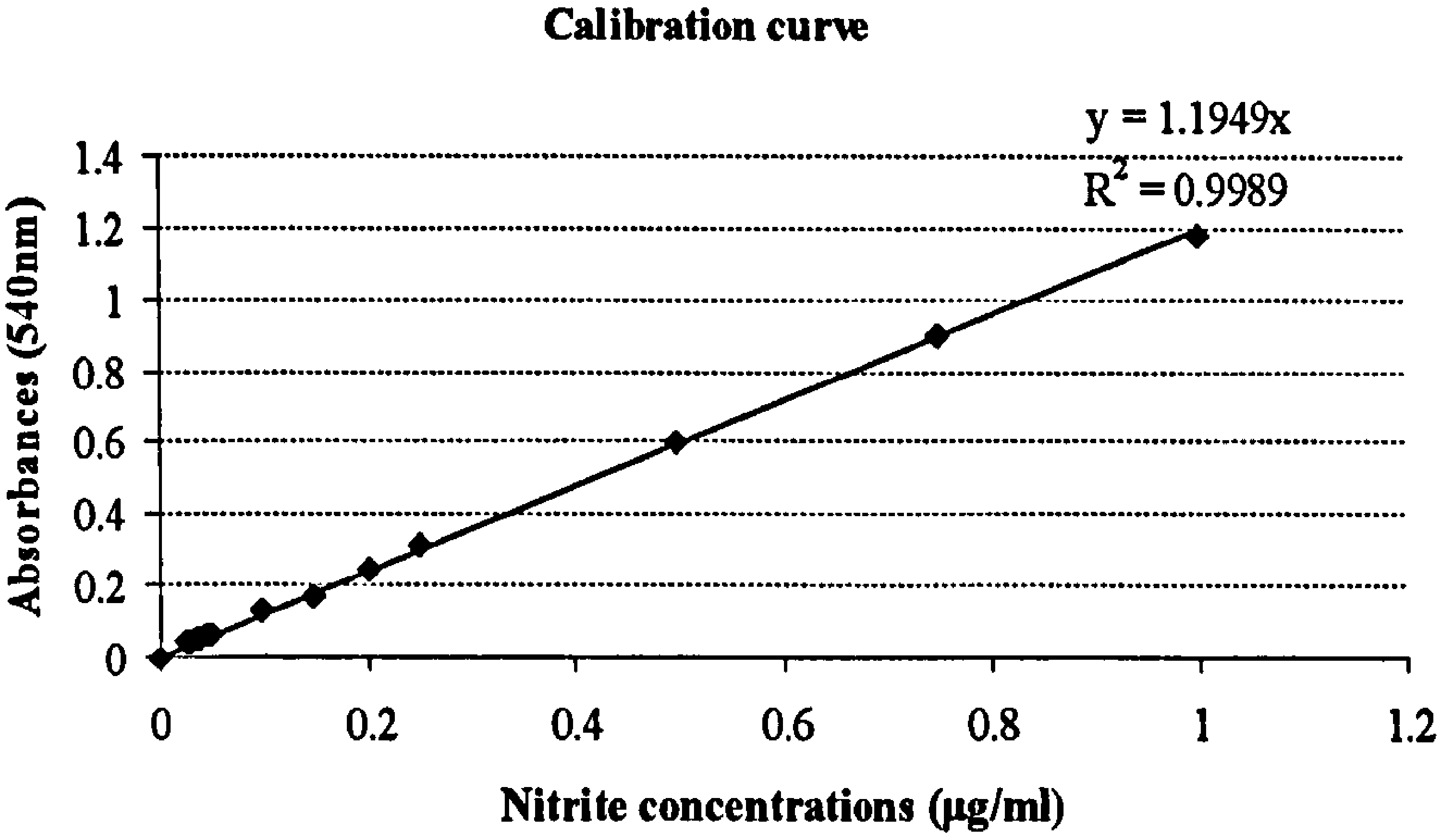


Figure 3.15 Calibration curve for low NO_2 concentrations.

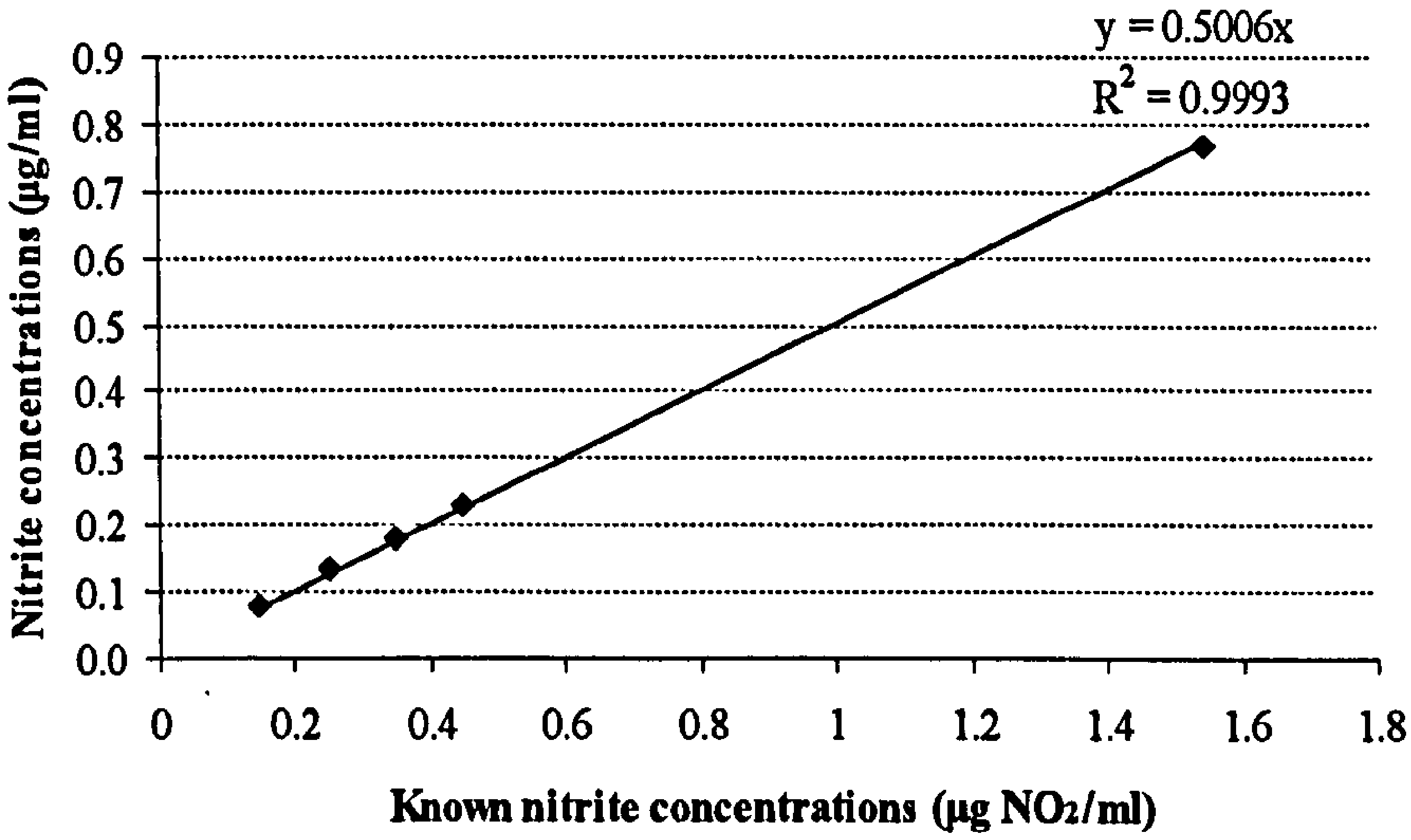


Figure 3.16 Nitrite concentrations for the known nitrite solution.

Experiment 9 Comparison of preparation methods for coating meshes

Overall, the development of the modified preparation for the diffusion tubes in previous experiments indicated that the modified preparation would be suitable for use in the experiment-sites. To quantify the difference between the two methods of coating, therefore, the average NO_2 concentration from the original preparation method was compared with the average NO_2 concentration from the modified method.

Twenty-four diffusion tubes for each method were prepared, in total forty-eight tubes. The tubes were positioned inside the UH gas boiler house and at a roadside (A1M) site for a 7-day period. The results are shown in Figure 3.17. F-test was used for checking variances of data from both methods. Then, t-test was used for comparing mean value of both methods (Table 3.11 and 3.12). Significant differences between both average NO_2 concentrations was found (p-value = 0.05), which means that the average NO_2 concentrations from the two methods were different. Moreover, the average NO_2 concentrations from the modified method from both indoors and outdoors sites showed a low range when compared with the average NO_2 concentrations from the original method. Therefore, the modified method is preferable to be used in this thesis.

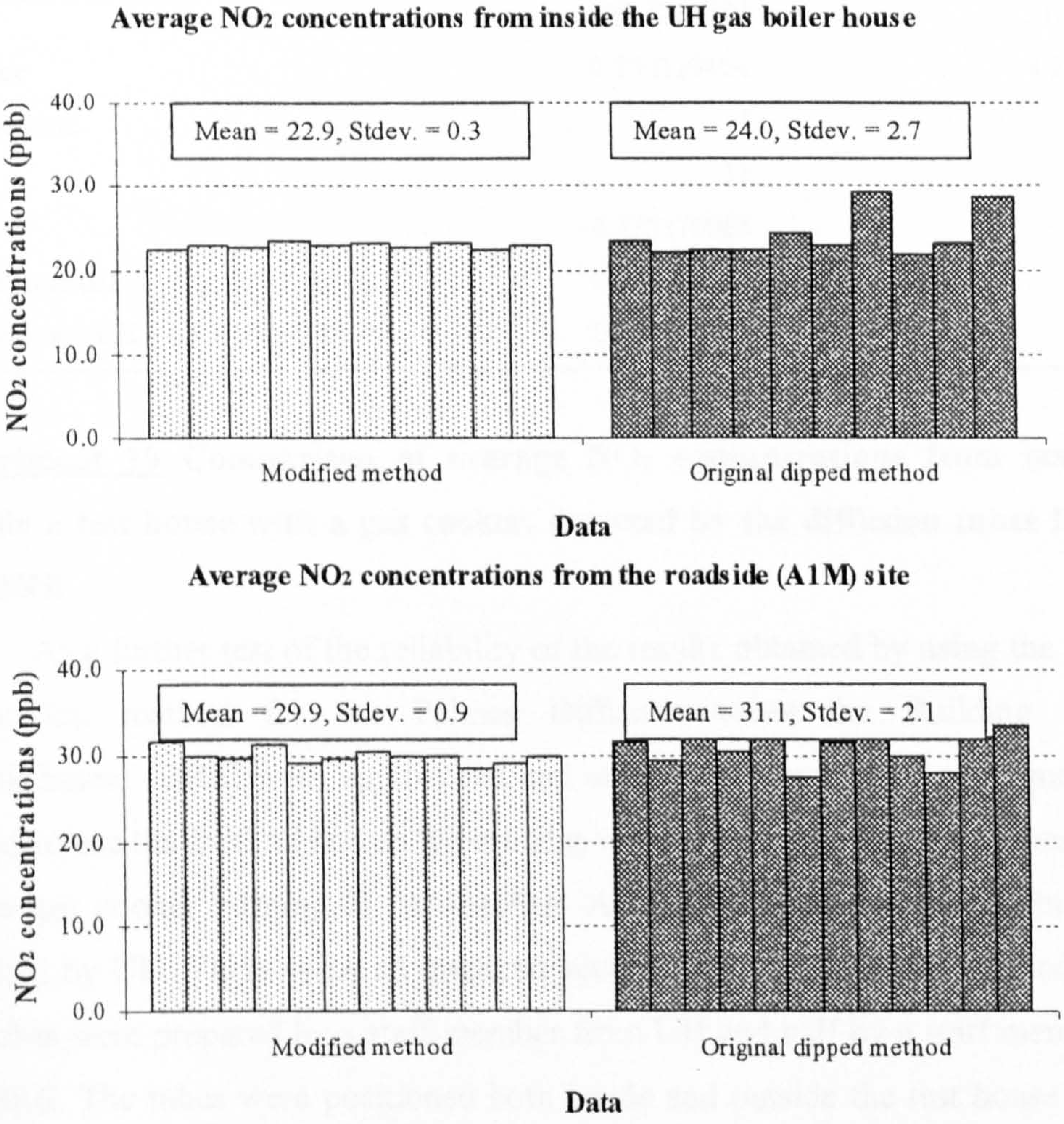


Figure 3.17 Average NO_2 concentrations from inside the UH gas boiler house and at the roadside (A1M) site over a 7-day period.

Table 3.11 Results of F-test

Average NO_2 concentrations from inside the UH gas boiler house

F-Test Two-Sample for Variances	Modified method	Original dipped method
Mean	22.85277008	24.041056
Variance	0.107565433	7.095352
Observations	10	10
df	9	9
F	0.015159986	
P(F<=f) one-tail	0.000000	
F Critical one-tail	0.314575033	

Average NO_2 concentrations from the roadside (A1M) site

F-Test Two-Sample for Variances	Modified method	Original dipped method
Mean	29.9261687	31.05890524
Variance	0.750119104	4.282233329
Observations	12	12
df	11	11
F	0.175170068	
P(F<=f) one-tail	0.003744934	
F Critical one-tail	0.354869911	

Experiment 10 Comparison of average NO_2 concentrations from inside and outside a test house with a gas cooker, detected by the diffusion tubes from UH and BRE

As a further test of the reliability of the results obtained by using the modified preparation method for the Palmes Diffusion tubes the Building Research Establishment (BRE) were approached and asked to set up a joint experiment. They agreed to use the method and an experiment was set up in the BRE test house, which had a gas cooker burning in the kitchen. A total of sixteen diffusion tubes were supplied by UH. These were all prepared according to the modified method. Half of the tubes were prepared by a staff member from UH and half by a staff member from the BRE. The tubes were positioned both inside and outside the test house for an 8-day period. The participation of UH and BRE staff in the preparation of these tubes provided an independent check on the preparation and analysis of the results of this experiment. The average concentrations of NO_2 from both sites (in Table 3.13) gave good accuracy and low standard deviations.

Table 3.12 Results of t-test

Average NO_2 concentrations from inside the UH gas boiler house

t-Test: Two-Sample Assuming Unequal Variances	**Modified method**	**Original dipped method**
Mean	22.85277008	24.041056
Variance	0.107565433	7.095352
Observations	10	10
Hypothesized Mean Difference	0	
Df	9	
T Stat	-1.400124942	
P(T<=t) one-tail	0.097496201	
T Critical one-tail	1.833113856	
P(T<=t) two-tail	0.194992402	
T Critical two-tail	2.262158887	

Average NO_2 concentrations from the roadside (A1M) site

t-Test: Two-Sample Assuming Unequal Variances	**Modified method**	**Original dipped method**
Mean	29.9261687	31.05890524
Variance	0.750119104	4.282233329
Observations	12	12
Hypothesized Mean Difference	0	
Df	15	
T Stat	-1.749178017	
P(T<=t) one-tail	0.050343087	
t Critical one-tail	1.753051038	
P(T<=t) two-tail	0.100686174	
t Critical two-tail	2.131450856	

Table 3.13 Average NO_2 concentrations from inside and outside the BRE test house.

	Inside the BRE test house		Outside the BRE test house	
	Average NO_2 conc. (ppb)	Stdev.	Average NO_2 conc. (ppb)	Stdev.
Prepared & analysed by UH	25.5	0.65	20.5	0.37
Prepared by BRE & analysed by UH	25.9	0.35	20.7	0.40
Prepared by UH & analysed by BRE	24.9	0.51	20.0	0.69

3.2.3 Survey of indoor and outdoor NO_2 concentrations in urban, semi-urban and rural area (in collaboration with BRE).

Experiment 11 Reliability test of the modified preparation method

For a further test of the reliability of the results obtained by using the modified preparation method for the Palmes diffusion tubes the Building Research Establishment (BRE) were approached and asked to set up the second joint experiment. The aim of this experiment was to measure the NO_2 levels in some gas cooker kitchens located in urban, semi-urban and rural area using two different preparation methods of the diffusion tubes. For the modified method, 60 µl of the TEA:acetone mixture solution was controlled by using micropipette. For tubes prepared by Gradko International Ltd each mesh was dipped in the mixture TEA:brij-35 solution. Four tubes of each method were located for a week in eleven houses with gas cookers, five houses in urban, one house in semi-urban and five houses in rural areas. Two tubes were placed in the kitchen and the other tubes were placed outdoors. The average concentration of NO_2 from the 11 houses is shown in Table 3.14.

The results showed that for current method (coated the tubes with 60 µl of the TEA:acetone solution), indoor NO_2 concentrations from the houses in urban and rural area to be higher than outdoors, except house 1 in an urban area. For Gradko tubes, indoor NO_2 levels from the houses in urban and rural area were higher than outdoors, except houses 1 and 3 in urban area.

F-test and T-test were chosen for comparing indoor and outdoor NO_2 concentrations from the 2 preparation methods of the Palmes diffusion tube. Normally, F-test is used to compare 2 population variances to be equal or not (Mason *et al.*, 1999). F-calculations of indoor NO_2 concentrations and outdoor NO_2 concentrations from both methods were found to be more than F-critical value (95% confidence interval). Thus, variances of NO_2 concentrations from both methods of Palmes diffusion tube preparation are statistically different. Then, T-test, for 2 samples assuming unequal variances, was tested.

T-test for comparing 2 population means is used for testing the means of two normal populations to be equal or not. T-calculations of indoor NO_2 concentrations and outdoor NO_2 concentrations from both methods were found to be lower than T-critical value (95% confidence interval). Hence, mean values of NO_2 concentrations from the two methods of Palmes diffusion tube preparation are not statistically different.

Table 3.14 Average NO_2 concentration from 11 houses located in urban, semi-urban and rural area.

House no./site	**Average indoor NO_2 levels ($\mu g/m^3$)**		**Average outdoor NO_2 levels ($\mu g/m^3$)**	
	CK*	**GK***	**CK***	**GK***
2/urban	45.4	40.7	49.9	51.3
3/urban	51.7	52.8	43.7	31.4
4/urban	46.2	41.7	45.5	50.2
6/urban	83.9	85.2	41.0	48.8
7/urban	50.9	60.3	34.9	42.5
2/semi	47.2	58.7	16.3	18.9
1/rural	38.4	38.7	17.9	17.5
2/rural	35.1	38.9	23.1	12.6
3/rural	32.0	34.8	27.0	26.8
4/rural	45.1	46.6	8.6	8.1
5/rural	26.1	22.9	25.4	23.2

Note: Exposed time was a 7-day period.

CK* means the tubes were prepared using a micropipette control amount of TEA:acetone solution.

GK* means the tubes were prepared using dipped method by Gradko International Ltd.

Table 3.15 Results of F-test

F-Test Two-Sample for Variances	**Average indoor NO_2 levels**		**Average outdoor NO_2 levels**	
	CK*	**GK***	**CK***	**GK***
Mean	23	23.89091	15.25455	15.16364
Variance	58.112	69.74891	47.37673	63.58055
Observations	11	11	11	11
df	10	10	10	10
F	0.83316		0.745145	
P(F<=f) one-tail	0.38924		0.325319	
F Critical one-tail	0.335769		0.335769	

Note: CK* means the tubes were prepared using a micropipette control amount of TEA:acetone solution.

GK* means the tubes were prepared using dipped method by Gradko International Ltd.

Table 3.16 Results of t-test

T-Test: Two-Sample Assuming Unequal Variances	**Average indoor NO_2 levels**		**Average outdoor NO_2 levels**	
	CK*	**GK***	**CK***	**GK***
Mean	23	23.89091	15.25455	15.16364
Variance	58.112	69.74891	47.37673	63.58055
Observations	11	11	11	11
Hypothesized Mean Difference	0		0	
Df	20		20	
T Stat	-0.26131		0.028624	
P(T<=t) one-tail	0.398262		0.488724	
T Critical one-tail	1.724718		1.724718	
P(T<=t) two-tail	0.796523		0.977448	
T Critical two-tail	2.085962		2.085962	

Note: CK* means the tubes were prepared using a micropipette control amount of TEA:acetone solution.

GK* means the tubes were prepared using dipped method by Gradko International Ltd.

3.2.4 Comparison of average outdoors NO_2 concentrations using Palmes diffusion tubes with a chemiluminescence monitor.

Experiment 12 Comparison of Palmes diffusion tube and chemiluminescence methods

Chemiluminescence analysers have been used as the reference monitoring method of NO_2 in ambient air (Defra, 2004). Therefore, it is necessary to compare the average NO_2 concentrations from the Palmes diffusion tubes with a chemiluminescence monitor. In this experiment, monitoring of weekly NO_2 concentrations using Palmes diffusion tubes was carried out in parallel with a chemiluminescence monitor at an urban background site for six 7-day periods (30 tubes x 6 periods = 180 tubes in total). The chemiluminescence monitoring site was operated by Atmospheric Science Research Group (ASRG) at the University of Hertfordshire. As part of quality assurance and quality control (QA/QC) procedures regular span checks were made before undertaking the measurements. In addition the instrument was independently calibrated by the manufacturers during a maintenance schedule.

Weekly average concentrations of NO_2 from the chemiluminescence monitor and from Palmes diffusion tubes were calculated and given in Table 3.15. Bias of average NO_2 concentrations between both methods were also calculated and shown in Table 3.15. Not only a positive or overestimation of average NO_2 concentrations from Palmes diffusion tubes when compared with the chemiluminescence but also a negative bias were found. The average bias was +19.3% (in the range +16.8 to +23.2 %) and a negative bias (underestimation) was 12.5%. The positive bias was lower than the bias found in Heal et al., 2000 study (+24%). Also, the negative bias was below the bias (-25%) reported in Laxen and Wilson (2002) study.

The average value from Table 3.15 was plotted in Figure 3.18, which shows the relation between average NO_2 concentrations from the chemiluminescence monitor (y) and average NO_2 concentrations from the Palmes diffusion tubes (x). 83.85% of the total variation of the NO_2 concentrations from chemiluminescence monitor is accounted for by a linear relationship with the NO_2 concentrations from Palmes diffusion tube ($R^2 = 0.8385$).

Table 3.17 Weekly average of NO_2 concentrations from Palmes diffusion tubes compared with chemiluminecence monitor

Periods	Weekly average NO_2 concentrations (ppb)		
	Diffusion tubes	The chemiluminescence monitor	*Bias between diffusion tubes and chemiluminescence monitor (%)
1	17.9	15.7	+ 14.0%
2	14.9	12.2	+ 22.1%
3	10.0	8.3	+ 20.5%
4	11.8	10.1	+ 16.8%
5	10.1	8.2	+ 23.2%
6	9.1	10.4	- 12.5%

*Bias is defined as the percentage deviation of the diffusion tube (D) from the chemiluminesence (C) value. [Bias (%) = (D-C)/C]

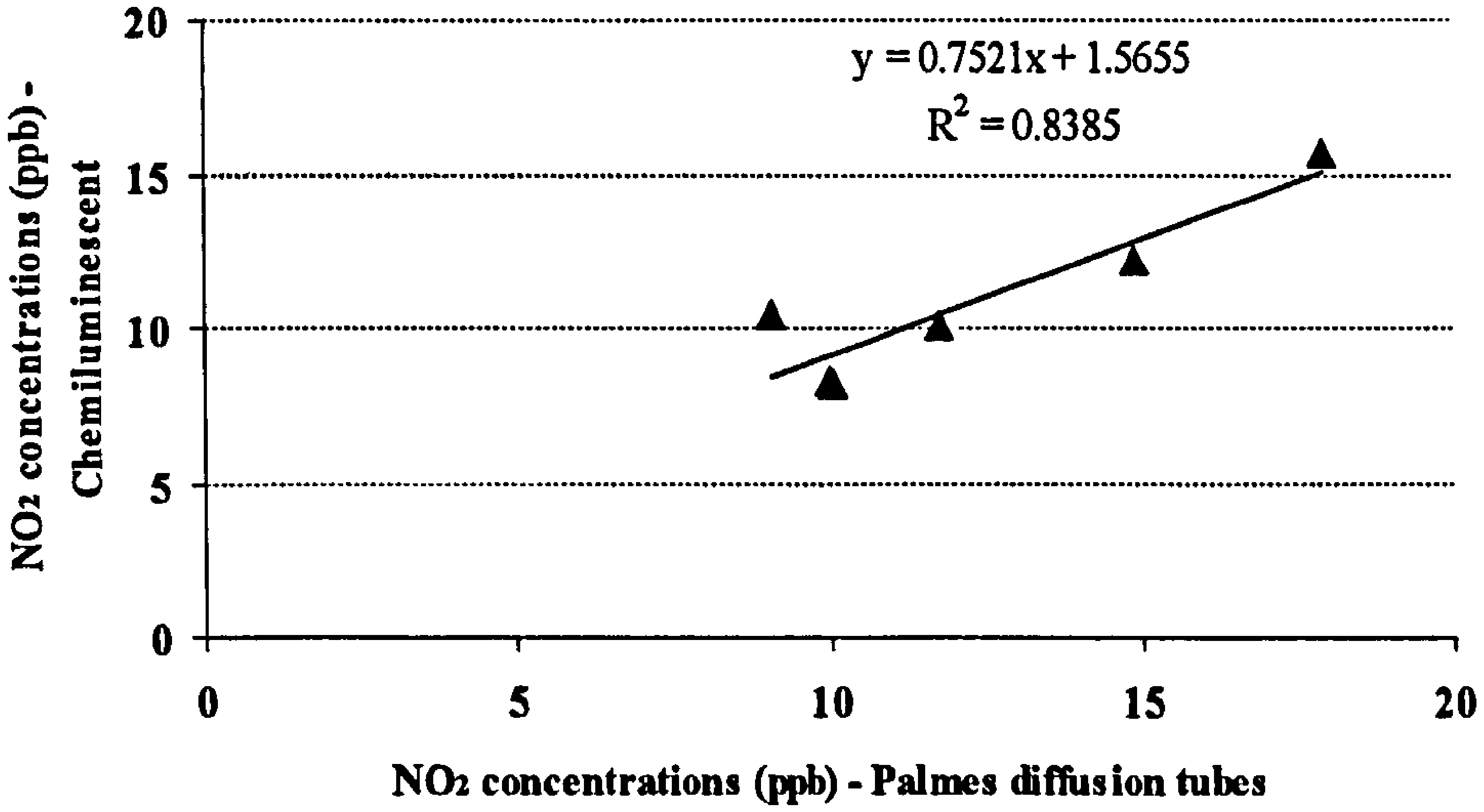


Figure 3.18 The comparison of average NO_2 concentrations from Palmes diffusion tubes and chemiluminescence monitor over six 7-day periods.

In conclusion, the modified preparation for the diffusion tubes described in this chapter showed good agreement with the chemiluminescence monitor and also gave more reliable results than the original method indicating that the modified preparation would be suitable for use in both the experiment-sites and field sites. Therefore, all Palmes diffusion tubes using through out this research programme were prepared using the modified preparation method.

Chapter 4

Methodology and Study Area

This chapter describes the methodology employed in this project. It provides details on the study area, the experimental campaigns and selection of subjects. The chapter also describes the questionnaire and time activity diaries filled in by the subjects. The chapter includes information of measurement regime, the type of data analysis performed as well as highlighting the main limitations of this study.

4.1 Overview of campaigns

Before attempting the full campaigns, two pilot studies of personal exposure measurements of NO_2 were carried out in the Hertfordshire areas during spring 2000 (April-May) with 15 subjects and summer 2000 (July-August) involving 31 subjects.

These pilot studies served the purpose of testing the sampling and analytical procedures to be used for the real field applications. Following the pilot studies the full campaigns were conduced as listed below:

(i) Autumn, 2000 (September – November); 55 subjects
(ii) Winter, 2000 (Dec 2000 - Feb 2001); 60 subjects
(iii) Summer 2001 (July-August); 30 subjects

The main campaigns were conducted over one year to identify any seasonal influences on NO_2 personal exposure measurements. The third campaign (in summer 2001) consisted of a subset of subjects from the winter study group.

4.2 Selection and description of the study area

There is scare information on measurements or modelling of personal exposure to air pollutants in the region of Hertfordshire. A small pilot study has been conducted previously in 1997 by the Building Research Establishment (BRE) in Hertfordshire to test and improve personal samplers for the continuous measurement of NO_2 and CO. The personal samplers were constructed and developed to measure peak short-term exposures for a group of 8 volunteers. Results showed that high peak of personal exposure to NO_2 were found during cooking using gas cookers and during of personal exposure to NO_2 were found during cooking using gas cookers and during travelling (Ross, 1997). Similarly, no other studies concerning personal exposure to NO_2 using passive diffusion sampling have been carried out in Hertfordshire area.

Hertfordshire, which consists of several small and medium sized towns, form part of a commuter belt to and from London (Figure 4.1). Hertfordshire is a county to the north of London in the UK, which covers an area of 1643km^2 and has a population of just over 1 million (http://www.statistics.gov.uk/). The county has excellent transport links, with the A1(M) and M1 for traffic travelling North/South and also the M25 to the south of the county, which allows traffic to get to other areas of the country using the wider Motorway system. Maximum temperatures average 22.2°C for July and minimum temperatures average 1.9°C for January. Rainfall average is 573.5 mm per year.

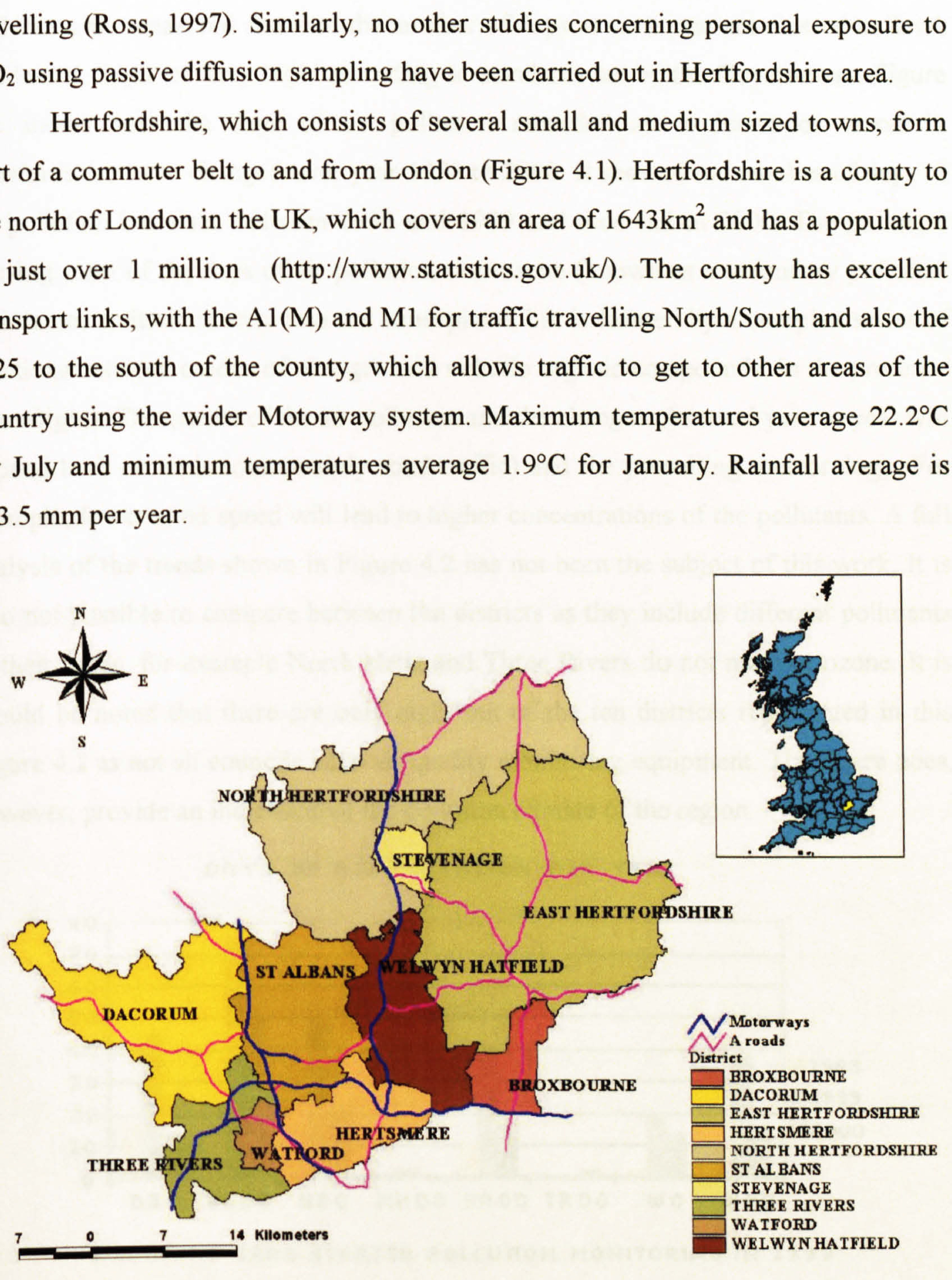
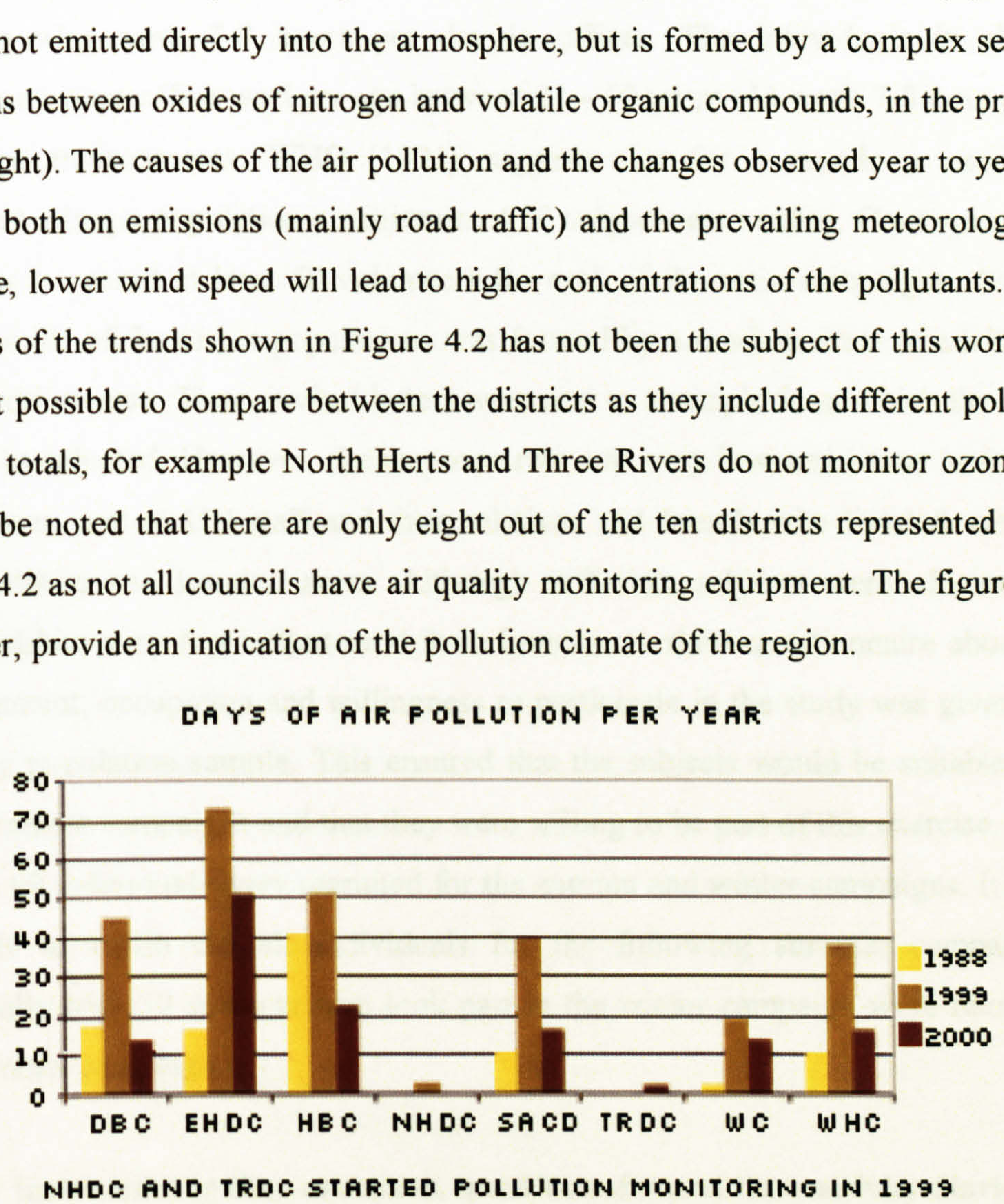


Figure 4.1 Study area

In Hertfordshire, four air pollutants, nitrogen dioxide, ozone, carbon monoxide and particulate matter (PM_{10}) are monitored (www.hertsdirect.org/yrccouncil/hcc/env/you/raiseaware/quallife/qol/invqol/qol2000/qolairpollution). Most of the ambient air pollution in the region arises from road traffic sources (Environmental Research Group, 2005). The concentration of these pollutants are measured and then the number of days in each year are classed as 'low', 'moderate', 'high' or 'very high' according to standards set by the Government. Figure 4.2 shows how the days of air pollution recorded as moderate or worse in Hertfordshire have changed over year 1998 to 2000. It showed the number of days of air pollution has risen between 1998 and 1999 and then fall in 2000. The pollutant causing most of the days of air pollution was ozone (known as a secondary pollutant as it is not emitted directly into the atmosphere, but is formed by a complex series of reactions between oxides of nitrogen and volatile organic compounds, in the presence of sunlight). The causes of the air pollution and the changes observed year to year will depend both on emissions (mainly road traffic) and the prevailing meteorology. For example, lower wind speed will lead to higher concentrations of the pollutants. A full analysis of the trends shown in Figure 4.2 has not been the subject of this work, It is also not possible to compare between the districts as they include different pollutants in their totals, for example North Herts and Three Rivers do not monitor ozone. It is should be noted that there are only eight out of the ten districts represented in this Figure 4.2 as not all councils have air quality monitoring equipment. The figure does, however, provide an indication of the pollution climate of the region.



DBC = Dacorum
NHDC = North Hertfordshire
WC = Watford
EHDC = East Hertfordshire
SACD = St.Albans
WHC = Welwyn Hatfield
HBC = Hertsmere
TRDC = Three River

Source: www.hertsdirect.org/yrccouncil/hcc/env/you/raiseaware/quallife/qol/invqol/qol2000/qolairpollution

Figure 4.2 Days of air pollution per year recorded in 1999-2000 as moderate or worse in Hertfordshire

4.3 Selection of Subjects

The target populations of this study were 21 - 60 year old office workers living and working in urban areas in the region. Although there are good train services to and from London, there is a heavy reliance on road transport for commuting journeys within the region. The first pilot study of exposure to NO_2 was conducted in spring 2000 for 15 volunteers. Then, the second pilot study was studied for 31 volunteers in summer 2000. The subjects for both pilot studies were mainly UH staff and PhD students who work 7-8 hours per day in offices. The individuals in all other campaigns were office workers age between 21 - 60 years old work 7-8 hour per day in office environments. WHO (1991) suggests that for a sample to statistically represent a target population a minimum of 50 subjects are needed. Consequently, the aim was to recruit at least 50 volunteers for each of the main campaigns. At first, a base sample of the target populations was formed by a random draw of adults in the Hertfordshire area. Then, invited letters were sent to a sample from which the subjects would be selected. However, the response rate was very low and hence invitation e-mails were sent to UH staff and their relatives and friends who lived & worked in Hertfordshire and London areas. Although sufficient subjects were obtained from Hertfordshire very few volunteered from London. A short questionnaire about home environment, occupation and willingness to participate in the study was given to this primary population sample. This ensured that the subjects would be suitable for the measurement campaigns and that they were willing to be part of this exercise. Finally, 55 and 60 individuals were recruited for the autumn and winter campaigns. It was not possible to retain the all individuals for the following summer campaign and eventually only 30 subjects who took part in the winter campaign were returned for the summer campaign.

4.4 Instruction to the volunteers, questionnaire and time activity diaries

The selected subjects were given instructions on the use of the samplers, (see Appendix). It was important to ensure that the instructions were easy to understand and follow especially regarding the placement of the samplers close to the breathing zone. Instructions were also provided where to place the samplers for indoors and outdoors measurements. An important consideration was not to place the samplers close to any NO_2 source, It was also important to place the samplers safely nearby when the subject was in the bathroom or when sleeping in the case of personal exposure measurements.

Questionnaires and time activity diaries diary were completed by the individuals and these are given in the Appendix. During the preparation of the questionnaire, the objectives of the study were clearly defined and the sampling group was determined. The questionnaire was then prepared and tested on a small number of volunteers. This was important to ensure that the meaning of each question was clear and unambiguous and would be understood by all participants before it was distributed.

The purposes of the questionnaire was as follows:

(i) To establish whether the subjects intended to participate for the whole campaign and to get some background information such as their occupation and age.

(ii) To collect data on factors that might influence personal exposure to NO_2 including characteristics of home, presence of smokers within home, types of cooking and heating system, the use of windows for ventilation, characteristics of office.

The purpose of the cooking time diary was to assess times when a cooking appliance was used in the household during the study period. The purpose of the time activity diaries was to estimate the times that individuals spent in the various microenvironments or undertaking other activities. Hence the following measurements of NO_2 were conducted:

(i) In different microenvironments.
(ii) Ambient environment (outside the home)
(iii) On the person

The individuals filled in the time activity diaries at 15 minute intervals. Usually the time activity diaries were collected from Monday morning to Monday morning or from Friday evening to Friday evening for 168 hours.

4.5 Measurement Regime

4.5.1 General protocols

NO_2 is measured as nitrite produced through chemical reactions with the reactive coated meshes inside the Palmes diffusion tubes (Palmes et al. 1976). The reactive coating meshes were analysed using a spectrophotometer at 540 nm and the integrated loadings of the reaction product were used to infer the average nitrite concentration. The analysis of the tubes was carried out at the University of Hertfordshire laboratory.

The Palmes diffusion tubes were prepared and placed in a sealed plastic bag and then kept in a fridge in a laboratory at the University of Hertfordshire ready to be used. Then, the diffusion tubes including blank tubes were given to the subjects a night before the start date. Blank tubes were kept in the fridge during the sampling period. An instruction booklet was also given to the volunteers to commencing the project. This included advice to avoid getting the tubes wet or damaged and always clipping the tubes onto the volunteers' collar and to keep the tubes outside of coats in the case personal exposure measurements. The tubes were exposured for one week (7 days) both for personal and microenvironment measurements. Concentrations of NO_2 were measured at the volunteers' houses (bedroom, living room and kitchen), their offices, inside their cars (if appropriate) and outside their houses (at the front door). Two passive Palmes diffusion tubes were used at each location. The volunteers were given instructions to uncap and place the Palmes tubes in the above microenvironments ready for exposure and then to recap the tubes at the end of the sampling period. Each volunteer was also asked to wear two Palmes diffusion tubes at breathing height for a 7-day period. Times of uncapping and recapping the diffusion tubes were documented by the volunteers on a record slip accompanying the instructions. The exposed tubes were placed in a plastic bag by the volunteers and returned to the researcher with the questionnaires and daily activities diaries.

4.5.2 Microenvironment measurements

Ideally, passive samplers would be placed at breathing height, but in order to reduce theft of tubes from outdoor sites, it is recommended that tubes are placed at a height 2-4 m, and in all cases no higher than 5 m (AEA Technology, 2003), also to avoid sampling in an area of higher than usual turbulence, the tube should not be located in the corner of a room or on the corner of a building. Moreover, to avoid any very localised sources or sinks of NO_2 or disturbances to the air flow, the tube should not located near heater flues, trees and other vegetation, air conditioning outlets, extractor vents and underground ventilation shafts. Also, tubes should not be mounted directly adjacent to surfaces due to the surfaces may act as absorbers for NO_2 leading to a thin layer of reduced atmospheric concentrations immediately adjacent to the surfaces. A spacer block of at least 5 cm should be used between the surface and the tubes. In this thesis, a stainless steel plate used as the spacer, as shown in Figure 3.1 in Section 3.1.

4.5.2.1 Indoor microenvironment measurements

For the purpose of this study, a microenvironment is a location where the air pollutant concentrations at any time can be considered relatively homogenous. The indoor microenvironments considered in this research were bedrooms, living rooms, kitchens, and offices. The indoor Palmes diffusion tubes were placed in the middle of the room and to avoid windows, corners and heating vents.

4.5.2.2 Outdoor microenvironment measurements

Average ambient NO_2 concentrations were measured using two diffusion tubes at the front door (outside) of the individuals' houses. The outdoor diffusion tubes were located at approximately 2 m above the ground away from possible localised pollutant sources such as driveways, roads and exhaust vents.

4.5.2.3 Other microenvironment measurements

Average NO_2 concentrations were measured using two diffusion tubes inside of the individuals' cars.

4.6 Data Analysis

The weekly average NO_2 concentrations from each diffusion tube was calculated according to Fick's law (Bird et al., 1960). Results of the weekly average NO_2 concentrations from each tube analysed were provided in ppb.

Statistical data analysis was performed using Microsoft EXCEL programme. Descriptive data or simple summary statistics such as mean, standard deviation and variance were derived to describe the distribution of NO_2 concentrations to which the individuals were exposed. Paired t-test was used to check the difference between the means estimated through time weighted average microenvironmental exposure and measurement of personal exposure to NO_2. Correlation coefficient was used to summarise the relationship between personal exposure and the exposure levels measured in microenvironments. Details of the statistical analysis can be found in a range of sources such as Ryan, 2000; Walpole, Myers and Myers 1998; Mason, Lind, and Marchal, 1999; Johnson, 1996. The statistics are briefly described below:

The sample mean

Mean ($\bar{x}$) is a numerical average which is calculated as the summation of all data divided by the number of data in the sample.

$$\bar{x} = \frac{\sum x_i}{n}$$

where, $\sum x_i$ is the summation of all data ($x_1 + x_2 + x_3 + ... x_n$)

n is the sample size, that is, the number of data in the sample.

(The population mean is represented by μ.)

The sample variance

Variance (s^2) represents the difference between a given value of x and the mean $\bar{x}$. It is the mean of the squared deviations, calculated using n-1 as the divisor as shown below (Johnson, 1996).

$$s^2 = \frac{\sum (x_i - \bar{x})^2}{n-1}$$

Where $(x_i - \bar{x})$ is the difference between the value of x and the mean $\bar{x}$. This deviation $(x_i - \bar{x})$ is zero when x_i is equal to the mean $\bar{x}$. It is positive if x is larger than $\bar{x}$ and negative if x is smaller than $\bar{x}$. n is the sample size, that is, the number of data in the sample. The population variance is normally represented as σ^2.

The sample standard deviation

Standard deviation (s) is a measure of variability calculated as the square root of the variance (s^2).

$$s = \sqrt{\frac{\sum (x_i - \bar{x})^2}{n-1}}$$

(The population standard deviation is σ.)

Single sample: tests concerning a single mean (known variance)

A hypothesis test on a population mean (μ) with known variance of the population (σ^2) is as follow:

H_0: $\mu = \mu_0$,

H_1: $\mu \neq \mu_0$

The random variables $x_1, x_2, ..., x_n$ represent a random sample from a normal distribution with known mean μ and variance $\sigma^2 > 0$. The test statistic is based on the random variable $\bar{x}$. As the random variable $\bar{x}$, has approximately a normal distribution with mean μ and variance σ^2/n for reasonably large sample sizes. Then, determine a two-tailed critical region based on the computed sample average $\bar{x}$. (The normal approximation for $\bar{x}$ will be good if $n \geq 30$ regardless of the shape of the population. If $n < 30$, the approximation is good only if the population is not too different from a normal distribution and if the population is known to be normal, the sampling distribution of $\bar{x}$ will follow a normal distribution, no matter how small the size of the samples is.)

It is convenient to standardise $\bar{x}$ and formally involve the standard normal random variable z, where

$$z = \frac{\bar{x} - \mu}{\sigma / \sqrt{n}}$$

Rejection of H_0 at significance level α results (such as 0.05) when a computed test statistic exceeds $z_{\alpha/2}$ or is less than $- z_{\alpha/2}$ ($z > z_{\alpha/2}$ or $z < - z_{\alpha/2}$). If $- z_{\alpha/2} < z < z_{\alpha/2}$, do not reject H_0. Rejection of hypothesis H_0 means hypothesis H_1 is accepted as $\mu \neq \mu_0$.

Two samples t-test on the difference between two means

In this case, the hypothesis test on two populations means (μ_1 and μ_2) with known two population variances (σ^2_1 and σ^2_2). The hypothesis is as follow:

H_0: $\mu_1 = \mu_2$,
H_1: $\mu_1 \neq \mu_2$

An estimator of the difference between μ_1 and μ_2 is given by the statistic $\bar{x}_1$-$\bar{x}_2$.

$$z = \frac{(\bar{x}_1 - \bar{x}_2) - (\mu_1 - \mu_2)}{\sqrt{(\sigma_1^2 / n_1) + (\sigma_2^2 / n_2)}}$$

The sampling distribution of $\bar{x}_1$-$\bar{x}_2$ to be approximately normally distributed with mean $\mu_{\bar{x}_1 - \bar{x}_2} = \mu_1 - \mu_2$ and standard deviation $\sigma_{\bar{x}_1 - \bar{x}_2} = \sqrt{(\sigma_1^2 / n_1 + (\sigma_2^2 / n_2)}$. Therefore, a probability of 1–α can be stated that the standard normal variable will fall between $-z_{\alpha/2}$ and $z_{\alpha/2}$. Rejection of H_0 at significance level α results (such as 0.05) when a computed test statistic exceeds $z_{\alpha/2}$ or is less than $- z_{\alpha/2}$ ($z > z_{\alpha/2}$ or $z < - z_{\alpha/2}$). If $- z_{\alpha/2} < z < z_{\alpha/2}$, do not reject H_0. Rejection of hypothesis H_0 means hypothesis H_1 is accepted as $\mu_1 \neq \mu_2$.

Correlation analysis

Correlation analysis attempts to measure the strength of relationships between two variables by means of a single number called a correlation coefficient (*r*). Value of $r = \pm 1$ only occur when $\sigma^2 = 0$, in which a perfect linear relationship between the two variables can be observed. A value of *r* equal to +1 implies a perfect linear relationship with a positive slope, while a value of *r* equal to -1 results from a perfect linear relationship with a negative slope, as $-1 \leq r \leq 1$. The sample estimates of *r* close to unity in magnitude imply good correlation or linear association between x and y, whereas values near zero indicate little or no correlation.

The measure of linear association between two variables *x* and *y* is estimated by from the following expression for *r*:

$$r = \frac{S_{xy}}{\sqrt{S_{xx} S_{yy})}}$$

where, $S_{xy} = \sum (x_i - \bar{x})(y_i - \bar{y})$; $S_{xx} = \sum (x_i - \bar{x})^2$; $S_{yy} = \sum (y_i - \bar{y})^2$

In data interpretation, for example, values of r equal to 0.3 and 0.6 mean that the results found two positive correlations, the latter representing a stronger correlation than the other. r^2 represents the proportion of the variation of S_{yy} explained by the regression of y on x. r^2 expresses the proportion of the total variation in the values of the variable y that can be accounted for or explained by a linear relationship with the values of the random variable x. thus a correlation of 0.6 means that 0.36, or 36% of the total variation of the values of y in the sample is accounted for by a linear relationship with values of x.

4.7 Limitations of the study

In this current study, it should be noted that subjects are not representative of the UK population as a whole, but are representative of the adult population (21-60 years old) working 7-8 hour/day in office environments.

There are a number of limitations to this study that can be identified. The main sources of high exposure to NO_2 are usually gas cooking and transport emissions. However, the questionnaires revealed that subjects were using a variety of cooker types (gas, electric and microwave) during the study campaigns. The subjects also were of different ages and hence would normally exhibit different activity patterns. The transport methods and journeys to work also differed as did occupation and workplace. Overall, it was difficult to recruit sufficient volunteers to ensure statistically significant representation of the all the above variations.

There was also limitation due to some of questionnaires and time activity diary not being returned (11 % and 13%, respectively). In a few cases (5 % of the returns) the volunteers did not record their time activities diary properly. For example, the activity diary was not completed for the whole period. Those missing questionnaires and time activities diaries led to under representation of personal exposure to NO_2 for passive smokers and smokers as the number of subjects was very low to make statistically significant conclusions.

It was not possible to measure exposure levels at all the environments visited by the subjects. For example, measurements were not conducted at locations such as public transportation (eg buses), shopping centres, leisure centres or public houses. The responses to the activity questionnaires and the subsequent data analysis showed that whilst these areas could be important they were not critical in determining the overall personal exposure of the individuals.

Chapter 5

Results and Discussion

This chapter presents the results and discussion of the NO_2 personal exposure measurements from the pilot and main campaigns. It was necessary to undertake preliminary campaigns to test the components of the overall methodology, including sampling, chemical analysis and the activity questionnaire. This chapter also presents the results and discussion of the NO_2 personal exposure measurement campaigns of office workers in Hertfordshire. The chapter discusses the relationship between personal exposure to NO_2 and indoor and outdoor sources and activity patterns. Although 'personal exposure' is defined as concentration multiplied by time, it is treated here as concentration (in ppb or $\mu g/m^3$) measured on the individuals. In section 5.5 exposure is considered in units of ppb.h. The datasets discussed in this chapter include the personal exposure to NO_2, NO_2 concentrations measured inside and outside houses and the time budget reported by volunteers through a time activities diary. The time budget and NO_2 concentrations from each microenvironment were then correlated to calculate weighted average personal exposures. Then, the weighted average personal exposures were compared with the personal exposure measurement data from the individuals during the campaigns.

5.1 Pilot studies of personal exposure to NO_2

Two pilot studies of personal exposure to NO_2 were designed and run in spring and summer 2000. The main purpose of the pilot studies was to test that the Palmes diffusion tubes preparation method and the overall methodology in real field situations. Details on these studies campaigns have been given in Section 4.1 (Chapter 4). In spring, the exposure of 15 volunteers to NO_2 was estimated in two different ways: personal exposure measurements of NO_2 concentrations and the time weighted average micro-environmental exposure modelling (TWME) (calculation of weighted average exposures using data on time spent in each microenvironment: bedrooms, living rooms, kitchens, front door, at work, in transit, and outdoors, respectively and NO_2 concentrations measured from those microenvironments for a 7 day-period). At the same time, questionnaires and activity patterns were filled in and recorded by the volunteers. The second pilot study was followed up with a larger subject group of 31 volunteers in summer (as shows in Table 5.1).

Table 5.1 Total number of volunteers includes only those who had completed the time activities diaries and questionnaires used for pilot studies and main campaigns.

	Pilot studies		Main campaigns			Total
	Spring 2000	Summer 2000	Autumn 2000	Winter 2000	Summer 2001*	Number of datasets
Total invited volunteers	15	31	55	60	30	191
Total completed time activities pattern diaries	15	31	40	55	25	166
Total completed questionnaires	15	30	40	55	30	170

5.2 Pilot study in spring 2000

5.2.1 Questionnaires & Activity Daily Diaries

During the first pilot study of personal exposure to NO_2 carried out in spring 2000 all 15 questionnaires and time activities diaries were completed and returned. Results from the questionnaires are reported in Table 5.2. The 15 subjects consisted of 6 male and 9 femal. Eleven of the subjects lived in Hertfordshire and 4 lived in London. The details also showed 9 volunteers used gas cookers and 6 volunteers used electric cookers. 2 volunteers were smokers, 3 volunteers were passive smokers and 10 volunteers were non-smokers.

Individual' ages were grouped from 21-25, 26-30, 31-35, 36-40, 41-45, 46-50, 51-55, and 56-60 years. The results showed that 33.3% of the population was in groups 21-25 and 26-30 years. Most of the volunteers (46.7%) lived in flats. Over 80% of the properties had double glazed windows, while less than 20% of the windows were mixed glazing (double glazing mixed with single glazing). Most of the individuals (66.5%) were commuters who travelled by buses, trains, underground, and bicycles and also on foot. Less than 40% of the volunteers were car owners. 56.3% of the volunteers said their cars were parked at the residents' car parks, followed by 43.8% of those who parked their cars at the kerbside of the roads. 66.7% of the individuals worked in separate offices, followed by 33.3% that worked in open plan offices. All of the offices had windows.

All of the subjects lived in urban areas such as London, Hatfield, St. Albans, Hertford, Welwyn Garden Citiy (WGC), Stevenage and Harpenden. 73.3% of their residences were located on the outside the town centres, followed by 26.7% of those located in the inner town regions. Most of volunteers shared their properties with another person. Most (90%) of the subjects did not have children. All properties had the central heating systems powered by natural gas but these were not in use during the study period (except for hot water). Location of the central heating/hot water boilers were mainly located in kitchen but some were in the hallway, living room and bedroom. In all cases, the location of boiler outlet pipes was outdoors. The properties did not have any extra boilers for hot water. Only 26.7% of the kitchens were equipped with kitchen fans (filter and recirculation) or extractors which were in used frequently during cooking and 5-10 minute after cooking.

Results from the activity patterns showed that all volunteers spent more than 80% of their time indoors (as shows in Figure 5.1) including 54.6% in house, 25.1% at work, 5.3% in transport vehicles, and also spent about 6.0% in other non-smoking areas (such as in shopping malls, at cinemas), 3.3% in other smoking areas (such as in restaurants, public houses). The individuals also spent 5.6% of their time outdoors.

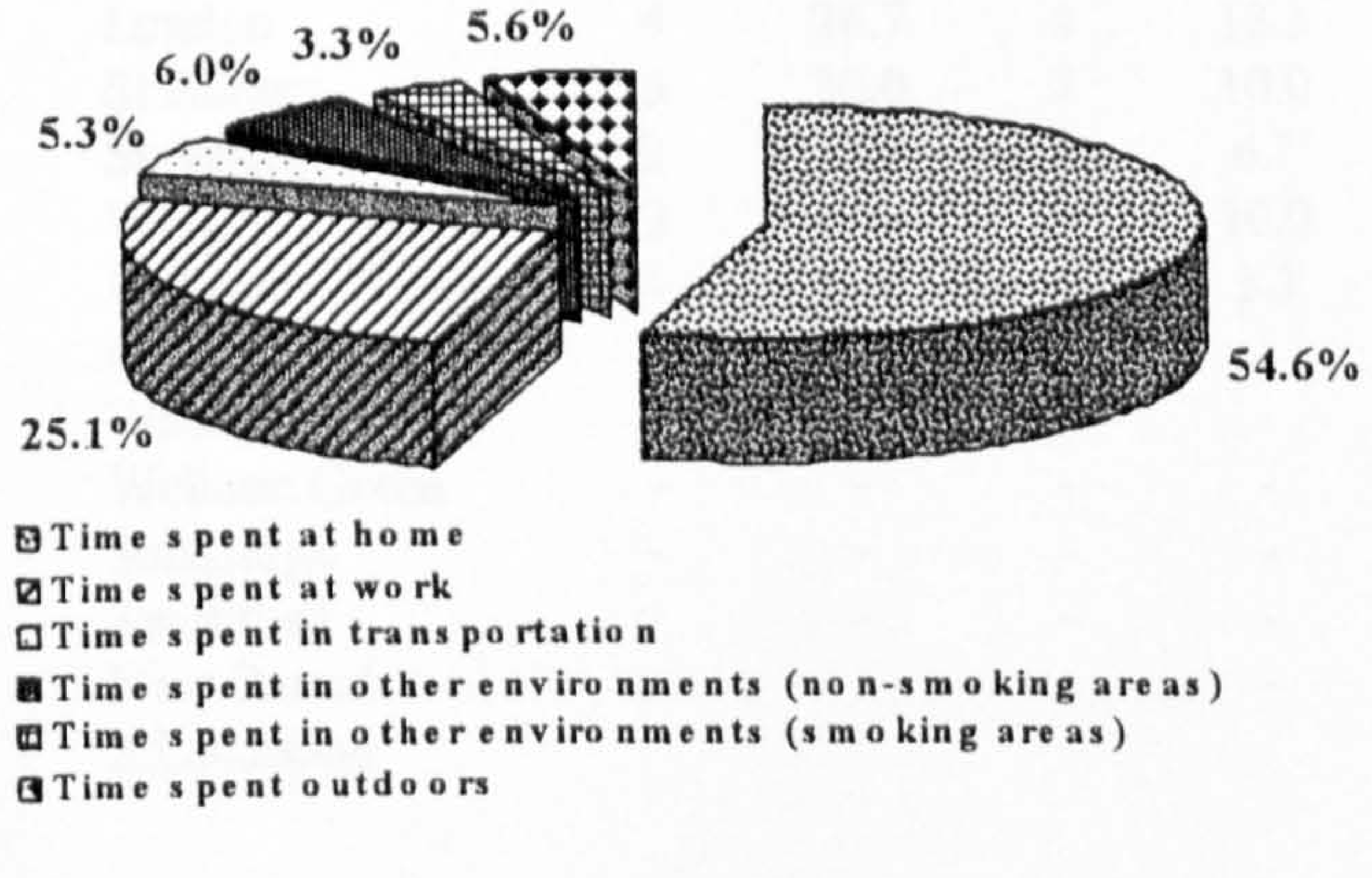


Figure 5.1 Average time activity patterns in microenvironments for all volunteers for a 7-day exposure period during pilot studies in spring

Table 5.2a. Results from the questionnaires for pilot studies and main campaigns providing gender and smoking details.

	Pilot studies				**Campaigns**					
	Spring 2000		Summer 2000		Autumn 2000		Winter 2000		Summer 2001*	
Total completed	N	%	N	%	N	%	N	%	N	%
questionnaires	15		30		40		55		30	
Details o individuals										
1.Gender										
Male	6	40.0	13	43.3	15	37.5	24	43.6	13	43.3
Female	9	60.0	17	56.7	25	62.5	31	56.4	17	56.7
2.Smoking habit										
Non-smoker	10	66.7	23	76.7	29	72.5	37	67.3	21	70.0
Passive smoker	3	20.0	4	13.3	7	17.5	11	20.0	7	23.3
Smoker	2	13.3	3	10.0	4	10.0	7	12.7	2	6.7
3.Age groups										
21-25yr	5	33.3	13	43.3	14	35.0	9	16.4	3	10.0
26-30yr	5	33.3	9	30.0	17	42.5	15	27.3	6	20.0
31-35yr	2	13.3	4	13.3	3	7.5	10	18.2	4	13.3
36-40yr	1	6.7	2	6.7	2	5.0	-	-	-	-
41-45yr	1	6.7	1	3.3	2	5.0	10	18.2	9	30.0
46-50yr	-	-	-	-	1	2.5	5	9.1	4	13.3
51-55yr	1	6.7	1	3.3	1	2.5	4	7.3	3	10.0
56-60yr	-	-	-	-	-	-	2	3.6	1	3.3

Table 5.2b. Results from the questionnaires for pilot studies and main campaigns providing details on location.

	Pilot studies				**Campaigns**					
	Spring 2000		Summer 2000		Autumn 2000		Winter 2000		Summer 2001*	
Total completed	N	%	N	%	N	%	N	%	N	%
questionnaires	15		30		40		55		30	
Location of houses										
1.Cities/Towns										
Harpenden	1	6.7	1	3.3	1	2.5	-	-	-	-
Hatfield	3	20.0	16	53.3	13	32.5	14	25.5	8	26.7
London	4	26.7	4	13.3	1	2.5	-	-	-	-
St.Albans	3	20.0	3	10.0	11	27.5	11	20.0	8	26.7
Stevenage	2	13.3	2	6.7	2	5.0	-	-	-	-
WGC*	2	13.3	3	10.0	5	12.5	7	12.7	5	16.7
Hertford	-	-	1	3.3	7	17.5	7	12.7	4	13.3
Pottersbar	-	-	-	-	-	-	3	5.5	1	3.3
Watford	-	-	-	-	-	-	2	3.6	-	-
Welham Green	-	-	-	-	-	-	2	3.6	2	6.7
Sandridge	-	-	-	-	-	-	1	1.8	-	-
Smallford	-	-	-	-	-	-	3	5.5	2	6.7
New Barnet	-	-	-	-	-	-	5	9.1	-	-
2.Locations										

Outer town	11	73.3	17	56.7	38	95.0	55	100	30	100
City centre	4	26.7	13	43.3	2	5.0	-	-	-	-
3.Types of street										
Minor single carriageway	2	13.3	2	6.7	3	7.5	3	5.5	2	6.7
Minor estate road	10	66.7	24	80.0	34	85.0	51	92.7	27	90.0
Main estate road	3	20.0	4	13.3	3	7.5	1	1.8	1	3.3

*WGC = Welwyn Garden City

Table 5.2c. Results from the questionnaires for pilot studies and main campaigns providing details on accommodation.

	Pilot studies				**Campaigns**					
	Spring 2000		**Summer 2000**		**Autumn 2000**		**Winter 2000**		**Summer 2001***	
	N	%	N	%	N	%	N	%	N	%
Total completed questionnaires	15		30		40		55		30	
4.Types of property										
Centre terrace house		20.0		30.0		32.5		25.5		26.7
End terrace house		6.7		3.3		2.5		5.5		10.0
Semi-detached house		26.7		26.7		32.5		40.0		30.0
Flat		46.7		40.0		32.5		29.1		33.3
5.Total adults in houses										
1 person	1	6.7	1	3.3	2	5.0	-	-	-	-
2 people	6	40.0	10	33.3	25	62.5	55	100	30	100
3 people	5	33.3	8	26.7	7	17.5	-	-	-	-
4 people	3	20.0	7	23.3	2	5.0	-	-	-	-
5 people	-	-	4	13.3	4	10.0	-	-	-	-
6.Total children in houses										
None	14	93.3	27	90.0	34	85.0	24	43.6	10	33.3
1 child	1	6.7	3	10.0	4	10.0	10	18.2	4	13.3
2 children	-	-	-	-	2	5.0	18	32.7	14	46.7
3 children	-	-	-	-	-	-	3	5.5	2	6.7
7.Types of glazing										
Double glazing	12	80.0	22	73.3	37	92.5	52	94.5	28	93.3
Mixed	3	20.0	8	26.7	3	7.5	3	5.5	2	6.7

Table 5.2d. Results from the questionnaires for pilot studies and main campaigns providing details on cookers, ventilation and travel.

	Pilot studies				**Campaigns**					
	Spring 2000		Summer 2000		Autumn 2000		Winter 2000		Summer 2001*	
	N	%	N	%	N	%	N	%	N	%
Total completed questionnaires	15		30		40		55		30	
8.Types of cooker										
Natural gas cooker	9	60.0	17	56.7	24	60.0	27	49.1	15	50.0
Electric cooker	6	40.0	13	43.3	16	40.0	28	50.9	15	50.0
9.Ventilation in kitchen										
Windows	11	73.3	21	70.0	25	62.5	34	61.8	17	56.7
Windows & an extractor fan	4	26.7	9	30.0	15	37.5	21	38.2	13	43.3
10.Car owners /commuters										
Commuters	10	66.7	14	46.7	18	45.0	26	47.5	6	20.0
Car owners	5	33.3	16	53.3	22	55.5	29	52.7	24	80.0
11.Petrol types										
U/L petrol	5	100	15	93.8	19	86.4	24	82.8	19	79.2
Diesel	-		1	6.3	3	13.6	5	17.2	5	20.8
12.Locations of car park										
Road kerbside	3	60.0	7	43.8	9	40.9	10	34.5	7	29.2
Resident car park	2	40.0	9	56.3	11	50.0	11	37.6	9	37.5
Garage	-	-	-	-	2	9.1	8	27.6	8	33.3

Table 5.2e. Results from the questionnaires for pilot studies and main campaigns providing details on work place.

	Pilot studies				**Campaigns**					
	Spring 2000		Summer 2000		Autumn 2000		Winter 2000		Summer 2001*	
	N	%	N	%	N	%	N	%	N	%
Total completed questionnaires	15		30		40		55		30	
13.Types of office										
Separate office	10	66.7	7	76.7	11	27.5	16	29.1	9	30.0
Open plan	5	33.3	23	23.3	29	72.5	39	70.9	21	70.0
14.Quantity of people in the office										
1 person	2	13.3	-	-	4	10.0	6	10.9	4	13.3
2 people	4	26.7	5	16.7	5	12.5	9	16.4	4	13.3
3 people	4	26.7	2	6.7	2	5.0	1	1.8	1	3.3
4 people	-	-	2	6.7	3	7.5	7	12.7	4	13.3
5 people	2	13.3	6	20.0	7	17.5	13	23.6	7	23.3
6 people	1	6.7	4	13.3	6	15.0	12	21.8	6	20.0
7 people	2	13.3	7	23.3	5	12.5	6	10.9	3	10.0
8 people	-	-	4	13.3	3	7.5	1	1.8	1	3.3
9 people	-	-	-	-	3	7.5	-	-	-	-
10 people	-	-	-	-	2	5.0	-	-	-	-

15.Ventilation in office										
A/C	-	-	5	16.7	-	-	4	7.3	2	6.7
Windows	15	100	23	76.7	37	92.5	46	83.6	24	80.0
Windows & A/C	-	-	2	6.7	3	7.5	5	9.1	4	13.3

5.2.2 Personal exposure and average NO_2 concentrations from each microenvironment

Total numbers of Palmes diffusion tubes for measuring NO_2 concentrations during the campaigns are given in Table 5.3. The personal exposure to NO_2 concentrations and the average of NO_2 concentrations from several microenvironments which were measured during pilot study are presented in Table 5.4. Three facts can be readily observed, (i) the weekly personal exposure to NO_2 of volunteers who used gas cookers was over two times higher than those who had electric cookers and than the average outdoor NO_2 concentration, (ii) the weekly average of NO_2 concentrations in kitchens and living rooms in houses with gas cookers were higher than those with electric cookers, and (iii) the weekly ambient NO_2 concentration was clearly lower than the UK National Air Quality Strategy Standard limit values for NO_2 of 21 ppb or 40 $\mu g/m^3$, measured as annual average (AQEG, 2004). For two houses the weekly average was 21.1 and 23.7 ppb – these were located in the town centre areas. It is appreciated that the comparison should strictly be based on annual measurements but it does give an indication of the exposure levels in relation to air quality standards.

Table 5.3 Total number of Palmes diffusion tubes used for measuring NO_2 concentrations from pilot studies and main campaigns.

Studies	Personal exposure	Microenvironments						Total
		Bedrooms	Living rooms	Kitchens	Front doors	Offices	Cars	
Spring 2000	30	30	30	30	30	30	10	190
Summer 2000	62	62	62	62	62	62	32	404
Autumn 2000	110	110	110	110	110	110	44	704
Winter 2000	120	120	120	120	120	120	58	778
Summer 2001*	60	60	60	60	60	60	48	408

Personal exposure to NO_2 concentrations for all volunteers (as shows in Table 5.4) ranged from 9.1 to 17.3 ppb. The weekly average NO_2 concentrations in bedrooms, living room, kitchens and front doors ranged from 6.5 to 18.6 ppb, 7.5 to 25.6 ppb, 7.8 to 33.8 ppb, and 10.4 to 23.7 ppb respectively. The weekly average NO_2 concentrations in offices and cars ranged from 6.4 to 15.6 ppb and 6.6 to 8.5 ppb. As can be observed in Table 5.4 the highest concentrations were measured in kitchens.

Table 5.4 Personal exposure to NO_2 and weekly average NO_2 concentrations measured from each microenvironment in pilot study during spring.

Cooker types	Personal exposure	Weekly average NO_2 concentrations in microenvironments (ppb)					
		Bedrooms	Living rooms	Kitchens	Front doors	Offices	Cars
Gas	12.4	13.1	15.9	**33.8***	17.0	9.3	-
Gas	10.3	10.7	**25.6***	**29.7***	15.9	9.8	-
Gas	15.4	15.5	20.7	**22.2***	17.1	12.1	-
Gas	17.3	13.7	12.7	16.5	**21.1***	15.6	-
Gas	14.1	18.6	16.9	**22.4***	19.0	9.5	-
Gas	10.6	10.7	14.3	20.5	10.8	8.3	7.3
Gas	16.5	13.5	16.2	**24.1***	**23.7***	8.8	-
Gas	16.9	18.0	18.8	20.3	18.6	9.6	6.6
Gas	14.0	13.4	17.0	**22.0***	16.8	6.4	-
Electric	9.7	6.5	8.1	9.8	16.9	9.9	-
Electric	9.1	8.6	9.6	10.7	11.9	9.9	7.9
Electric	14.2	12.7	12.8	10.0	13.3	10.2	7.0
Electric	14.6	11.9	12.7	11.2	16.8	11.9	-
Electric	12.9	7.6	8.8	9.6	16.7	11.6	-
Electric	11.4	6.7	7.5	7.8	10.4	10.2	8.5
Min.	**9.1**	**6.5**	**7.5**	**7.8**	**10.4**	**6.4**	**6.6**
Max.	**17.3**	**18.6**	**25.6**	**33.8**	**23.7**	**15.6**	**8.5**
Average	**13.3**	**12.1**	**14.5**	**18.0**	**16.4**	**10.2**	**7.4**
Stdev.	**2.7**	**3.7**	**5.0**	**8.0**	**3.6**	**2.1**	**0.4**

Note: * Concentrations higher than the UK National Air Quality Strategy Standard for NO_2 (21 ppb).

As also shown in Table 5.4, personal exposure to NO_2 concentrations of volunteers living in houses with gas cookers ranged from 10.3 to 17.3 ppb (average 14.2 ppb, as presented in Figure 5.2) while the NO_2 concentrations in bedrooms, living rooms and kitchens ranged from 10.7 to 18.6 (average 14.1 ppb), 12.7 to 25.2 ppb (average 17.6 ppb), and 16.5 to 33.8 ppb (average 23.5 ppb), respectively. In addition, average personal exposure to NO_2 concentrations of volunteers living in houses with electric cookers was

12.0 ppb (ranged from 9.1 to 14.2 ppb) while the NO_2 concentrations in bedrooms, living rooms and kitchens ranged from 6.5 to 12.7 (average 9.0 ppb), 7.5 to 12.8 ppb (average 9.9 ppb), and 7.8 to 11.2 ppb (average 9.9 ppb), respectively. The main finding here is that higher concentrations of NO_2 are found in houses with gas cookers compared to electric cookers. This would be expected as gas cookers are key source of NO_2.

As highlighted above the average NO_2 concentration in all rooms in houses with gas cookers was found to be higher than those with electric cookers, especially in kitchens where the value was 2.5 time higher (as shown in Figure 5.2). Personal exposure to NO_2, on the other hand, for volunteers living in houses with gas cookers was only slightly higher when compared with those living in houses with electric cookers. One reason could be because the volunteers (living in houses with gas cookers) did not spend much time in the kitchens. Another reason could be due to the fact that the volunteers, who lived in houses with electric cookers, were exposed to NO_2 from other sources such as public houses and transportations which were not measured in this study.

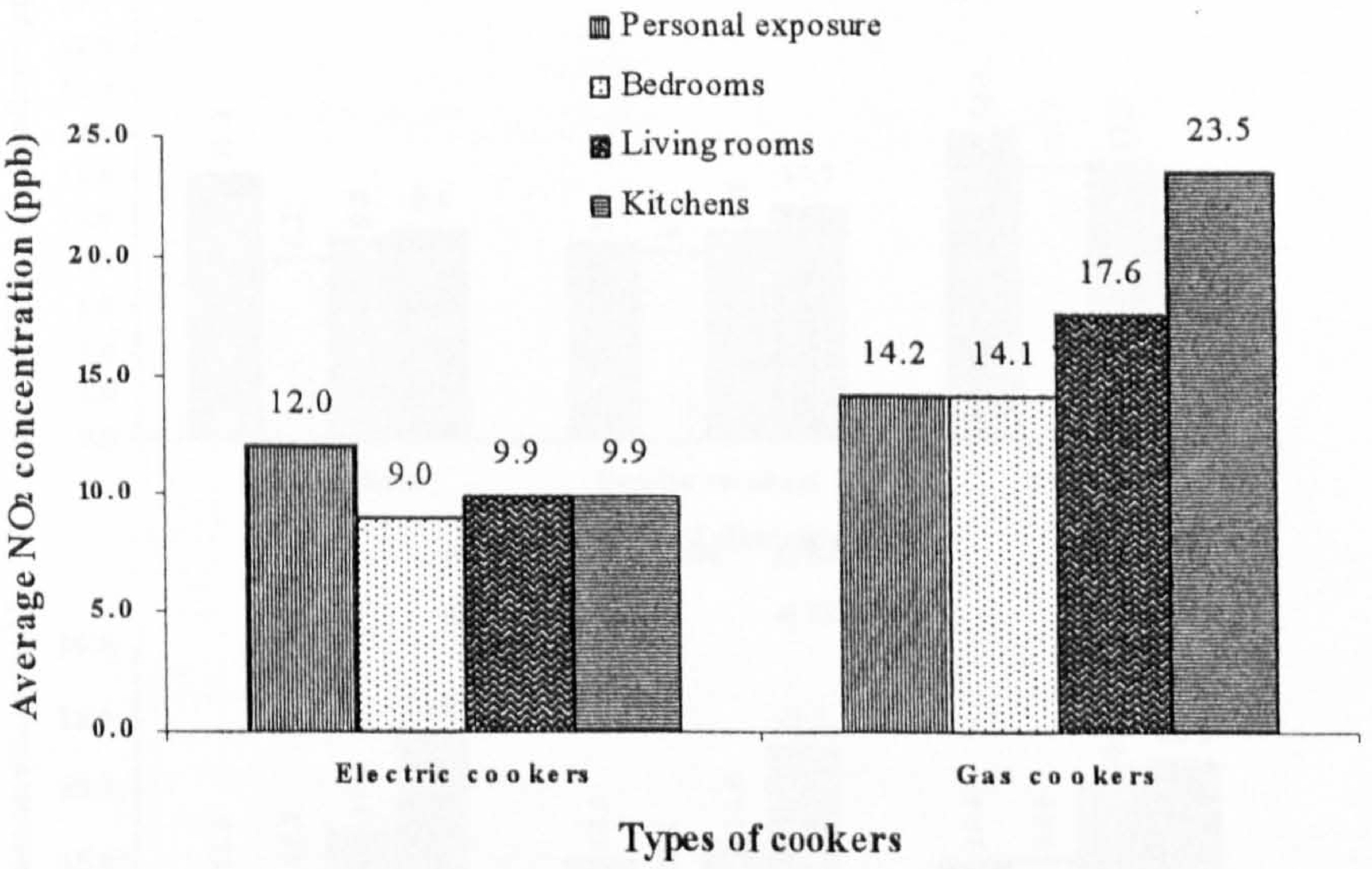


Figure 5.2 Personal exposure to NO_2 and average NO_2 concentrations measured in bedrooms, living rooms and kitchens with electric and gas cookers during pilot study in spring.

Average personal exposure to NO_2 of smokers (14.2 ppb) was higher than average personal exposure to NO_2 of non-smokers (12.2 ppb) and passive smokers (9.1 ppb), as well as, average NO_2 concentration in bedrooms and living rooms of smokers were higher than those rooms of non-smokers and passive smokers (as shows in Figure 5.3), which can be seen clearly in houses with electric cookers without other NO_2 sources (such as gas cookers) to interfered. The number of subjects was too low to make statistical significant conclusions on the results for smokers and passive smokers (see Table 5.2a). However, the micro-environmental NO_2 levels were similar for non-smokers and passive smokers. Personal exposure levels however, were higher for passive smokers compared to non-smokers. Interpretation of these results is difficult as mentioned above the number of subjects were low. In addition activity patters would need to be examined to arrive at any possible explanation.

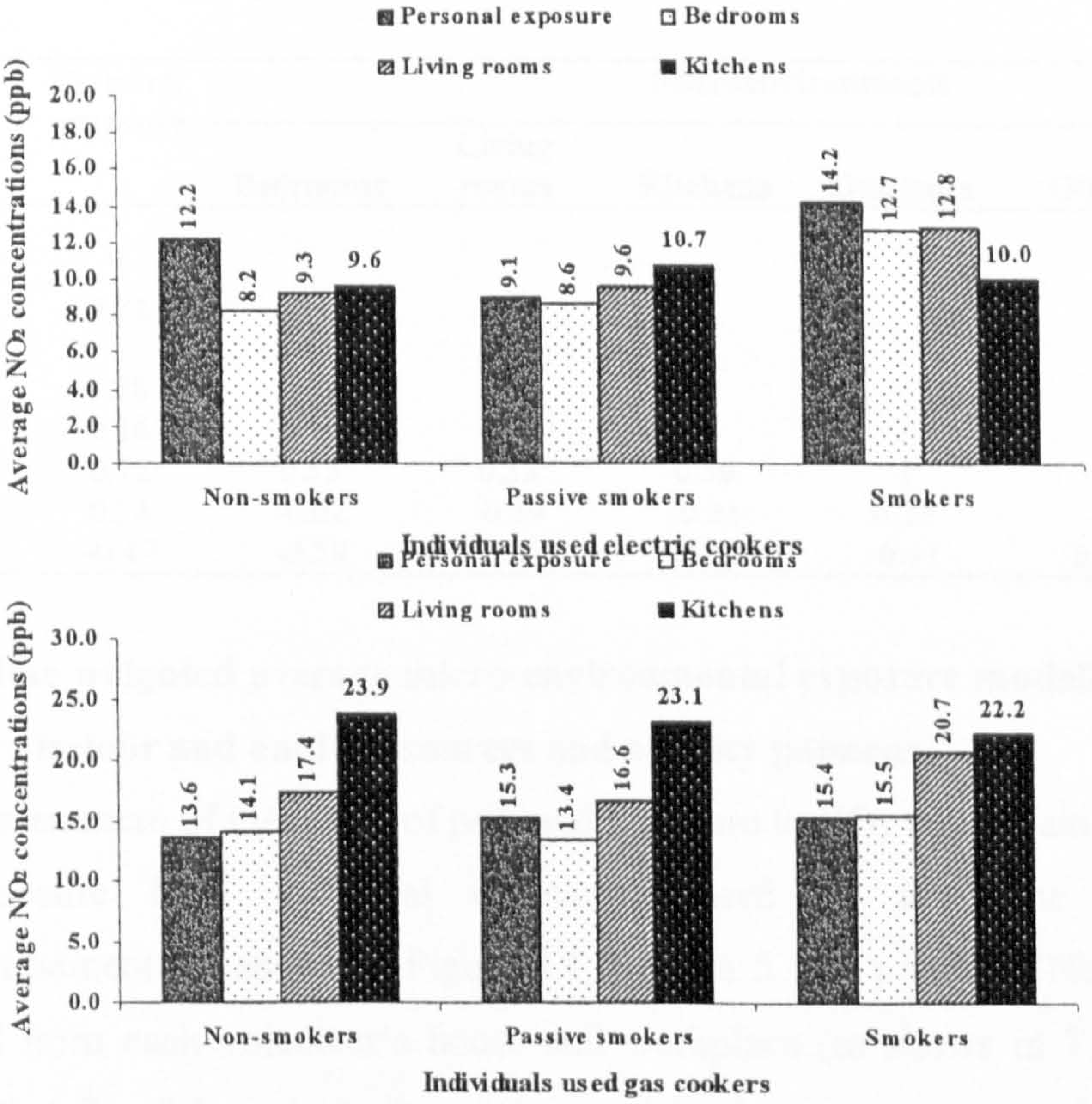


Figure 5.3 Average personal exposure of non-smokers, passive smokers and smokers to NO_2 concentrations and average NO_2 concentrations in microenvironments measured during pilot study in spring.

5.2.3 The relationship between personal exposure to NO_2 concentrations in relation to indoor and outdoor sources and activity patterns

An attempt to measure the strength of the relationship between personal exposure to NO_2 concentrations and average NO_2 concentrations in each microenvironment was made by calculating the correlation coefficients (r). Values of r are always between -1 and 1 ($-1 \leq r \leq 1$). Results from the Correlation analysis is shown in Table 5.5. The good correlation between personal exposure to NO_2 and average NO_2 concentrations in bedrooms and outdoors were found (r = 0.72 and 0.71, respectively), as well as, strong correlation between average NO_2 concentrations in living rooms and kitchens was also found (r = 0.81).

Table 5.5 Coefficient of correlation (r) results between personal exposure to NO_2 concentrations and NO_2 concentrations in each microenvironment used for pilot study in spring.

	Personal exposure	**Microenvironments**					
		Bedrooms	**Living rooms**	**Kitchens**	**Outdoors**	**Offices**	**Cars**
Personal exposure	1						
Bedrooms	0.72	1					
Living rooms	0.28	0.64	1				
Kitchens	0.16	0.54	0.81	1			
Outdoors	0.71	0.53	0.33	0.39	1		
Offices	0.34	-0.02	-0.19	-0.31	0.23	1	
Cars	-0.47	-0.59	-0.45	-0.30	-0.41	0.05	1

5.2.4 Time weighted average micro-environmental exposure modelling (TWME) in relation to indoor and outdoor sources and activity patterns

Assessment of the levels of personal exposure to NO_2 was obtained by calculating total exposure from fractional exposures based on the time spent in each microenvironment (as shows in Figure 5.1, Section 5.1.1.1) and the NO_2 concentrations measured from each volunteer's house and workplace (as shows in Table 5.4, Section 5.1.1.2). Details of the calculation of time weighted average exposure has been given in Section 2.3.2 (Chapter 2). Then, the time-weighted average micro-environmental exposures were plotted against the personal exposure to NO_2 concentrations as result is shows in Figure 5.4. The time weighted average gave a fair approximation but underestimates ($y = 0.9182x$, $R^2 = 0.7785$) when compared with the personal exposure to NO_2 concentrations. The reason could be probably due to the fact that individuals spent their time in other microenvironments which were not included in this study. Additionally, their time reporting in the time activity diaries was inaccurate.

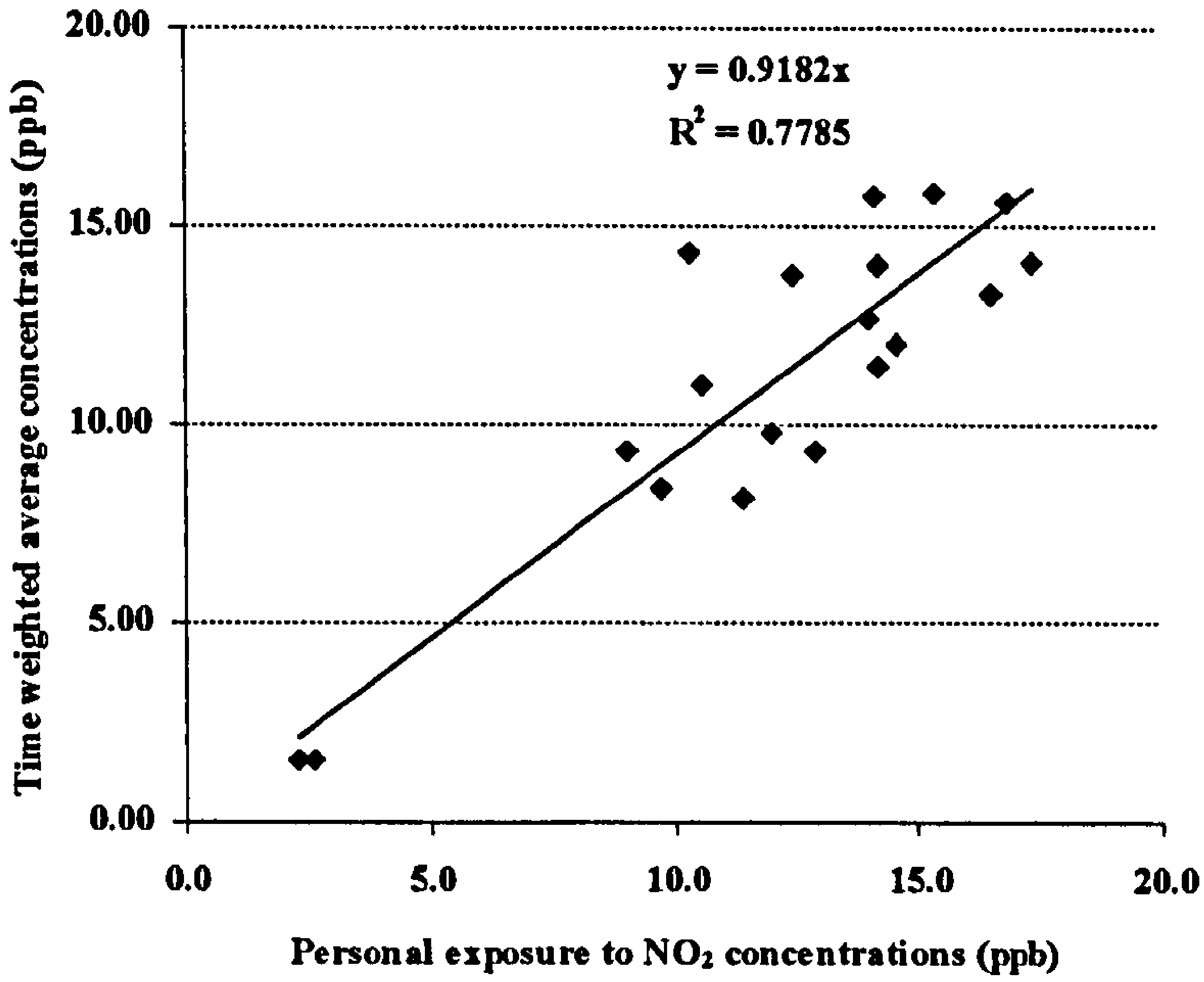


Figure 5.4 Comparisons between the personal exposure to NO_2 and time weighted average microenvironmental exposure calculated from pilot study data in spring.

Also paired t-test was analysed (as details have been given in Section 4.6 in Chapter 4). The paired t-test was used to find out that the mean values of personal exposure to NO_2 and the mean values of time weighted average were or were not significantly different. The result of paired t-test (p-value < 0.05) as shows in Table 5.6 was confirmed that non significant difference has been found between the time weighted average micro-environmental exposure and the personal exposure to NO_2 concentrations of overall volunteers. As well as the time weighted average exposure did not show significantly different from the personal exposure to NO_2 concentrations of volunteers used gas cookers and also non significant difference has been found between the time weighted average micro-environmental exposure and the personal exposure to NO_2 concentrations of volunteers using electric cookers (as shown in Table 5.7).

Table 5.6 Paired t-Test between time weighted average micro-environmental exposure and personal exposure to NO_2 for all volunteers in pilot studies during spring and summer.

	Pilot study in spring 2000		Pilot study in summer 2000	
	Time weighted average NO_2 concentrations	Personal exposure to NO_2	Time weighted average NO_2 concentrations	Personal exposure to NO_2
Mean	12.4	13.3	13.3	13.6
Variance	7.0	7.0	1.6	2.1
Observations	15	15	25	25
Pearson Correlation	0.6		0.9	
Hypothesized Mean Difference	0		0	
Degree of Freedom	14		24	
t Stat	-1.62		-2.31	
P(T<=t) one-tail	0.06		0.01	
t Critical one-tail	1.76		1.71	
P(T<=t) two-tail	0.13		0.03	
t Critical two-tail	2.14		2.04	

Note: t stat < t critical, therefore both means are not significantly different (both equal means)

Table 5.7 Paired t-Test between time weighted average micro-environmental exposure and personal exposure to NO_2 concentrations for volunteers using gas cookers and electric cookers from pilot study in spring.

	Gas cookers		Electric cookers	
	Time weighted average NO_2 concentrations	Personal exposure to NO_2	Time weighted average NO_2 concentrations	Personal exposure to NO_2
Mean	14.1	14.2	9.8	12.0
Variance	2.5	6.8	2.6	5.3
Observations	9	9	6	6
Pearson Correlation	0.5		0.8	
Hypothesized Mean Difference	0		0	

Degree of Freedom	8	5
t Stat	-0.15	-3.65
P(T<=t) one-tail	0.44	0.01
t Critical one-tail	1.86	2.02
P(T<=t) two-tail	0.89	0.01
t Critical two-tail	2.31	2.57

Note: t stat < t critical, therefore both means are not significantly different (both equal means)

5.3 Pilot study in summer 2000

5.3.1 Questionnaires & Activity Daily Diaries

Although the number of subjects was low, the first pilot study indicated the robustness of the methods and the procedures followed for calculating the concentrations. A second pilot study was carry out in summer 2000 for 31 individuals. 30 out of 31 questionnaires (Table 5.1) were analysed and the results are presented in Table 5.2. The outcome showed that all 13 male and 17 female volunteers lived in urban areas. The result also found that 26 individuals lived in Hertfordshire and 4 in London, as well as 17 individuals used gas cookers and 13 used electric cookers. Also, 4 volunteers were smokers, 3 were passive smokers and 23 were non-smokers. Most of the individuals (43.3%) were aged between 21-25 years followed by 30% with ages between 26-30 years. The results showed that 40% of the volunteers lived in semi-detached houses, followed by 30% who lived in centre terrace houses. Over 73% of the properties were double glazing windows and about 17% had mixed glazing windows. 53% of the individuals were car owners using mostly unleaded petrol. Most of the cars (60%) were parked at the kerbside of the roads, followed by 40% which were parked at the resident car park. Over 76.7% of the individuals were working in an open plan office and 23.3% working in a separate office. 76.7% of the offices had windows, 16.7% of those had only A/C (with no windows) and 6.7% had both windows and A/C.

Most of volunteers' houses (56.7 %) were located in the outer town areas, followed by 43.3 % located in town centre. Most of volunteers shared their properties with another person and only small number lived alone. Over 90% of the individuals did not have children. All properties had central heating systems which were run on natural gas but were not being used during this study period. The central heating/hot water boiler was located in either in the kitchen, hall, living room or bedroom. Also, location of the boiler outlet pipe was outdoors. None of the properties had any extra boilers for hot water. Only 30% of the kitchens were equipped with kitchen fans (filter and recirculation) or extractors. The kitchen extract fans were frequently in used during cooking and 5-10 minute after cooking.

The results from 31 activities diaries showed that all volunteers spent more than 80% of their time indoors (as shows in Figure 5.5). The time spent in different microenvironments was as follows: 49% in house, 29.7% at work, 3.5% in transportations, 5.8% in other non-smoking areas and 1.5% in other smoking areas not classified in the questionnaires. The individuals spent 10.2% of their time outdoors which was twice higher than time spent outdoors during the pilot study in spring.

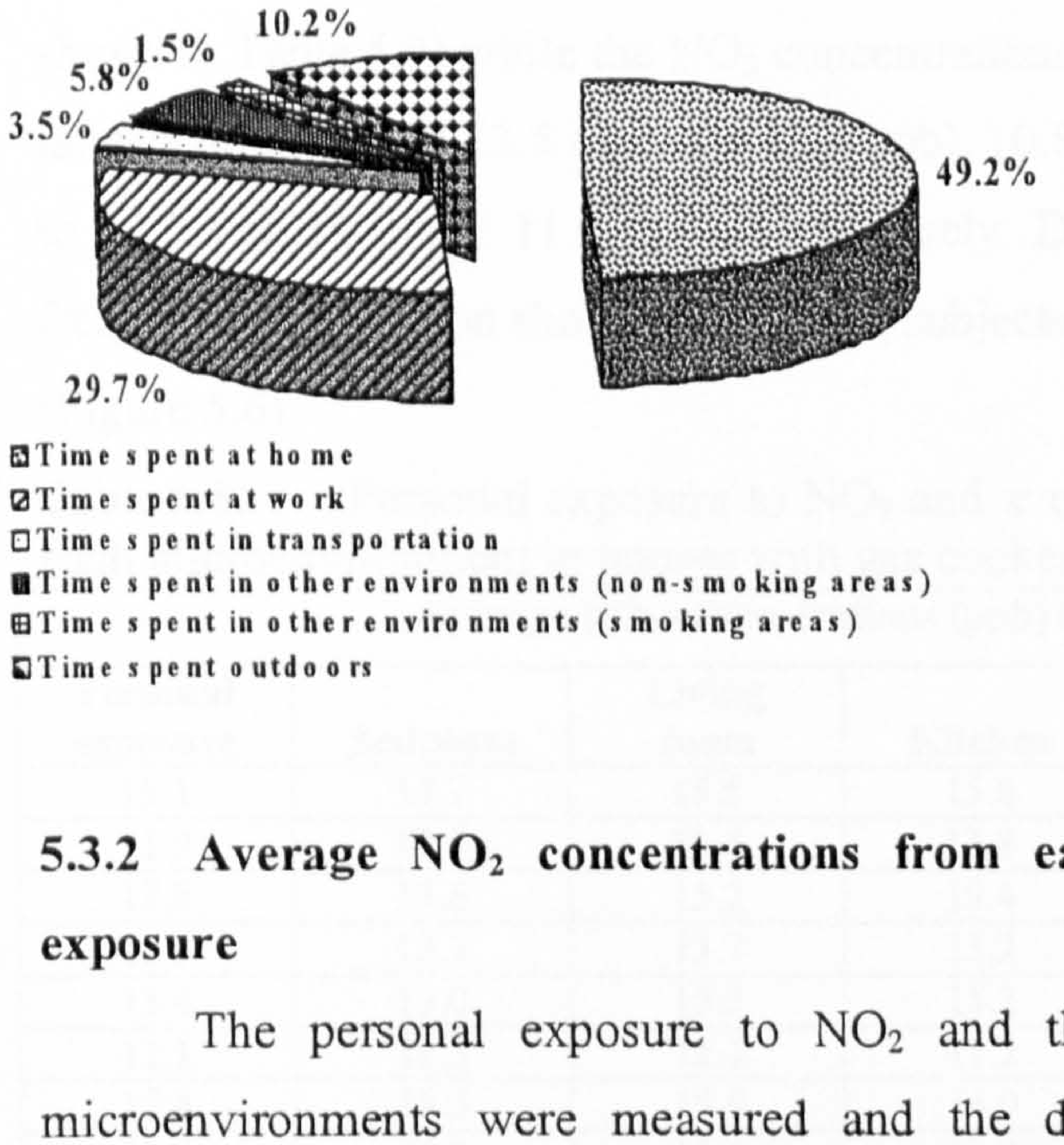


Figure 5.5 Average time activity patterns in microenvironments for all volunteers for a 7-day exposure period during pilot studies in summer

5.3.2 Average NO_2 concentrations from each microenvironment and personal exposure

The personal exposure to NO_2 and the average of NO_2 concentrations in microenvironments were measured and the data is presented in Table 5.9. Three observations can be made: (i) the personal exposure to NO_2 of volunteers who uses gas cookers were higher than those volunteers who used electric cookers, (ii) the average of NO_2 concentrations in bedroom, living room and kitchen of houses with gas cookers and with electric cookers were lower than the average outdoor NO_2 concentrations and (iii) the ambient NO_2 concentrations was lower than the annual standard value of NO_2 stated by the UK National Air Quality Strategy.

Personal exposure to NO_2 concentrations for all volunteers ranged from 10.5 to 17.4 ppb. The NO_2 concentrations in bedrooms, living room, kitchens and outdoor ranged from 10.3 to 17.0 ppb, 10.8 to 19.3 ppb, 9.6 to 18.9 ppb, and 10.8 to 20.3 ppb respectively. The NO_2 concentrations in offices and cars ranged from 9.3 to 15.0 ppb and 8.3 to 14.4 ppb (as shown in Table 5.8). Table 5.8, also showed that the personal exposure concentrations of volunteers who lived in houses with gas cookers ranged from 11.9 to 17.4 ppb (average 14.0 ppb, as presents in Figure 5.7) while the NO_2 concentrations in bedrooms, living rooms and kitchens ranged from 12.3 to 17.0 (average 14.0 ppb), 12.1 to 19.3 ppb (average 14.8 ppb), and 11.2 to 18.9 ppb (average 14.4 ppb), respectively. Average personal exposure to NO_2 concentrations of volunteers lived in houses with electric cookers was 12.5 ppb as shows in Figure 5.6 (ranged from 10.5 to 14.2 ppb, as shows in Table 5.9) while the NO_2 concentrations in bedrooms, living rooms and kitchens ranged from 10.3 to 13.5 (average 12.4 ppb), 10.8 to 13.5 ppb (average 12.5 ppb), and 9.6 to 13.5 ppb (average 11.9 ppb), respectively. Data in Table 5.8 is also displayed as a frequency distribution showing that most subjects were exposed to levels of 11.6-14.5 ppb (Figure 5.6).

Table 5.8a Personal exposure to NO_2 and average NO_2 concentrations measured from each microenvironment in houses with gas cookers during pilot study in summer.

Average NO_2 concentrations (ppb) in houses with gas cookers						
Personal exposure	**Bedroom**	**Living room**	**Kitchen**	**Outdoor**	**Work**	**Car**
15.1	14.7	15.5	15.8	16.0	12.4	-
11.9	12.3	13.5	13.8	14.7	11.0	-
13.5	13.6	15.2	15.4	16.3	13.0	-
13.3	13.3	13.7	13.2	14.6	13.3	8.8
13.4	13.0	15.3	15.2	16.4	11.0	-
12.1	12.3	12.1	11.2	12.8	12.2	-
15.4	15.5	15.9	14.0	17.0	13.9	-
12.8	13.2	13.4	13.0	14.9	12.9	11.4
13.6	13.7	14.4	12.1	15.4	14.2	-
14.4	14.6	14.7	14.5	15.7	11.3	-
12.8	12.8	13.0	13.2	14.2	11.4	11.9
14.6	14.6	14.4	14.2	14.4	13.7	12.8
14.1	13.8	13.3	13.3	14.6	9.3	8.8
13.6	13.7	14.7	14.4	15.1	12.8	10.8
16.0	16.0	17.4	17.7	18.9	13.2	13.9
17.4	17.0	19.3	18.9	20.3	14.4	11.4
14.9	13.8	16.2	15.0	16.8	13.2	-

Table 5.8b Personal exposure to NO_2 and average NO_2 concentrations measured from each microenvironment in houses with electric cookers during pilot study in summer.

Average NO_2 concentrations (ppb) in houses with electric cookers						
Personal exposure	**Bedroom**	**Living room**	**Kitchen**	**Outdoor**	**Work**	**Car**
12.9	12.8	12.6	12.5	13.3	10.3	-
12.6	12.7	13.4	13.1	14.2	12.1	-
12.7	13.4	13.1	12.4	14.0	11.7	-
10.5	10.9	11.0	9.6	10.8	10.3	-
13.0	13.5	13.1	13.5	13.9	9.8	-
12.2	12.0	12.3	11.1	13.8	13.5	9.3
13.7	13.4	13.5	12.4	15.0	10.8	13.7
10.9	10.3	10.8	11.4	11.5	12.9	14.1
13.3	13.4	12.6	11.9	13.9	13.8	8.3
14.2	13.0	13.5	12.3	13.6	11.9	10.0
12.2	12.3	12.1	11.5	13.5	12.5	9.7
13.2	13.2	13.2	12.3	13.9	10.0	14.4
12.3	10.9	11.2	10.8	11.4	15.0	-
11.8	12.2	11.9	11.6	11.7	10.2	10.0

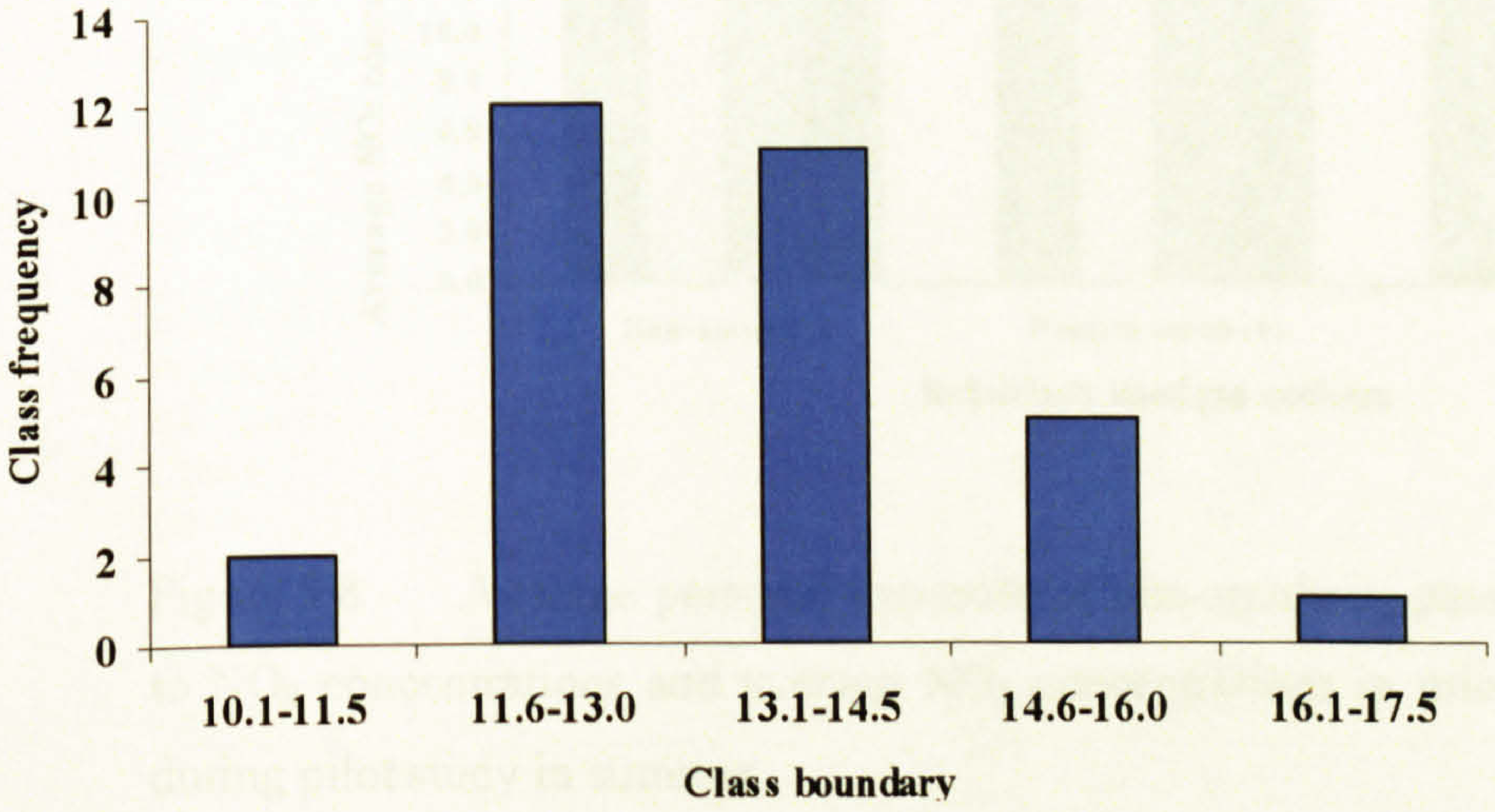


Figure 5.6 Frequency distribution for the NO_2 concentration (ppb) data in Table 5.8

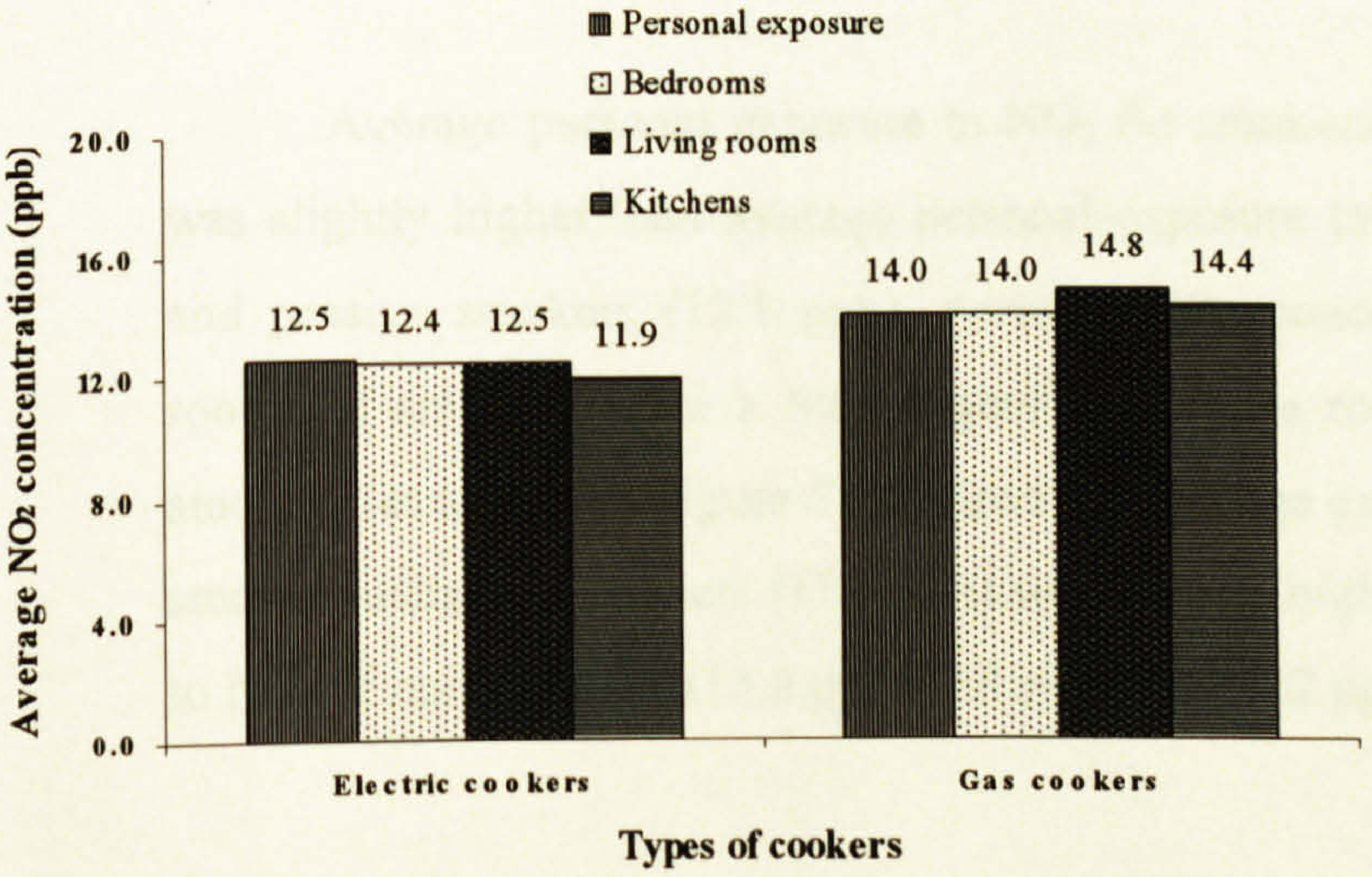


Figure 5.7 Personal exposure to NO_2 and average NO_2 concentrations measured in bedrooms, living rooms and kitchens with electric and gas cookers during pilot study in summer.

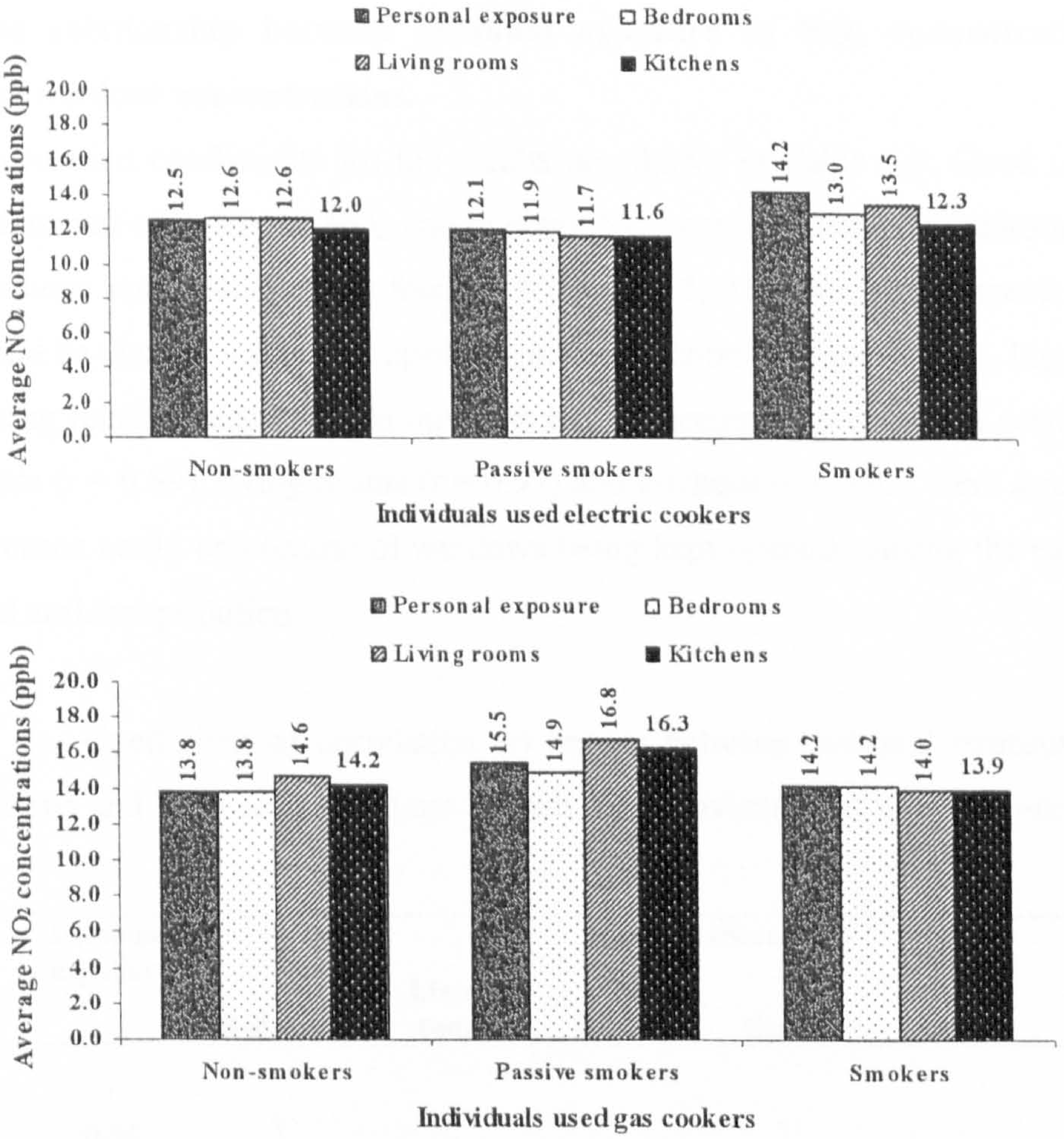


Figure 5.8 Average personal exposure of non-smokers, passive smokers and smokers to NO_2 concentrations and average NO_2 concentrations in microenvironments measured during pilot study in summer.

Average personal exposure to NO_2 for smokers using electric cookers (14.2 ppb) was slightly higher than average personal exposure to NO_2 for non-smokers (12.5 ppb) and passive smokers (12.1 ppb). Average NO_2 concentration in bedrooms and living rooms of smokers were a little higher than those rooms of non-smokers and passive smokers (as shows in Figure 5.8). However, average personal exposure to NO_2 of passive smokers using gas cookers (15.5 ppb) was slightly higher than average personal exposure to NO_2 of non-smokers (13.8 ppb) and smokers (14.2 ppb).

5.3.3 The relationship between personal exposure to NO_2 concentrations and indoor and outdoor concentrations.

Correlation coefficients for the results are shown in Table 5.9. Good correlation between personal exposure to NO_2 and average NO_2 concentrations in bedrooms, living rooms, kitchens and outdoors were found (r = 0.94, 0.92, 0.84 and 0.88, respectively). The reason could be that the volunteers spent significant amount of time (49.2%, Figure 5.5) at home. Strong relationships between outdoors NO_2 concentrations and NO_2 concentrations in bedrooms (r = 0.89), living rooms (r = 0.97) and kitchens (r = 0.92) were also found. A possible reason could be because of windows being kept opened causing the exchange of indoor and ambient pollution.

Table 5.9 Coefficient of correlation (r) results between personal exposure to NO_2 concentrations and NO_2 concentrations in each microenvironment used for pilot study in summer.

	Personal exposure	**Microenvironments**					
		Bedroom	**Living room**	**Kitchen**	**Outdoor**	**Work**	**Car**
Personal exposure	1						
Bedroom	0.94	1					
Living room	0.92	0.91	1				
Kitchen	0.84	0.84	0.94	1			
Outdoor	0.88	0.89	0.97	0.92	1		
Work	0.33	0.23	0.32	0.21	0.31	1	
Car	0.09	0.08	0.15	0.19	0.13	-0.06	1

Comparisons between personal exposure to NO_2 and average NO_2 concentrations (from front door, bedrooms and living rooms) are shown as a scatter plots in Figure 5.9. Good relationships between the personal exposure to NO_2 concentrations and the average NO_2 concentrations in bedrooms, living rooms and front door were determined (R^2 = 0.8908, 0.8285 and 0.7715, respectively). The strong relationship found between personal exposure and bedroom concentrations is probably due to individuals spending several hours sleeping in on this microenvironment. NO_2 concentrations from bedrooms, living rooms and front door could be all used together to estimate the personal exposure.

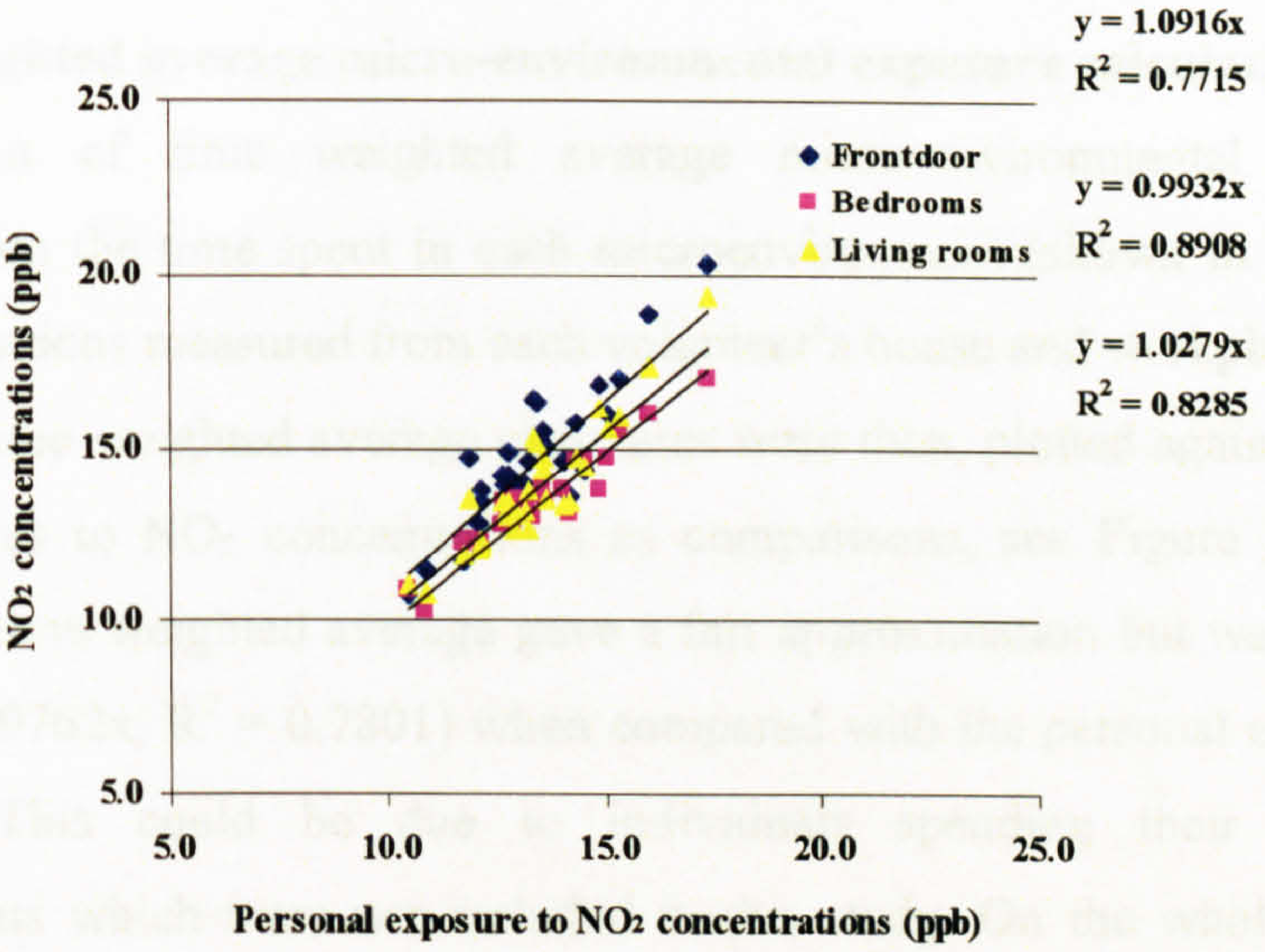


Figure 5.9 Comparisons between personal exposure to NO_2 and average NO_2 concentrations (front door, bedrooms and living rooms) used for pilot study in summer.

Relationships between the outdoor and indoor NO_2 concentrations (bedrooms, living rooms and kitchens) are plotted as a scatter plot in Figure 5.10. Good relationships were found in living rooms, kitchens and bedrooms (R^2 = 0.94, 0.8315 and 0.6193) again possibly due to the windows being kept opened introducing exchange of indoor and outdoor pollution.

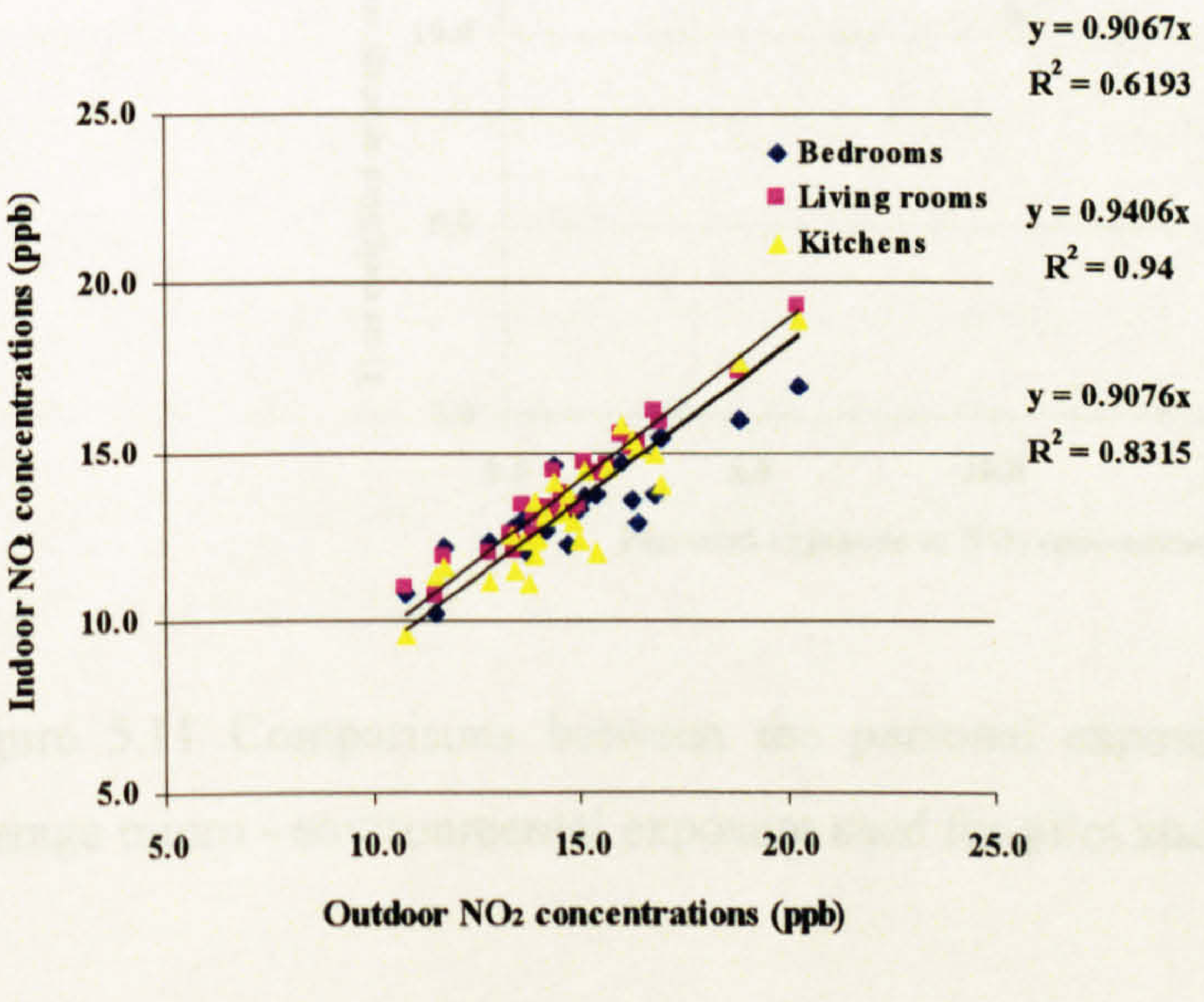


Figure 5.10 Comparisons between outdoor and indoor NO_2 concentrations (bedrooms, living rooms and kitchens) used for pilot study in summer.

5.3.4 Time weighted average micro-environmental exposure calculations

Calculation of time weighted average micro-environmental exposure was computed based on the time spent in each microenvironment (shown in Figure 5.5) and the NO_2 concentrations measured from each volunteer's house and workplace (as shows in Table 5.8). The time-weighted average exposures were then, plotted against the measured personal exposures to NO_2 concentrations as comparisons, see Figure 5.11. The plots showed that the time weighted average gave a fair approximation but was slightly under estimated ($y = 0.9762x$, $R^2 = 0.7801$) when compared with the personal exposure to NO_2 concentrations. This could be due to individuals spending their time in other microenvironments which were not included in this study. On the whole, however, the pilot study indicated that most of the exposure can be explained by the concentrations in the microenvironments included in this project. The results from paired t-test ($p\text{-value} < 0.05$) verified that significant differences were not observed between the overall time weighted average exposure and the personal exposure to NO_2 concentrations, shown in Table 5.10. This was the case for volunteers using gas and electric cookers.

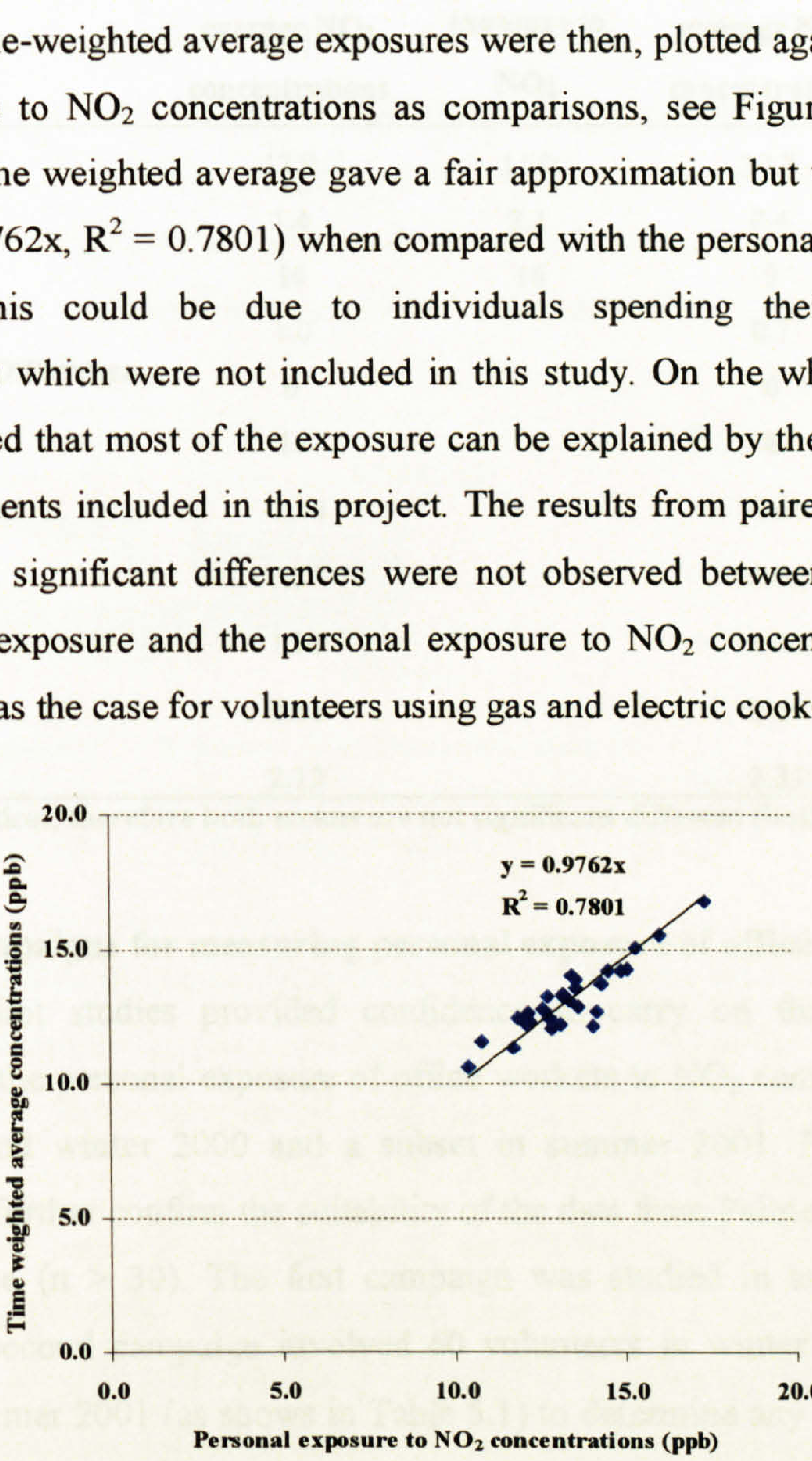


Figure 5.11 Comparisons between the personal exposure to NO_2 and time weighted average micro - environmental exposure used for pilot study in summer.

Table 5.10 Paired t-test between time weighted average micro-environmental exposure and personal exposure to NO_2 concentrations for volunteers using gas cookers and electric cookers from pilot study in summer.

	Gas cookers		Electric cookers	
	Time weighted average NO_2 concentrations	**Personal exposure to NO_2**	**Time weighted average NO_2 concentrations**	**Personal exposure to NO_2**
Mean	13.9	14.0	12.3	12.7
Variance	1.4	2.1	0.4	1.1
Observations	16	16	9	9
Pearson Correlation	1.0		0.7	
Hypothesized Mean Difference	0		0	
df	15		8	
t Stat	-1.68		-1.56	
P(T<=t) one-tail	0.06		0.08	
t Critical one-tail	1.75		1.86	
P(T<=t) two-tail	0.11		0.16	
t Critical two-tail	2.13		2.31	

Note: t stat < t critical, therefore both means are not significant different (both equal means)

5.4 Main Campaigns for measuring personal exposure of office workers to NO_2

As the pilot studies provided confidence to carry on the main campaigns, measurements of the personal exposure of office workers to NO_2 campaigns were carried out in autumn and winter 2000 and a subset in summer 2001. Purpose of the first campaign was to further confirm the suitability of the data from Palmes diffusion tubes for larger sample size (n > 30). The first campaign was studied in autumn involving 55 volunteers. The second campaign involved 60 volunteers in winter and a subset of 30 volunteers in summer 2001 (as shows in Table 5.1) to determine any seasonal differences in personal exposure levels.

5.4.1 Campaign study of autumn 2000

5.4.1.1 Questionnaires & Activity Daily Diaries

40 out of 55 questionnaires & time activities pattern from autumn campaign were completed, returned and analysed (as shows in Table 5.1). Results from 40 questionnaires showed that all volunteers (15 male and 25 female) lived in urban areas, out of which 39 lived in Hertfordshire and 1 in London (see Table 5.2). 24 volunteers used gas cookers and 16 used electric cookers. Out of the total returns 4 volunteers were smokers, 7 were passive smokers and 29 were non-smokers. 16 volunteers (11 non-smokers, 3 passive smokers and 2 smokers) used electric cookers and 24 volunteers (18 non-smokers, 4 passive smokers and 2 smokers) used gas cookers (Figure 5.12).

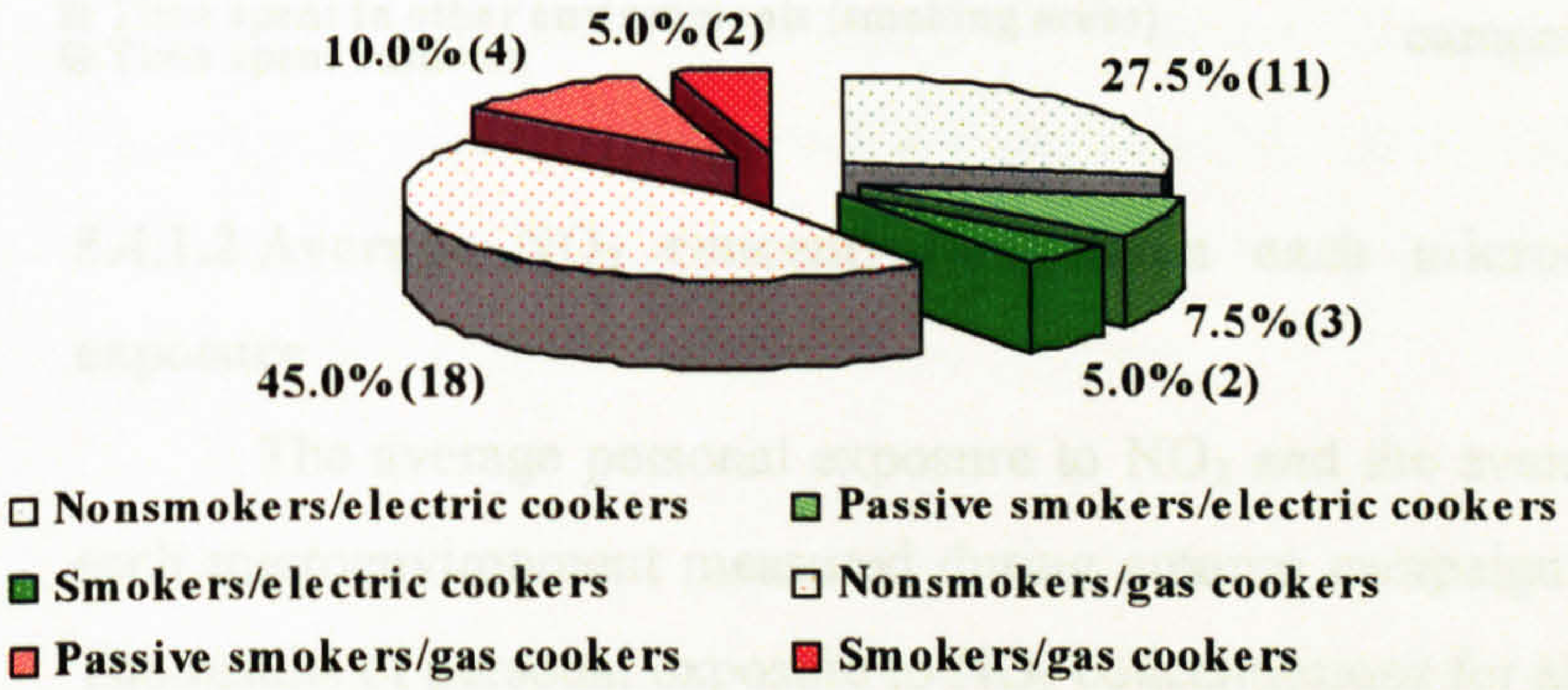


Figure 5.12 Percents of non-smokers, passive smokers and smokers using electric and gas cookers for the autumn campaign.

Most of the individuals (42.5%) were of ages between 26-30 years, followed by 35% who were between 21-25 years old. Nearly a third (32.5%) of the individuals lived in central terrace house, flat or semi-detached house. Most of volunteers shared the property with another adult person, though, over 90% of the individuals did not have children living with them. All properties had central gas heating system with the water boiler being located in different rooms (kitchens, bedrooms, halls and living rooms). Over 70% of the individuals did not have any the additional heaters. The questionnaire returns revealed that 12.5% used electricity radiator followed by 10% and 5% using electricity warm air heaters and wood/coal fireplace, respectively, as the additional heating device. More than 50% of the individuals were car owners using unleaded petrol. 50% of the cars were parked at the resident car park, followed by 40% at the kerbside of the road and lest than 10% in garage. These findings are similar to those of the pilot campaign (section 5.3.1).

Results from the activities patterns showed that all volunteers spent most of their time at home (54.1%), followed by 30.5% of their time at work (Figure 5.13). Also they spent their time in other indoors environments such as non-smoking (4.8%) and smoking (2.7%) areas. The results also showed that the individuals spent only 3.5 % and 4.3% of their time in transportation and outdoors.

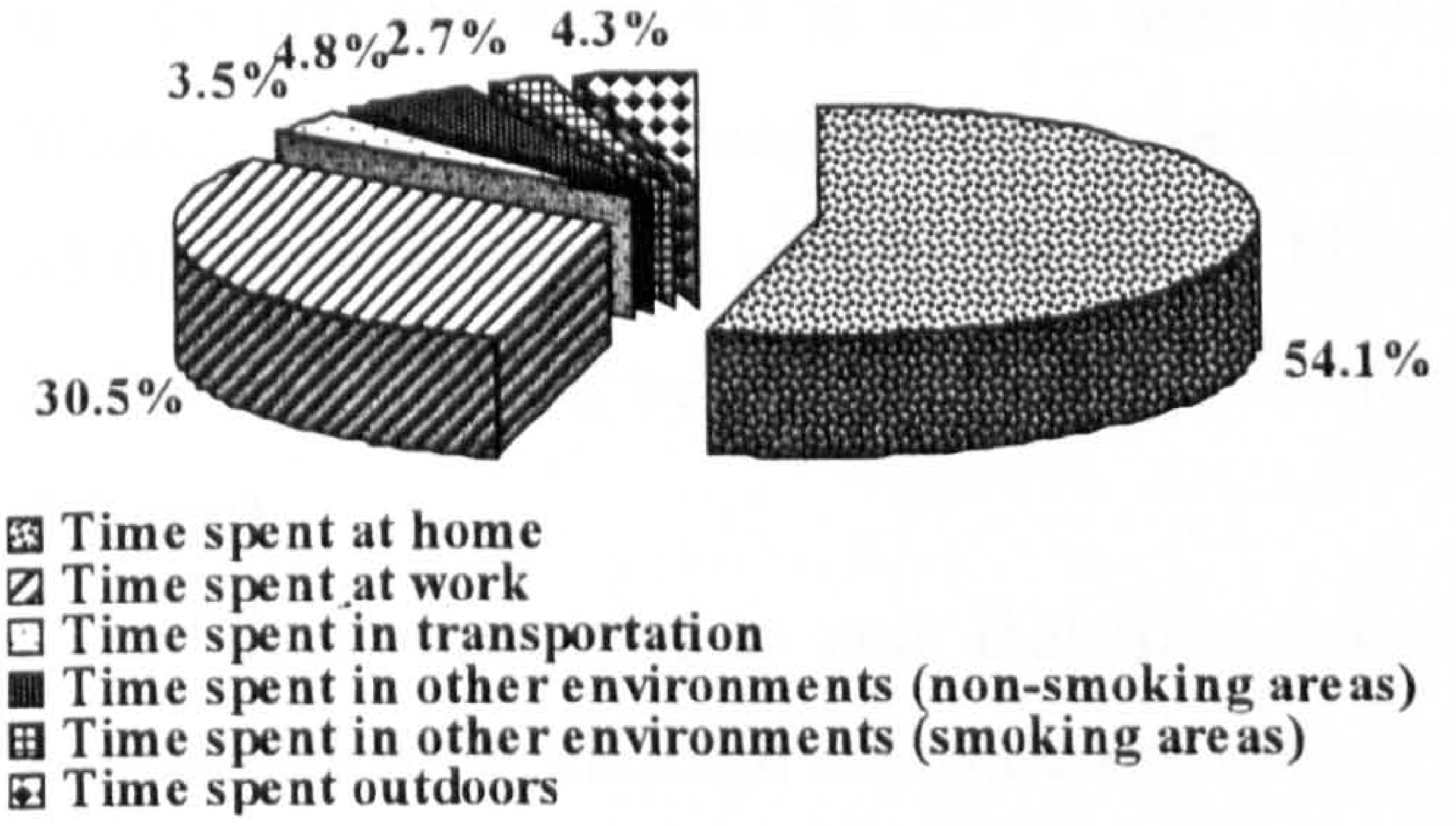


Figure 5.13 Average time activity patterns in microenvironments for all volunteers during a 7-day exposure period in autumn campaign

5.4.1.2 Average NO_2 concentrations from each microenvironment and personal exposure

The average personal exposure to NO_2 and the average of NO_2 concentrations in each microenvironment measured during autumn campaign are presented in Table 5.11. The results of personal exposure to NO_2 concentrations for all volunteers ranged from 6.2-15.9 ppb. NO_2 concentrations in overall bedrooms, living rooms and kitchens ranged from 5.8-15.3 ppb, 4.5-28.8 ppb and 4.4-43.0 ppb, respectively. Outdoor NO_2 concentrations ranged from 8.5-19.5 ppb. Also, weekly mean NO_2 concentrations in all offices ranged from 6.4-12.8 ppb. As well as average NO_2 concentrations in cars ranged from 7.6-12.6 ppb.

Table 5.11 Overall average personal exposure to NO_2 concentrations and average NO_2 concentrations in microenvironments measured during the autumn campaign.

	Personal exposure to NO_2 (ppb)	**Average NO_2 concentrations (ppb)**					
		Bedrooms	**Living rooms**	**Kitchens**	**Outdoors**	**Offices**	**Cars**
Min.	6.2	5.8	4.5	4.4	8.5	6.4	7.6
Max.	15.9	15.3	28.8	43.0	19.5	12.8	12.6
Average	11.1	10.7	13.6	17.0	14.3	8.8	9.0
Stdev.	2.2	2.0	5.4	9.5	1.9	1.4	1.3

Personal exposure to NO_2 concentrations for volunteers using gas cookers ranged from 8.2 to 15.9 ppb (as shows in Table 5.12), which were slightly higher than for those using electric cookers (6.2 to 13.5 ppb). NO_2 concentrations in bedrooms (in houses with gas cookers) ranged from 8.5 to 15.3 ppb and 5.8 to 13.2 ppb in house with electric cookers. NO_2 concentrations in living rooms (houses with gas cookers) ranged from 10.6 to 28.8 ppb and from 4.5 to 12.9 in those living rooms in houses with electric cookers. Weekly mean NO_2 concentrations in the kitchen with gas cookers ranged from 13.0 to 43.0 ppb (average 24.5 ppb, as shown in Figure 5.14). These values were dramatically higher by a factor of nearly three than those with electric cookers (4.4 to 11.2 ppb, average 8.5 ppb).

It is interesting to note that for subjects using electric cookers the variation in concentrations in personal exposure and different microenvironments is small. In contrast for subjects using gas cookers the variation is significant with the highest concentrations measured in kitchens. The mean personal exposure for subjects using gas cookers is also 25% higher than those using electric cookers.

Table 5.12 Average personal exposure to NO_2 concentrations (of volunteers using electric and gas cookers) and average NO_2 concentrations in houses measured during autumn campaign

	Average NO_2 concentrations (ppb)							
	Electric cookers				**Gas cookers**			
	Min.	**Max.**	**Mean**	**Stdev.**	**Min.**	**Max.**	**Mean**	**Stdev.**
Personal exposure to NO_2	6.2	13.5	9.8	2.0	8.2	15.9	12.3	1.7
Bedrooms	5.8	13.2	9.6	2.0	8.5	15.3	11.6	1.6
Living rooms	4.5	12.9	9.7	2.3	10.6	28.8	17.1	4.9
Kitchens	4.4	11.2	8.5	1.4	13.0	43.0	24.5	6.9

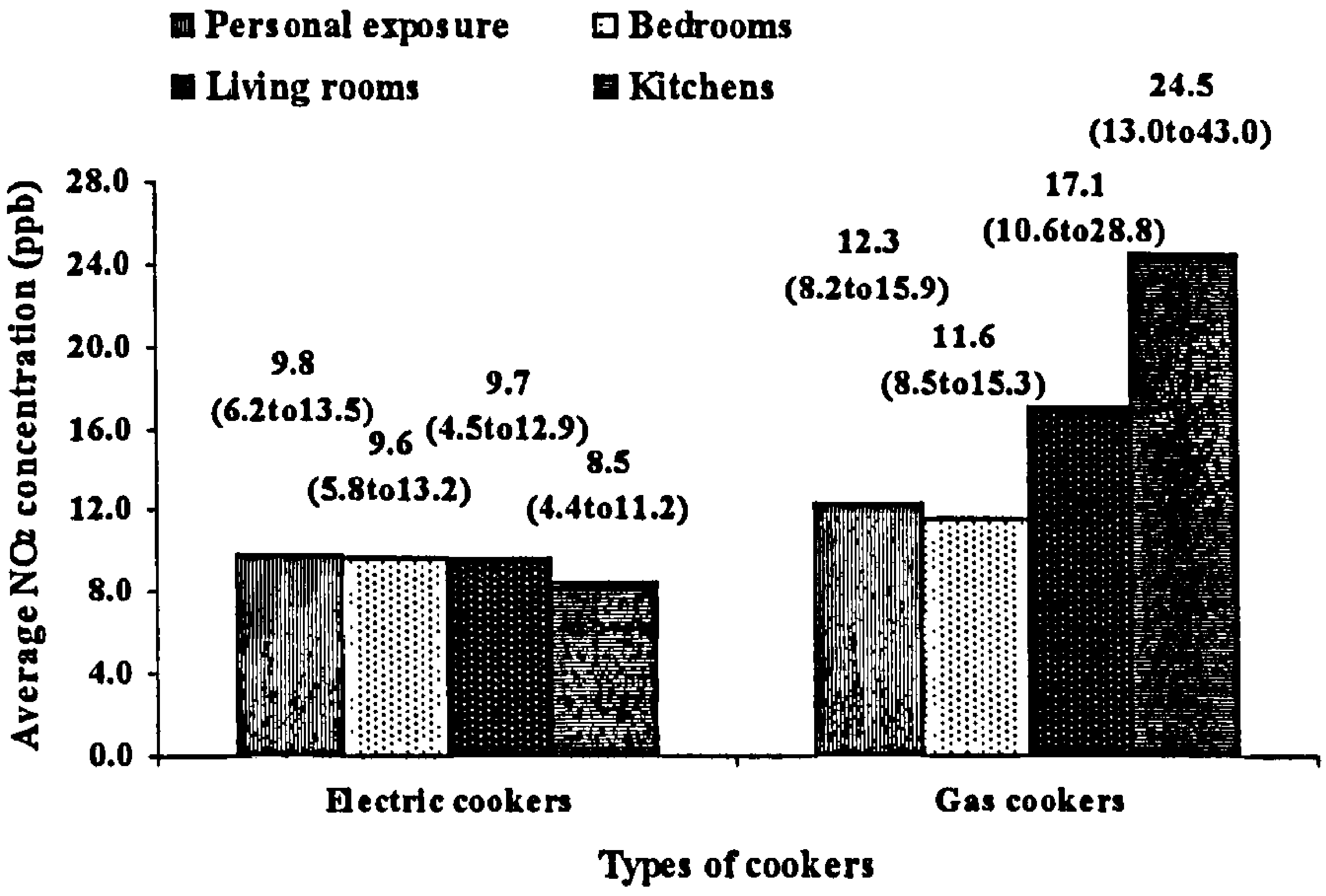


Figure 5.14 Personal exposure to NO_2 and average NO_2 concentrations measured in bedrooms, living rooms and kitchens with electric and gas cookers during the autumn campaign.

In houses with electric cookers and gas cookers, average personal exposure to NO_2 of smokers (14.2 ppb/15.3 ppb) were slightly higher than average personal exposure to NO_2 of non-smokers (12.5 ppb/12.7 ppb) and passive smokers (12.1 ppb/11.7 ppb). The average NO_2 concentrations in rooms from houses of smokers using electric cookers were similar to those rooms from houses of non-smokers and passive smokers (as shown in Figure 5.15). In the case of houses with gas cookers, however, average NO_2 concentrations in rooms of smokers from houses with gas cookers was higher than those for passive smokers but similar to those for non-smokers. Information on ventilation regimes was limited and hence it is difficult to fully interpret these findings.

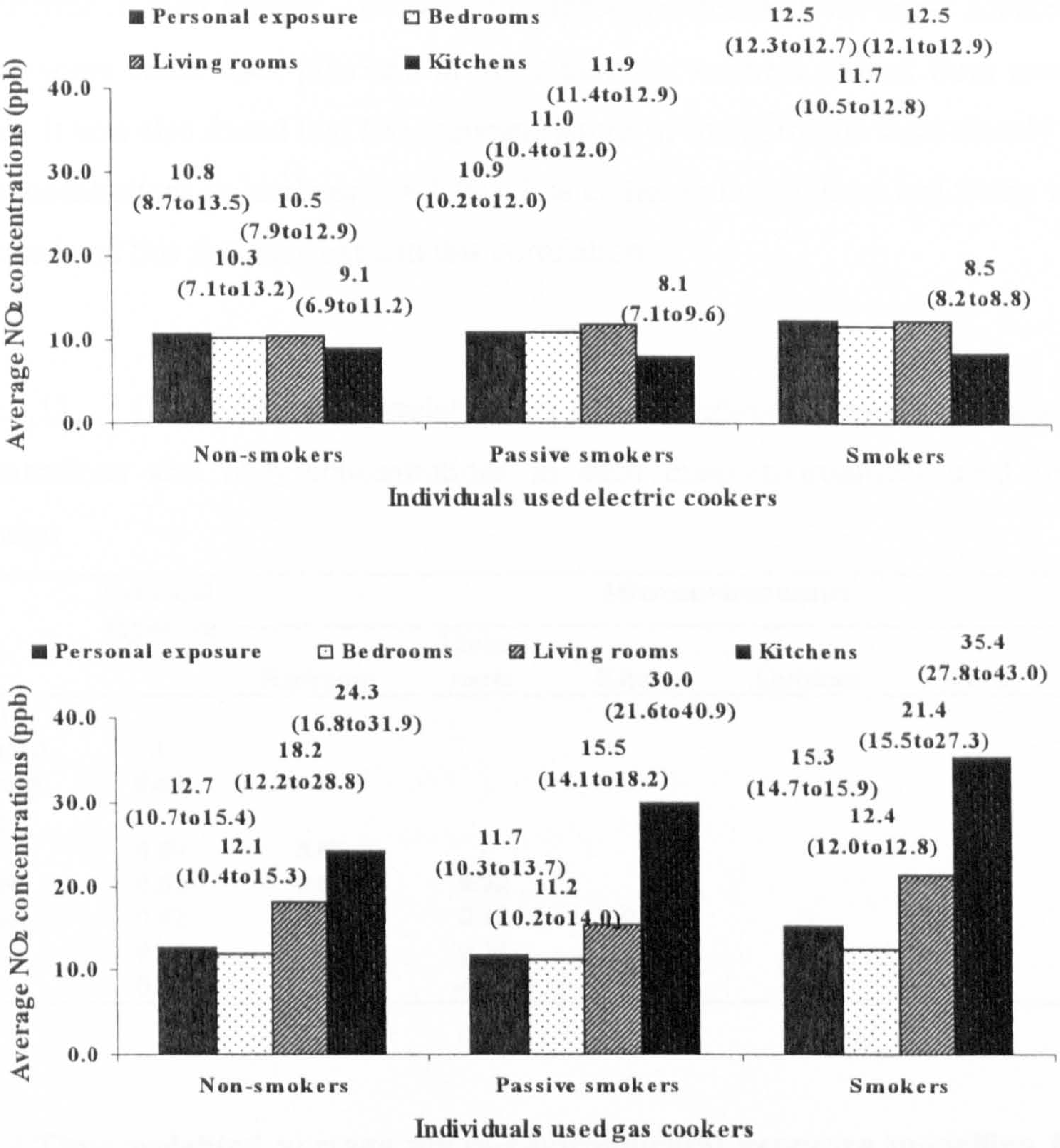


Figure 5.15 Average personal exposure of non-smokers, passive smokers and smokers to NO_2 concentrations and average NO_2 concentrations in microenvironments measured during autumn campaign.

5.4.1.3 The relationship between personal exposure to NO_2 concentrations in relation to indoor and outdoor sources and activity patterns

Correlation analysis was conducted to identify any relationships between personal exposure and concentrations in microenvironments. Result of this analysis is shown in Table 5.13. It showed good correlation between personal exposures to NO_2 concentrations in bedrooms, living rooms, kitchens, front door and offices (r = 0.69, 0.69, 0.62, 0.42 and 0.22, respectively). This is may be explained by the fact that the subjects spent a majority of their time in their houses. The largest contribution comes from home sources. Offices were in some cases open plan and in other case the workers moved from one office to another. It was also found that NO_2 concentrations in living rooms were closely related to NO_2 concentrations in kitchens (r = 0.92). It is common for kitchens and living areas to be connected and this fact may explain this correlation.

Table 5.13 Coefficient of correlation (r) results between personal exposure to NO_2 concentrations and NO_2 concentrations in each microenvironment used for autumn campaign

	Personal exposure	**Microenvironments**					
		Bedroom	**Living room**	**Kitchen**	**Outdoor**	**Work**	**Car**
Actual measured	1						
Bedroom	0.69	1					
Living room	0.69	0.67	1				
Kitchen	0.62	0.67	0.92	1			
Outdoor	0.42	0.22	0.17	0.08	1		
Work	0.22	0.11	0.14	0.10	0.31	1	
Car	0.06	0.03	-0.04	-0.07	-0.01	-0.03	1

5.4.1.4 Time weighted average micro-environmental exposure modelling in relation to indoor and outdoor sources and activity patterns

Calculation of the weighted average micro–environmental exposure from fractional exposures based on time spent in each microenvironment and the NO_2 concentration data measured in the microenvironments (in each volunteer's house and office) was carried out (see section 2.3.2). The results, as presented in Table 5.14, showed that average of time weighted micro-environmental exposure of non-smokers, passive smokers and smokers using electric cookers (10.0, 10.5 and 10.8 ppb respectively) were slightly lower than those using gas cookers (12.5, 12.2 and 15.0 ppb respectively). Moreover, the time weighted average of volunteers using electric cookers ranged from 8.2 to 12.2 ppb (average 10.2 ppb) and from 10.8 to 15.4 ppb for those using gas cookers (average 12.6 ppb).

Table 5.14 Time weighted average micro-environmental exposure of volunteers calculated from autumn campaign data

	Time weighted average NO_2 concentrations (ppb) (overall ranged from 6.6 to 15.4, average 10.9 ppb)							
	Electric cookers (average 10.9 ppb)				**Gas cookers** (average 12.6 ppb)			
	Min.	**Max.**	**Mean**	**Stdev.**	**Min.**	**Max.**	**Mean**	**Stdev.**
Non smokers	8.2	12.2	10.0	1.2	10.8	14.4	12.5	1.1
Passive smokers	9.8	10.9	10.5	0.6	11.2	13.9	12.2	1.2
Smokers	9.7	12.0	10.8	1.6	14.6	15.4	15.0	0.6

The time-weighted average micro-environmental exposures were also plotted against the personal exposure concentrations and the result are shows in Figure 5.16. The time weighted average gave a fair approximation but underestimated slightly when compared with the personal exposure to NO_2 concentrations ($y = 0.975x$, $R^2 = 0.7295$). The reason could be due to individuals spending their time in other micro-environments which were not included in this study. On the whole the time weighted approach based on the micro-environments gave a good approximation of the personal exposure measurements.

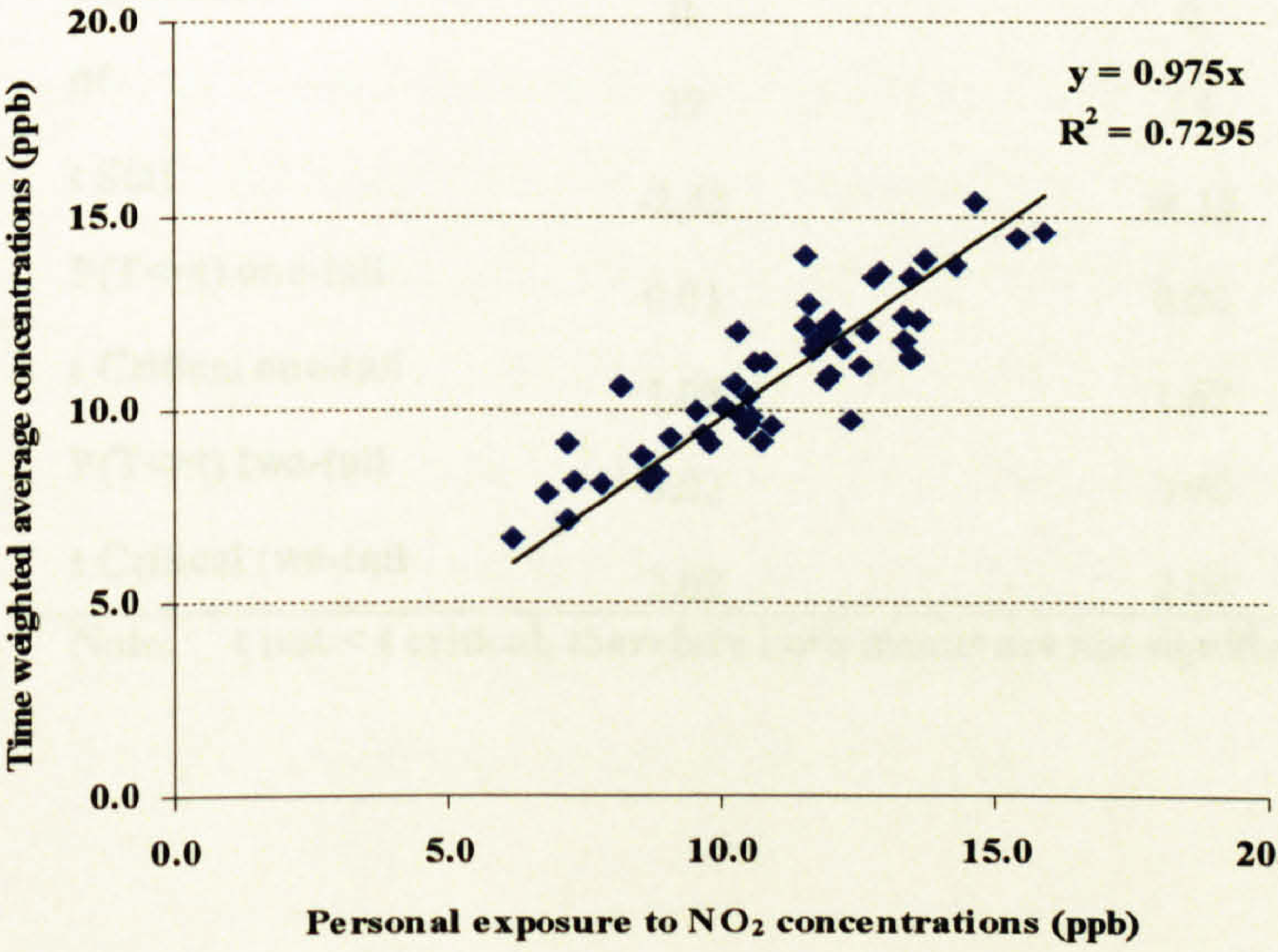


Figure 5.16 Comparisons between the personal exposure to NO_2 and time weighted average micro - environmental exposure used for autumn campaign

The differences between the time weighted average micro-environmental exposure and the personal exposure to NO_2 concentrations were calculated using Paired t–test (to analyse the difference between two mean data). The result from the paired t-test analysis (p-value < 0.05), as shown in Table 5.15 and Table 5.16, confirmed that the difference was non significant. This was also the case for volunteers using gas cookers and for those using electric cookers confirming that the time weighted approached worked well in representing the measured personal exposures.

Table 5.15 Paired t-Test between time weighted average micro-environmental exposure and personal exposure to NO_2 for all volunteers in main campaign studies during autumn, winter and summer.

	Autumn 2000		Winter 2000		Summer 2001	
	Time weighted average	**Personal exposure**	**Time weighted average**	**Personal exposure**	**Time weighted average**	**Personal exposure**
Mean	11.7	12.1	9.2	9.7	13.7	13.0
Variance	2.9	2.6	5.2	5.8	1.7	1.0
Observations	40	40	55	55	25	25
Pearson Correlation	0.8		0.9		0.8	
Hypothesized Mean Difference	0		0		0	
df	39		54		24	
t Stat	-2.42		-4.15		4.27	
P(T<=t) one-tail	0.01		0.00		0.00	
t Critical one-tail	1.68		1.67		1.71	
P(T<=t) two-tail	0.02		0.00		0.00	
t Critical two-tail	2.02		2.00		2.06	

Note: t test < t critical, therefore both means are not significant different (both equal means)

Table 5.16 Paired t-Test between time weighted average micro-environmental exposure and personal exposure to NO_2 concentrations for volunteers using gas cookers and electric cookers from autumn campaign.

	Gas cookers		Electric cookers	
	Time weighted average NO_2 concentrations	Personal exposure to NO_2	Time weighted average NO_2 concentrations	Personal exposure to NO_2
Mean	10.2	11.0	12.6	12.7
Variance	1.3	1.7	1.6	2.1
Observations	16	16	24	24
Pearson Correlation	0.8		0.7	
Hypothesized Mean Difference	0		0	
df	15		23	
t Stat	-4.09		-0.52	
P(T<=t) one-tail	0.00		0.30	
t Critical one-tail	1.75		1.71	
P(T<=t) two-tail	0.00		0.61	
t Critical two-tail	2.13		2.07	

5.4.2 Campaign study in winter 2000

5.4.2.1 Questionnaires & Activity Daily Diaries

55 questionnaires were analysed and the outcomes showed that the volunteers consisted of 24 male and 31 female individuals who all lived in urban areas. The majority (50 individuals) lived in Hertfordshire and 5 in North London (New Barnet). Also, 28 volunteers used gas cookers and 27 used electric cookers. In addition, 7 volunteers were smokers, 11 were passive smokers and 37 were non-smokers. 19 non-smokers, 4 passive smokers and 5 smokers used electric cookers and 18 non-smokers, 7 passive smokers and 2 smokers used gas cookers (Figure 5.17a).

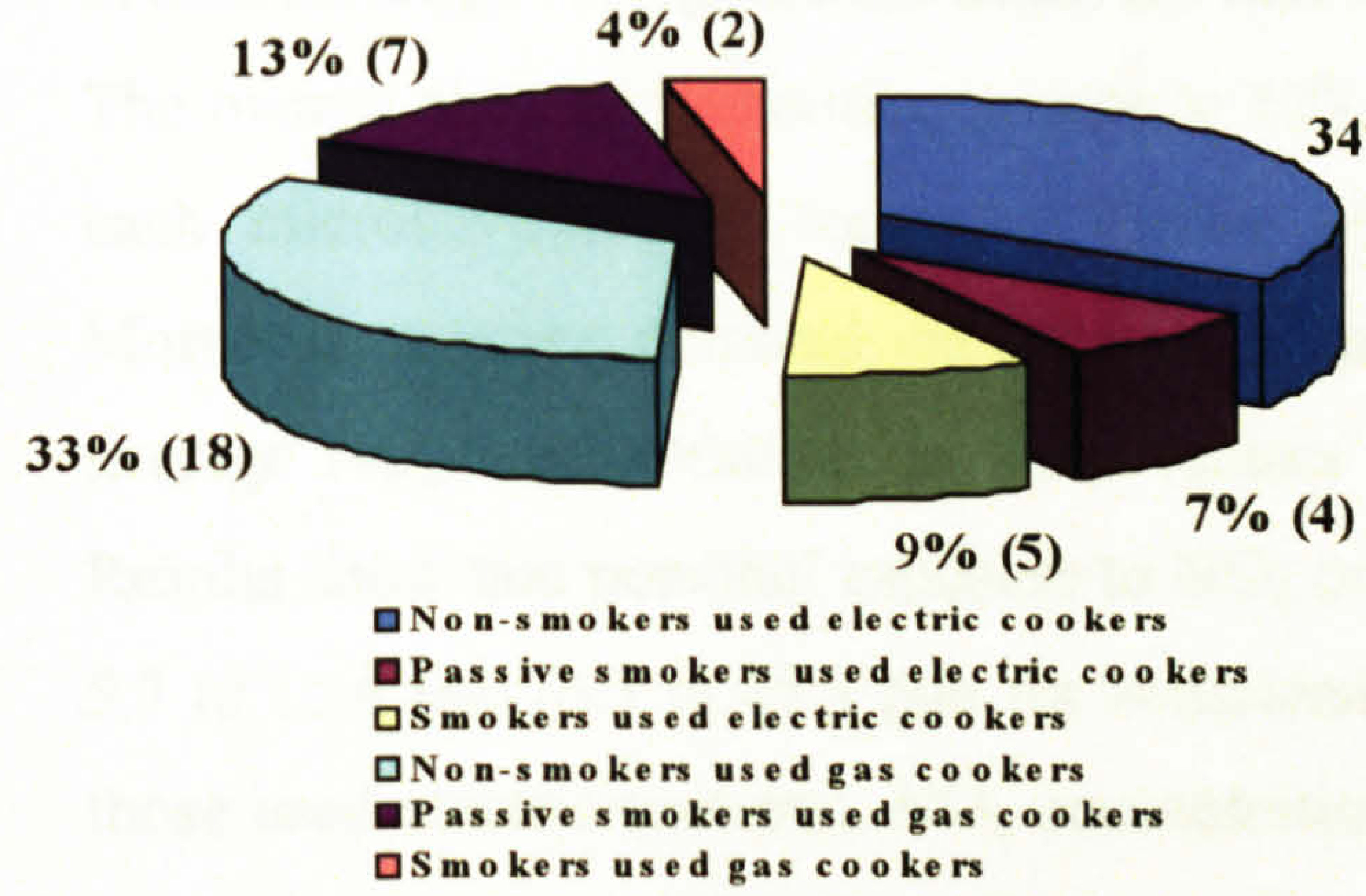


Figure 5.17a Percent of non-smokers, passive smokers and smokers used electric and gas cookers for winter campaign

27.3% of the volunteers were aged between 26-30 years, 18.2% were aged between 31-35, 38.1% were aged 36-49 and 16.4% were aged between 21-25 years. Most of the volunteers (40%) lived in flat, followed by 29.1% in semi-detached house and 25.5% in central terrace house. All volunteers shared the property with another person. 43.6% of individuals did not have children, 18.2% had one child and 32.7% had two children. Over 90% of the individuals did not have any additional heater but 12.5% used electric radiators followed by 5.5% and 3.6% who used wood/coal fire place and electricity warm air heater, respectively, as the additional heating. More than 50% of the individuals were car owners using mostly unleaded petrol. 37.9% of the cars were parked at the resident car park, followed by 34.5% at the kerbside of the road and 27.6% in a garage. Results from the activities diaries (as shown in Figure 5.17b) showed that all volunteers spent most of their time at home (52.8%), followed by 31.0% of their time at work. They also spent their time in other non-smoking indoors environments (5.5%) and smoking indoors environments (2.2%). The results also showed that the individuals spent only 4.5 % and 4.0% of their time in transportation and outdoors.

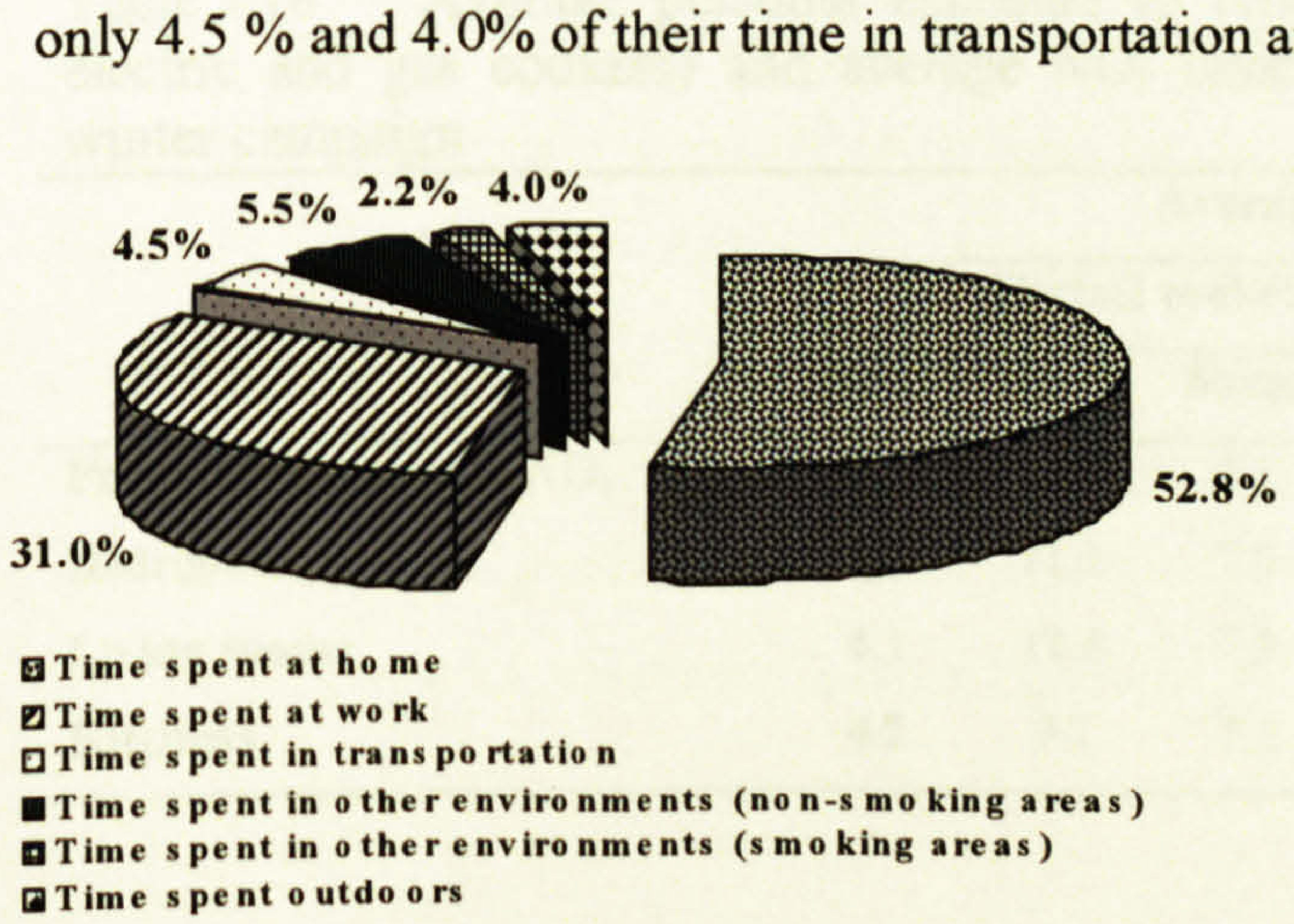


Figure 5.17b Average time activity patterns in microenvironments for all volunteers during a 7-day exposure period in winter campaign

5.4.2.2 Average NO_2 personal exposure and micro-environmental concentrations

The overall average personal exposure to NO_2 and the average of NO_2 concentrations in each microenvironment measured during winter campaign is given in Table 5.17. Moreover, average personal exposure of volunteers using electric and gas cookers and average NO_2 concentrations in those houses is shown in Table 5.18 and Figure 5.18. Results show that personal exposure to NO_2 concentrations for all volunteers ranged from 5.7 to 15.4 ppb (6.3 to 15.4 ppb for volunteers used gas cookers and 5.7 to 11.0 ppb for those used electric cookers). NO_2 concentrations in the bedroom ranged from 3.2 to 15.5 ppb (6.3 to 15.5 ppb in houses with gas cookers and 3.2 to 11.1 ppb in houses with electric cookers). NO_2 concentrations in the living room ranged from 4.1 to 30.1 ppb (from 6.1 to 30.1 in houses with gas cookers and from 4.1 to 11.4 in houses with electric cookers). The results also showed that weekly mean NO_2 concentrations in the kitchens with gas cookers ranged from 12.9 to 38.8 ppb. These values were higher than for the kitchens with electric cookers (4.2-9.7 ppb). Average front door NO_2 concentration was 12.9 ppb (range of 8.1 to 16.1 ppb). Also, weekly mean NO_2 concentrations in the offices and cars ranged from 5.6 to 13.5 ppb (average 8.8 ppb) and from 4.1 to 11.3 ppb (average 6.8 ppb), respectively.

Table 5.17 Overall average personal exposure to NO_2 concentrations and average NO_2 concentrations in microenvironments measured during winter campaign.

	Personal exposure to NO_2 (ppb)	Average NO_2 concentrations (ppb)					
		Bedrooms	Living rooms	Kitchens	Outdoors	Offices	Cars
Min.	5.7	3.2	4.1	8.1	8.1	5.6	4.1
Max.	15.4	15.5	30.1	13.4	16.1	13.5	11.3
Average	9.5	9.1	10.5	13.1	12.9	8.8	6.8
Stdev.	2.4	2.5	4.8	8.0	1.8	1.8	1.6

Table 5.18 Average personal exposure to NO_2 concentrations (of volunteers using electric and gas cookers) and average NO_2 concentrations in houses measured during winter campaign

	Average NO_2 concentrations (ppb)							
	Electric cookers				Gas cookers			
	Min.	Max.	Mean	Stdev.	Min.	Max.	Mean	Stdev.
Personal exposure to NO_2	5.7	11.0	8.1	1.8	6.3	15.4	11.2	2.3
Bedrooms	3.2	11.1	7.8	2.0	6.3	15.5	10.8	2.3
Living rooms	4.1	11.4	7.9	2.1	6.1	30.1	13.7	5.5
Kitchens	4.2	9.7	7.1	2.8	12.9	38.8	20.6	6.9

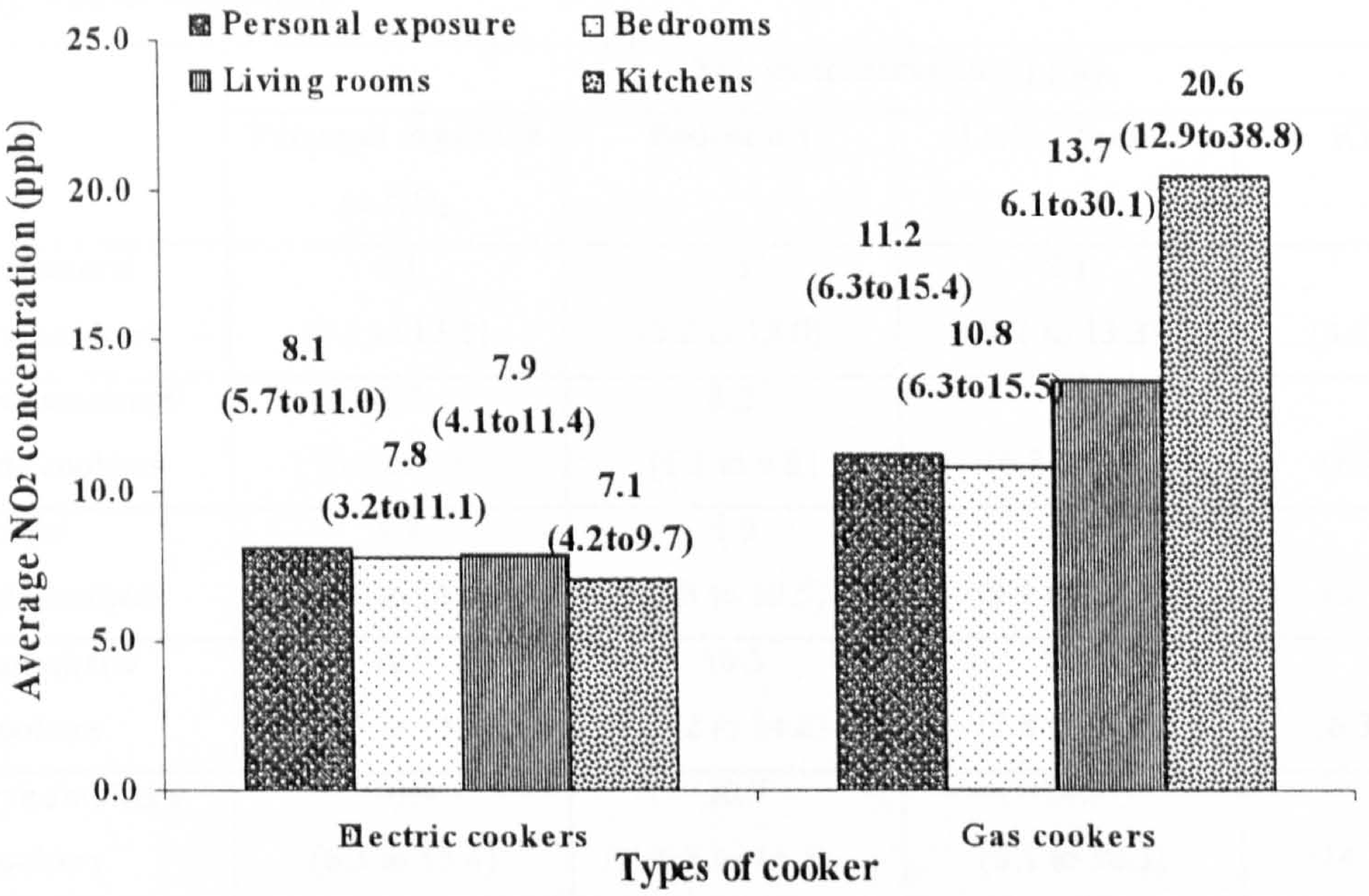


Figure 5.18 Personal exposure to NO_2 and average NO_2 concentrations measured in bedrooms, living rooms and kitchens with electric and gas cookers during the winter campaign

Personal exposure of non-smokers, passive smokers and smokers to NO_2 concentrations and NO_2 concentrations in houses with electric and gas cookers is given in Table 5.19 and Figure 5.19. The results clearly show that, average personal exposure to NO_2 of smokers in houses with gas cookers (13.6ppb) was higher than those non-smokers (10.8 ppb) and passive smokers (10.9 ppb). However, there was no significant difference between personal exposure of non-smokers, passive and smokers in houses with electric cookers (8.1, 8.7 and 9.4 ppb, respectively). Only average NO_2 concentration in bedrooms of smokers using gas cookers were found to be significantly different from those rooms of non-smokers and passive smokers while the other rooms of non-smokers and passive smokers using gas cookers and electric cookers did not show any significant difference.

Table 5.19 Personal exposure of non-smokers, passive smokers and smokers to NO_2 concentrations and NO_2 concentrations in houses with electric and gas cookers measured during winter campaign

	NO_2 concentrations (ppb)			
	Personal exposure to NO_2	Bedrooms	Living rooms	Kitchens
Non-smokers/ electric cookers	8.1 (5.7 to 13.1)	7.8 (3.2 to 13.0)	8.1 (4.1 to 13.3)	7.6 (4.2 to 19.8)
Passive smokers/ electric cookers	8.7 (6.6 to 9.8)	8.2 (6.5 to 9.8)	7.6 (6.3 to 9.7)	7.3 (6.2 to 9.6)
Smokers/ electric cookers	9.4 (7.1 to 11.0)	8.9 (6.8 to 10.5)	9.0 (8.1 to 10.0)	7.1 (6.1 to 8.3)
Non-smokers/ gas cookers	10.8 (7.5 to 14.6)	10.3 (7.2 to 14.2)	13.0 (7.8 to 24.1)	18.9 (6.3 to 38.8)
Passive smokers/ gas cookers	10.9 (6.3 to 15.4)	10.7 (6.3 to 15.5)	14.7 (6.1 to 30.1)	21.7 (14.3 to 34.6)
Smokers/ gas cookers	13.6 (13.1 to 14.2)	13.6 (13.2 to 13.9)	14.6 (13.5 to 15.7)	24.8 (21.4 to 28.2)

5.4.2.3 The relationship between personal exposure to NO_2 concentrations in relation to indoor and outdoor sources and activity patterns

Relationships between personal exposure to NO_2 and average NO_2 concentrations in each microenvironment were tested with correlation analysis (as shows in Table 5.20). Good correlation was found between personal exposure and NO_2 concentrations in bedrooms, living rooms, kitchens, front door and offices (r = 0.96, 0.86, 0.73, 0.21 and 0.44 respectively). However, no relationship was found between personal exposures to NO_2 and NO_2 concentrations in cars. Similar reasons also apply here as discussed for the autumn campaign. Good correlation also found between indoor concentrations for kitchens, living rooms and bedrooms.

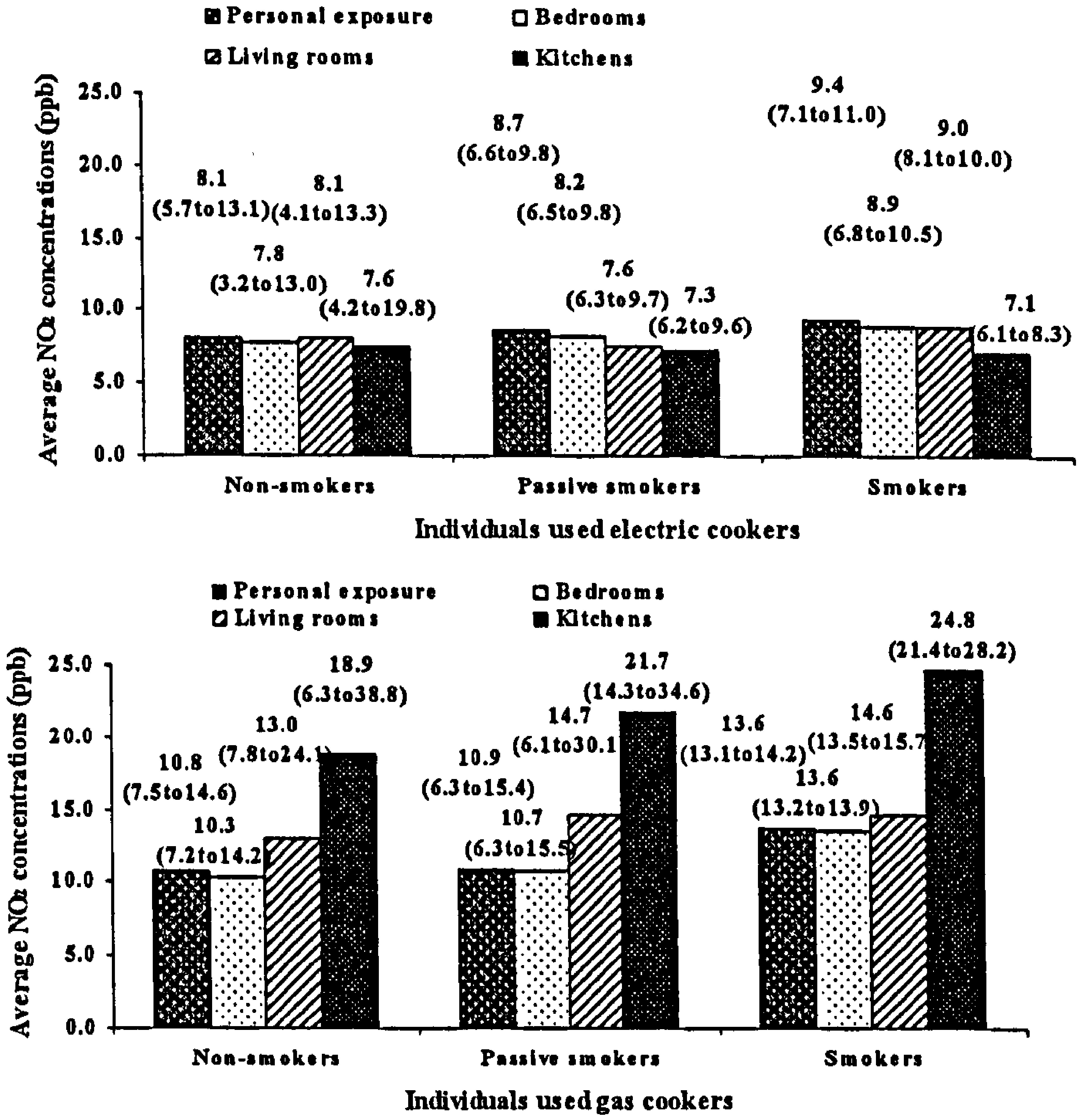


Figure 5.19 Average personal exposure of non-smokers, passive smokers and smokers o NO_2 concentrations and average NO_2 concentrations in microenvironments measured during winter campaign

Table 5.20 Coefficient of correlation (r) results between personal exposure to NO_2 concentrations and NO_2 concentrations in each microenvironment used for winter campaign

	Personal exposure	Microenvironments					
		Bedroom	Living room	Kitchen	Outdoor	Work	Car
Actual measured	1						
Bedroom	0.96	1					
Living room	0.86	0.83	1				
Kitchen	0.73	0.74	0.82	1			
Outdoor	0.21	0.21	0.15	-0.02	1		
Work	0.44	0.35	0.41	0.37	0.10	1	
Car	0.00	0.02	-0.08	-0.22	0.30	0.08	1

Comparisons between personal exposures to NO_2 concentrations and NO_2 concentrations in bedrooms, living rooms and kitchens are given in Figure 5.20. The relationship was found between personal exposures to NO_2 concentrations and NO_2 concentrations in bedrooms, living rooms and kitchens. The average NO_2 concentrations in bedrooms, living rooms and kitchens were accounted for 92.93%, 73.26% and 53.77% of the personal exposure (R^2 = 0.9293, 0.7326, 0.5377). The reason could be due to individuals spent more of their time in bedrooms and living rooms and spent little time in kitchen as data were recorded in time activity diaries. As a result, NO_2 concentrations from bedrooms, living rooms and kitchens could be used to estimate the personal exposure rather than NO_2 concentrations from other microenvironments.

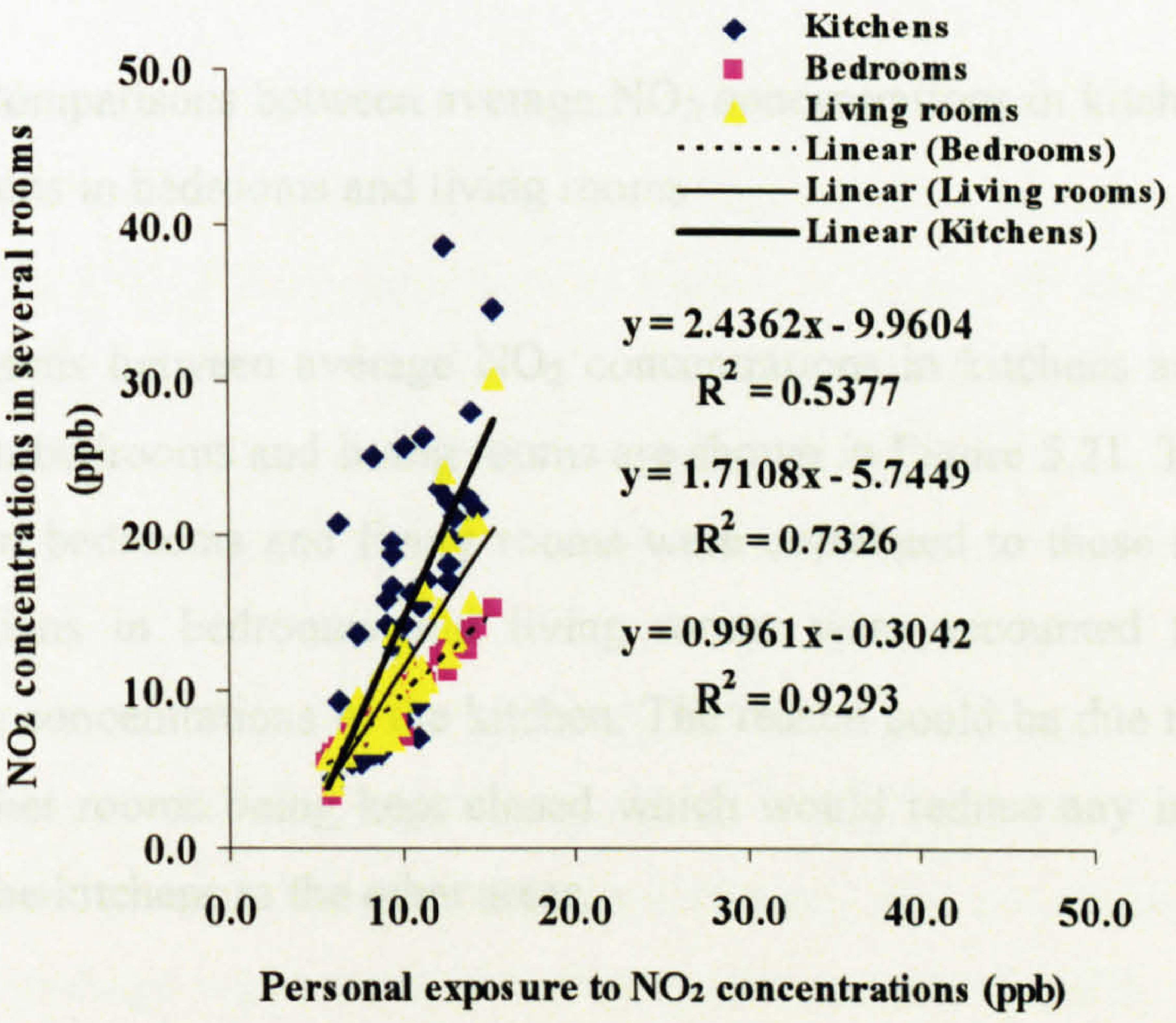


Figure 5.20 Comparisons between personal exposure to NO_2 concentrations and NO_2 concentrations in bedrooms, living rooms and kitchens

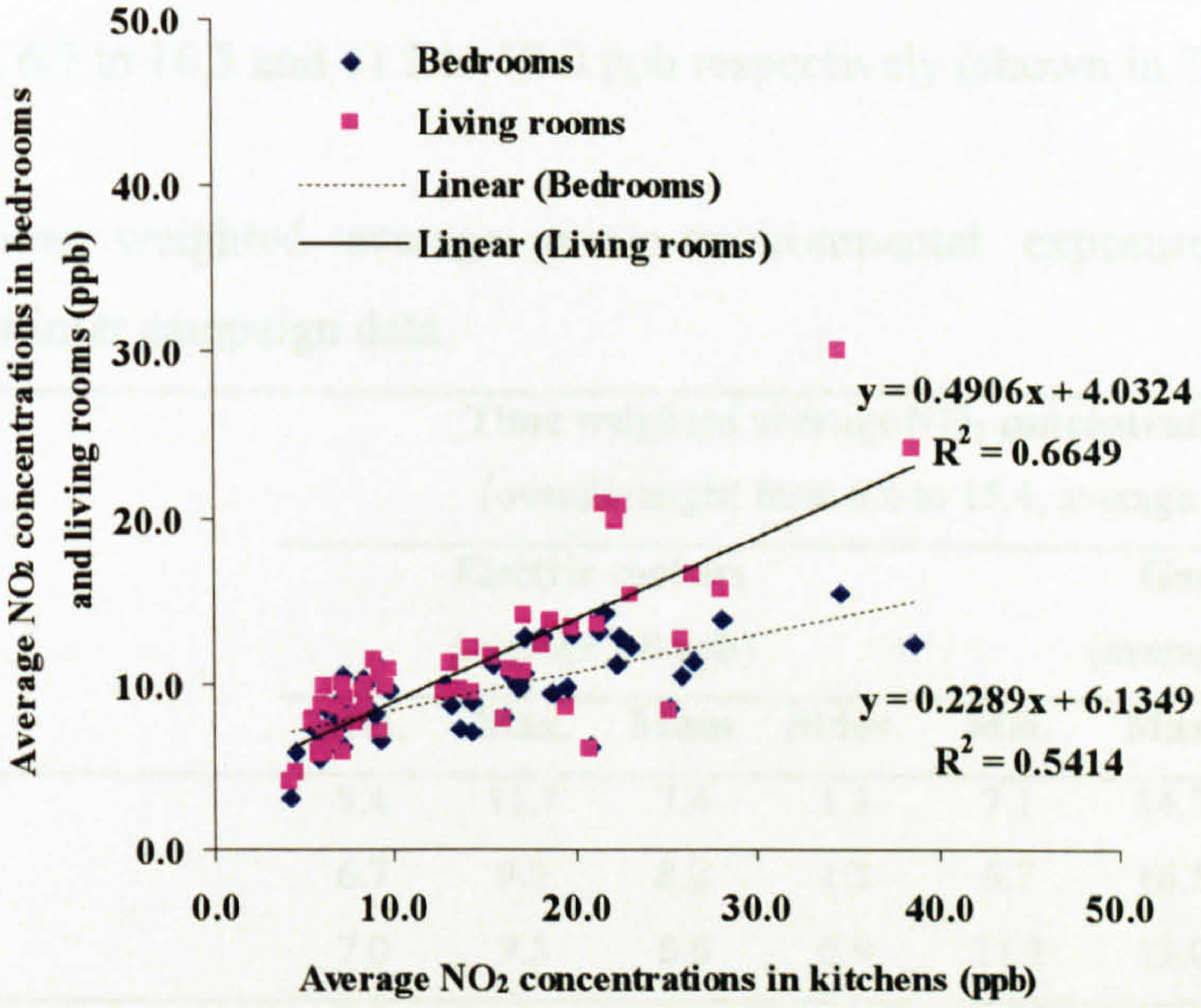


Figure 5.21 Comparisons between average NO_2 concentrations in kitchens and average NO_2 concentrations in bedrooms and living rooms

Comparisons between average NO_2 concentrations in kitchens and average NO_2 concentrations in bedrooms and living rooms are shown in Figure 5.21. The average NO_2 concentrations in bedrooms and living rooms were correlated to those in kitchens. The NO_2 concentrations in bedrooms and living rooms were accounted for 66.49% and 54.14% of those concentrations in the kitchen. The reason could be due to doors between kitchens and other rooms being kept closed which would reduce any infiltration of the pollution from the kitchens to the other areas.

5.4.2.4 Time weighted average micro-environmental exposure modelling in relation to indoor and outdoor sources and activity patterns

Time weighted average micro-environmental exposure were calculated using data from fractional exposures based on time spent in microenvironments and the NO_2 concentration data measured in those microenvironments. The results showed that overall time weighted average ranged from 6.6 to 15.4 ppb (average 10.9 ppb). Also, the time weighted average of non-smokers, passive smokers and smokers using electric cookers ranged from 5.4 to 11.7, 6.7 to 9.7 and from 7.0 to 9.3 ppb respectively. The time weighted average of non-smokers, passive smokers and smokers used gas cookers ranged from 7.1 to 14.7, 6.7 to 16.5 and 11.2 to 12.0 ppb respectively (shown in Table 5.21).

Table 5.21 Time weighted average micro-environmental exposure of volunteers calculated from winter campaign data

	Time weighted average NO_2 concentrations (ppb) (overall ranged from 6.6 to 15.4, average 10.9 ppb)							
	Electric cookers (average 7.8 ppb)				Gas cookers (average 10.5 ppb)			
	Min.	Max.	Mean	Stdev.	Min.	Max.	Mean	Stdev.
Non smokers	5.4	11.7	7.6	1.3	7.1	14.7	10.4	2.1
Passive smokers	6.7	9.7	8.2	1.3	6.7	16.5	10.5	3.1
Smokers	7.0	9.3	8.6	0.9	11.2	12.0	11.6	0.5

The time-weighted average exposure was also plotted against the personal exposure to NO_2 concentrations and is shown in Figure 5.22. The time weighted average gave a fair approximation but underestimated when compared with the personal exposure to NO_2 concentrations ($y = 0.9433x$, $R^2 = 0.8535$). This was a slightly worse relationship that for the autumn results (section 5.4.1.4). Again as in the case of the autumn campaign, individuals probably spent their time in other microenvironments which were not included in this study.

The differences between the time weighted average and the personal exposure to NO_2 concentrations were calculated using Paired t–test analysis. The result from the paired t-test (p-value < 0.05) showed that the difference was not significant between the time weighted average exposure and the personal exposure to NO_2 concentrations as shown in Table 5.18 (Section 5.2.1.4). The case was similar for the time weighted average of individuals using gas cookers and their personal exposure and for the time weighted average of individuals used electric cookers and their personal exposure (Table 5.22).

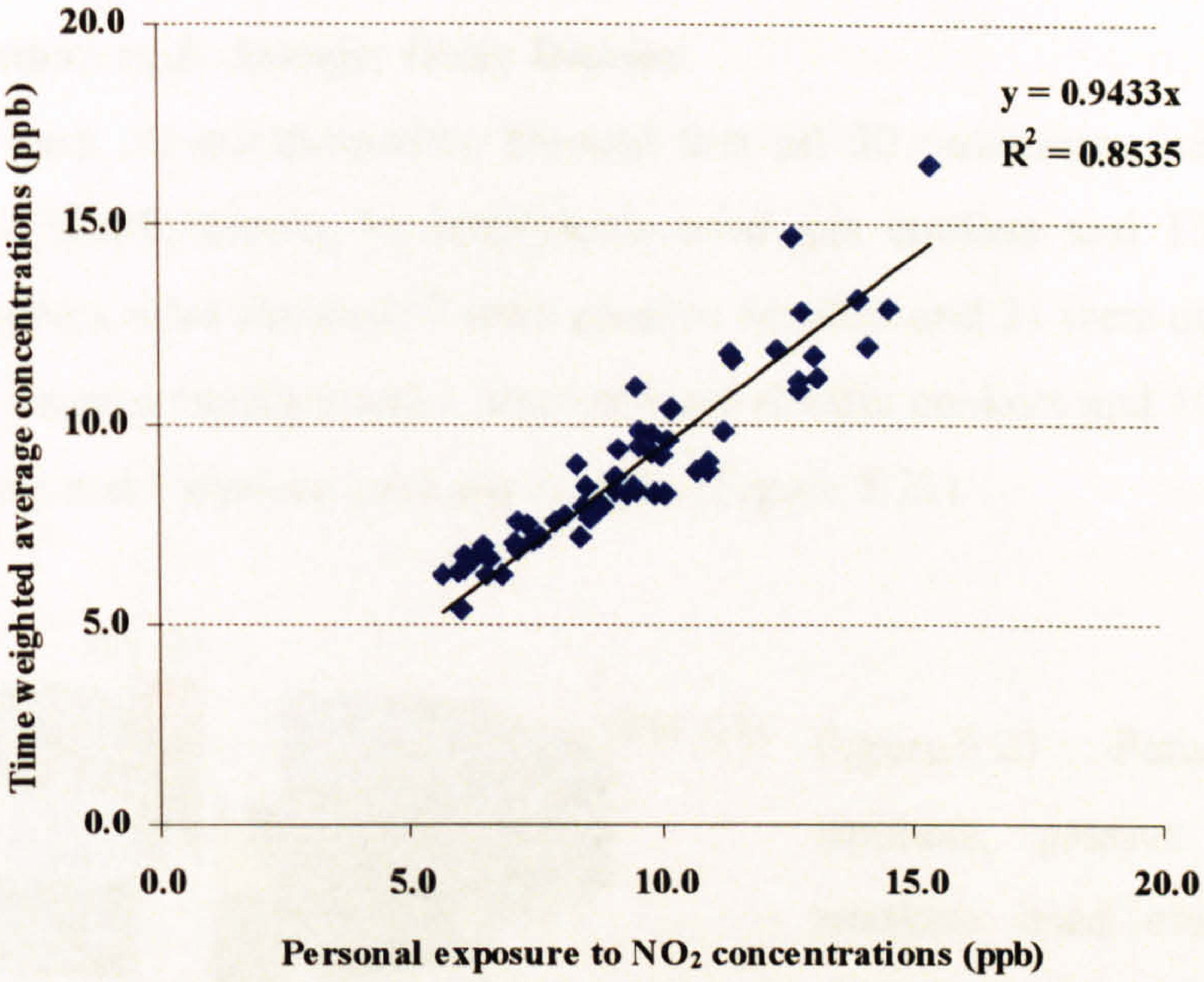


Figure 5.22 Comparisons between the personal exposure to NO_2 and time weighted average micro-environmental exposure used for winter campaign

Table 5.22 Paired t-Test between time weighted average micro-environmental exposure and personal exposure to NO_2 concentrations for volunteers using gas cookers and electric cookers from winter campaign.

	Gas cookers		**Electric cookers**	
	Time weighted average NO_2 concentrations	**Personal exposure to NO_2**	**Time weighted average NO_2 concentrations**	**Personal exposure to NO_2**
Mean	10.7	11.2	7.7	8.3
Variance	5.0	5.1	1.1	2.4
Observations	27	27	28	28
Pearson Correlation	0.9		0.9	
Hypothesized Mean Difference	0		0	
df	26		27	
t Stat	-2.29		-4.02	
P(T<=t) one-tail	0.02		0.00	
t Critical one-tail	1.71		1.70	
P(T<=t) two-tail	0.03		0.00	
t Critical two-tail	2.06		2.05	

5.4.3 Campaign study in summer 2001

5.4.3.1 Questionnaires & Activity Daily Diaries

Results from 30 questionnaires showed that all 30 volunteers (13 male and 17 female) lived in Hertfordshire. 15 individuals used gas cookers and 15 used electric cookers. 2 volunteers were smokers, 7 were passive smokers and 21 were non-smokers. 11 non-smokers, 3 passive smokers and 1 smoker used electric cookers and 10 non-smokers, 4 passive smokers and 1 smoker used gas cookers (Figure 5.23).

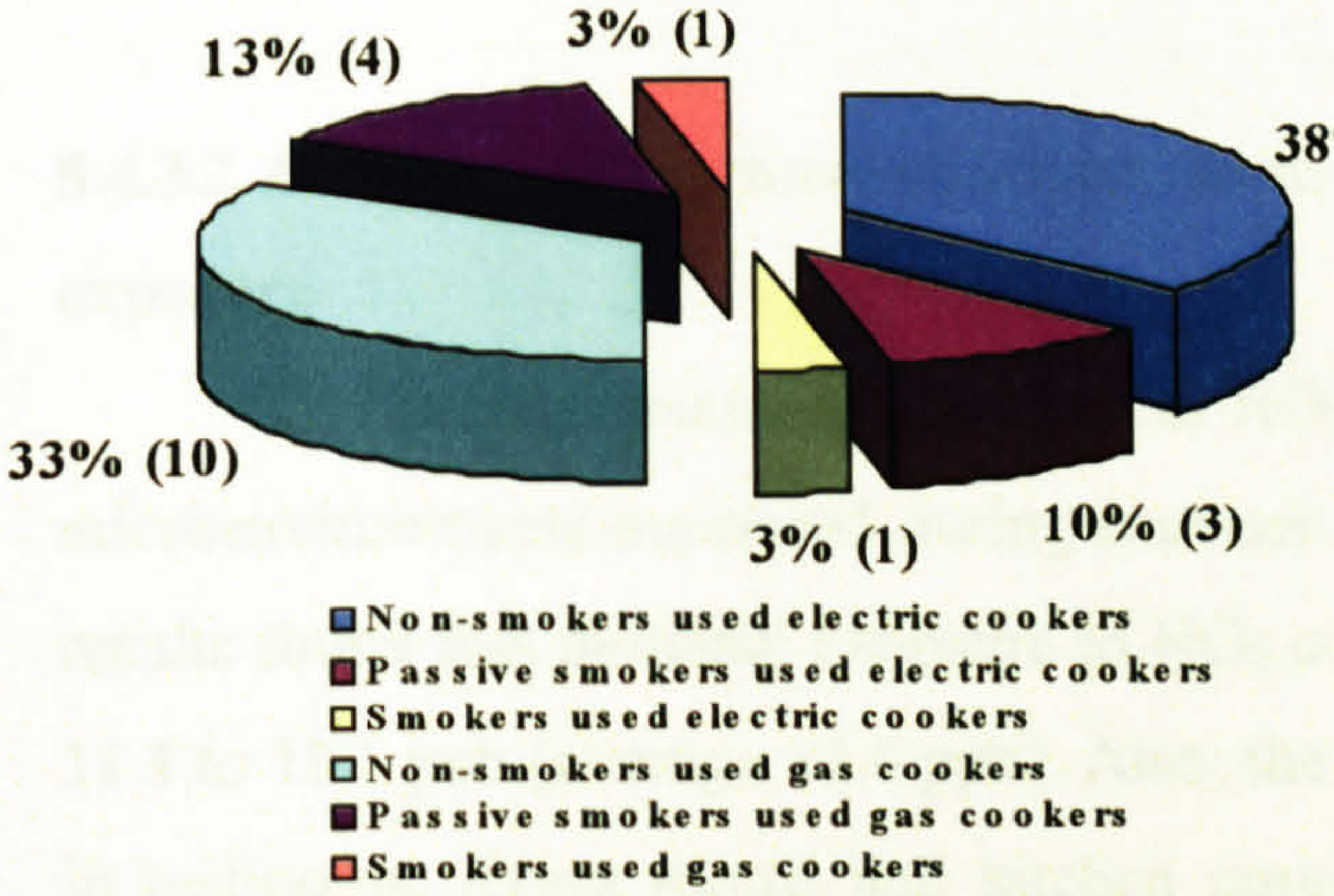


Figure 5.23 Percents of non-smokers, passive smokers and smokers used electric and gas cookers for summer campaign

The results showed that 30% of the subjects were aged between 41-45 years, followed by 20% being 26-30 years old. 33.3% of the individuals lived in semi-detached houses, followed by 30% in flats and 26.7% in central terrace houses. More than 80% of the individuals were car owners using mainly unleaded petrol. 37.5 % of the cars were parked at the resident car park, followed by 33.3% being parked in a garage and 29.2% at the kerbside of the road.

Results from 25 activities diaries showed that all volunteers spent much of their time at home (48.0%), followed by 29.3% of their time at work. Also they spent their time in other non-smoking indoors environments (4.6%) and smoking indoors environments (2.1%). The results also showed that the individuals spent 4.0 % of their time in transportation and 11.9 % outdoors (as shown in Figure 5.24).

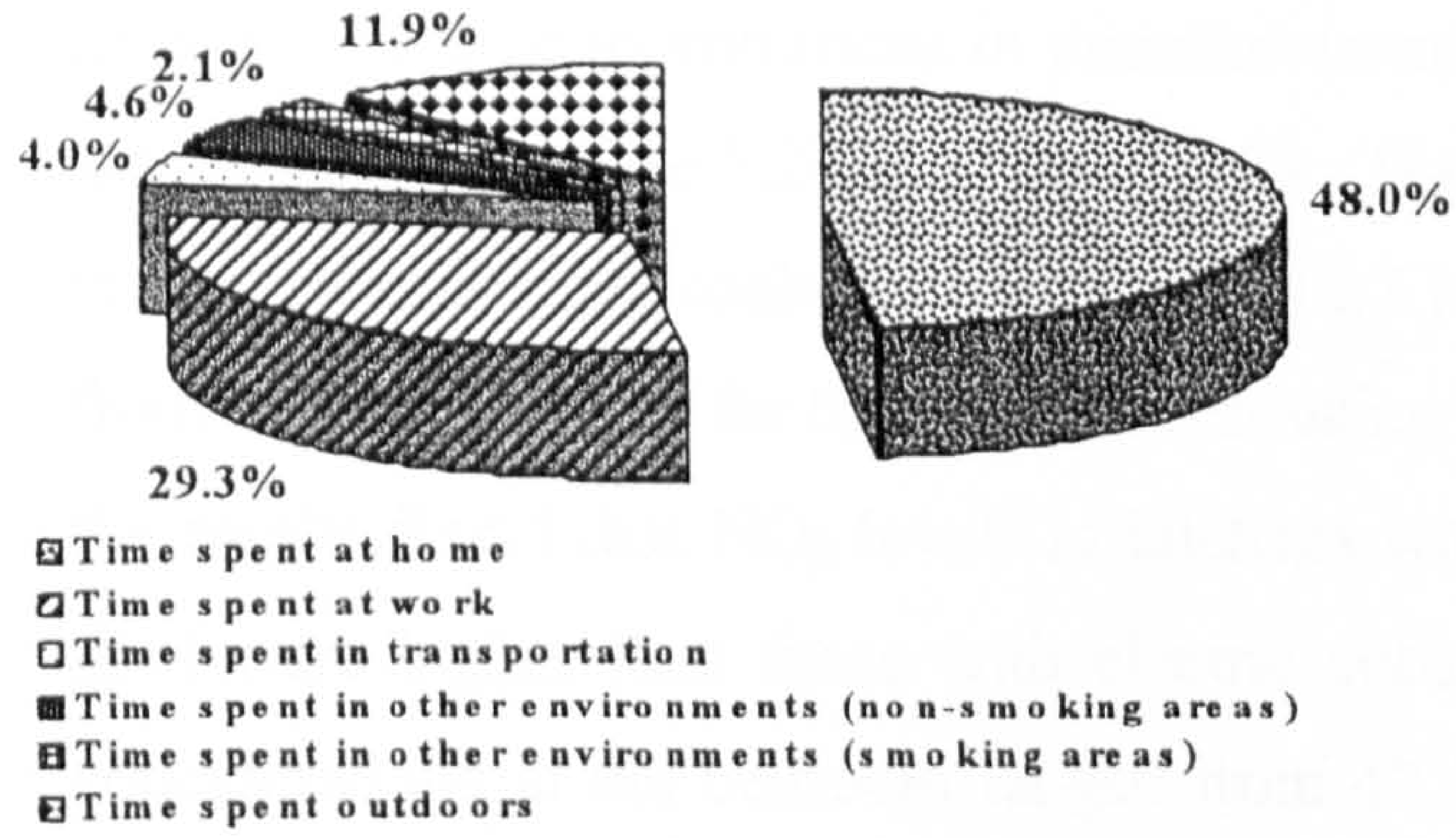


Figure 5.24 Average time activity patterns in microenvironments for all volunteers during a 7-day exposure period in summer campaign

5.4.3.2 Average NO_2 concentrations from each microenvironment and personal exposure

The average personal exposure to NO_2 and the average of NO_2 concentrations in microenvironments measured during summer campaign are presented in Table 5.23. The results found that personal exposure to NO_2 concentrations for all volunteers ranged from 11.3 to 18.1 ppb (average 14.0 ppb). Also, the results showed average NO_2 concentrations in bedrooms, living rooms and kitchen ranged 10.6-17.3 ppb (average 13.5ppb), 10.8-18.2ppb (13.9ppb) and 8.0-17.7 ppb (average 12.6 ppb) respectively. The outdoors concentrations ranged from 11.3 to 18.8 ppb (average 14.5 ppb). NO_2 concentrations in offices ranged from 9.2 to 15.2 ppb (average 12.2 ppb) and in cars ranged from 8.7 to 14.4 ppb (average 11.4 ppb).

Table 5.23 Overall average personal exposure to NO_2 concentrations and average NO_2 concentrations in microenvironments measured during summer campaign.

	Personal exposure to NO_2 (ppb)	Average NO_2 concentrations (ppb)					
		Bedrooms	Living rooms	Kitchens	Outdoors	Offices	Cars
Min.	11.3	10.6	10.8	8.0	11.3	9.2	8.7
Max.	18.1	17.3	18.2	17.7	18.8	15.2	14.4
Average	14.0	13.5	13.9	12.6	14.5	12.2	11.4
Stdev.	1.5	1.6	1.6	2.2	1.8	1.5	1.6

The average personal exposure of volunteers using electric and gas cookers and the average of NO_2 concentrations in microenvironments measured during summer campaign are presented in Table 5.24 and Figure 5.25. The results showed that personal exposure of volunteers using gas cookers ranged from 12.7 to 18.1 ppb (average 14.6 ppb) and ranged from 11.3 to 15.3 ppb for those volunteers using electric cookers (average 13.3 ppb). Also, the results found that NO_2 levels in kitchens with gas cookers (ranged from 12.8 to 17.7 ppb) were higher than those with electric cookers (ranged from 8.0 to 13.3 ppb). NO_2 concentrations in the bedroom ranged from 12.5 to 17.3 ppb in houses with gas cookers and 10.6 to 14.8 ppb in those with electric cookers. NO_2 concentrations in the living room ranged from 10.8 to 18.2 ppb (from 13.2 to 18.2 in house with gas cookers and from 10.8 to 15.4 in houses with electric cookers).

Comparison of concentrations in kitchens with gas cookers showed lower or similar values to those for other rooms. During the summer period, windows would be expected to be kept open more often giving increased ventilation rates than for winter times. This would lead to lower concentrations in kitchens than would be case in winter times.

Table 5.24 Average personal exposure to NO_2 concentrations (of volunteers using electric and gas cookers) and average NO_2 concentrations in houses measured during summer campaign

	Average NO_2 concentrations (ppb)							
	Electric cookers				**Gas cookers**			
	Min.	**Max.**	**Mean**	**Stdev.**	**Min.**	**Max.**	**Mean**	**Stdev.**
Personal exposure to NO_2	11.3	15.3	13.3	1.2	12.7	18.1	14.6	1.6
Bedrooms	10.6	14.8	12.7	1.3	12.5	17.3	14.3	1.4
Living rooms	10.8	15.4	13.1	1.5	13.2	18.2	14.7	1.4
Kitchens	8.0	13.3	11.0	1.7	12.8	17.7	14.2	1.3

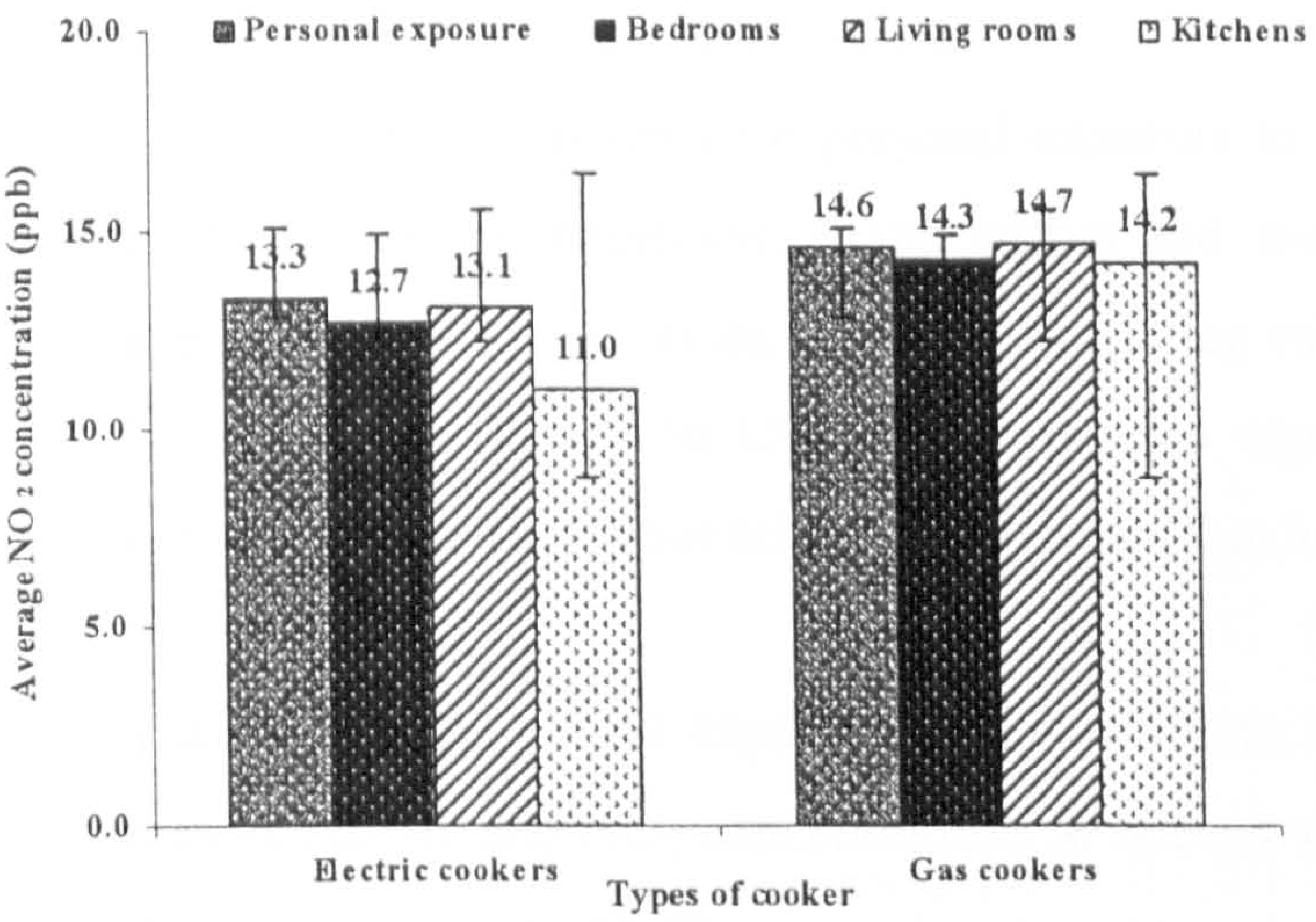


Figure 5.25 Personal exposure to NO_2 and average NO_2 concentrations measured in bedrooms, living rooms and kitchens with electric and gas cookers during summer campaign

Personal exposure of non-smokers, passive smokers and smokers to NO_2 concentrations and NO_2 concentrations in houses with electric and gas cookers is given in Table 5.25 and Figure 5.26. The results clearly showed that, average personal exposure to NO_2 of smokers in houses with gas cookers (17.0 ppb) was higher than those non-smokers (14.9 ppb) and passive smokers (13.7 ppb). However, there was no significant difference between personal exposure of non-smokers, passive and smokers in houses with electric cookers (13.1, 13.7 and 13.4 ppb, respectively). Significant differences were found between the average NO_2 concentration in bedrooms and living rooms of smokers using gas cookers and those for rooms of non-smokers and passive smokers. No difference was found for the other areas for non-smokers and passive smokers using gas cookers or electric cookers.

5.4.3.3 The relationship between personal exposure to NO_2 concentrations in relation to indoor and outdoor sources and activity patterns

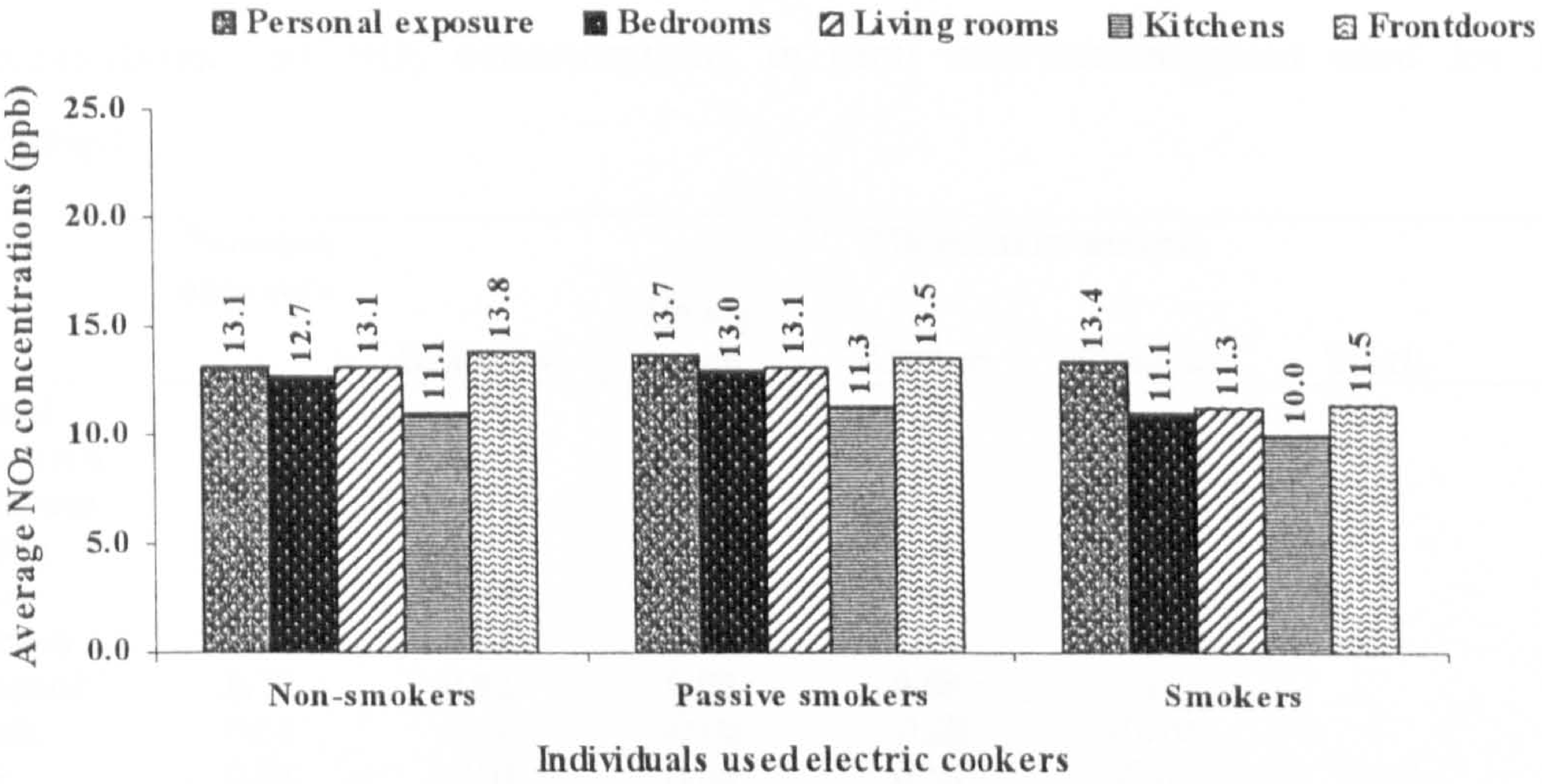
The relationship between the personal exposure to NO_2 and the average NO_2 concentrations in each microenvironment was analysed using Correlation analysis. Good correlation was found between personal exposure and NO_2 concentrations in bedrooms (r = 0.86), living rooms (r = 0.80), kitchens (r = 0.76) and also outdoors (r = 0.78) concentrations (Table 5.26). However, no correlation was found between personal exposures to NO_2 and NO_2 concentrations in offices and cars indicating that these were not significant contributors towards the overall personal exposure. The good correlation was also found between NO_2 concentrations from outdoors and NO_2 concentrations in bedrooms, living rooms and kitchens.

Comparisons between personal exposure to NO_2 concentrations and average NO_2 concentrations in bedrooms, living rooms and kitchens are given in Figure 5.27. The average NO_2 concentrations in bedrooms, living rooms and kitchens could represent for 72.45%, 62.26%, and 56.43% of the personal exposure. This means that must be NO_2 concentrations from other microenvironments that have an influence also.

Table 5.25 Personal exposure of non-smokers, passive smokers and smokers to NO_2 concentrations and NO_2 concentrations in houses with electric and gas cookers measured during summer campaign

	NO_2 concentrations (ppb)			
	Personal exposure to NO_2	**Bedrooms**	**Living rooms**	**Kitchens**
Non-smokers/ electric cookers	13.1 (11.3 to 14.7)	12.7 (11.3 to 14.5)	13.1 (11.5 to 15.4)	11.1 (8.7 to 13.3)
Passive smokers/ electric cookers	13.7 (12.6 to 14.8)	13.0 (10.6 to 14.6)	13.1 (10.8 to 14.7)	11.3 (8.0 to 13.0)
Smoker/ electric cooker*	13.4	11.1	11.3	10.0
Non-smokers/ gas cookers	14.9 (12.7 to 18.1)	14.3 (12.5 to 17.2)	14.7 (13.2 to 18.2)	14.0 (12.1 to 17.7)
Passive smokers/ gas cookers	13.7 (13.1 to 14.2)	13.6 (13.0 to 14.3)	14.4 (13.5 to 15.2)	14.0 (13.0 to 14.6)
Smoker/ gas cooker*	17.0	17.3	17.3	16.2

Note: *Only one person belonged to this group.



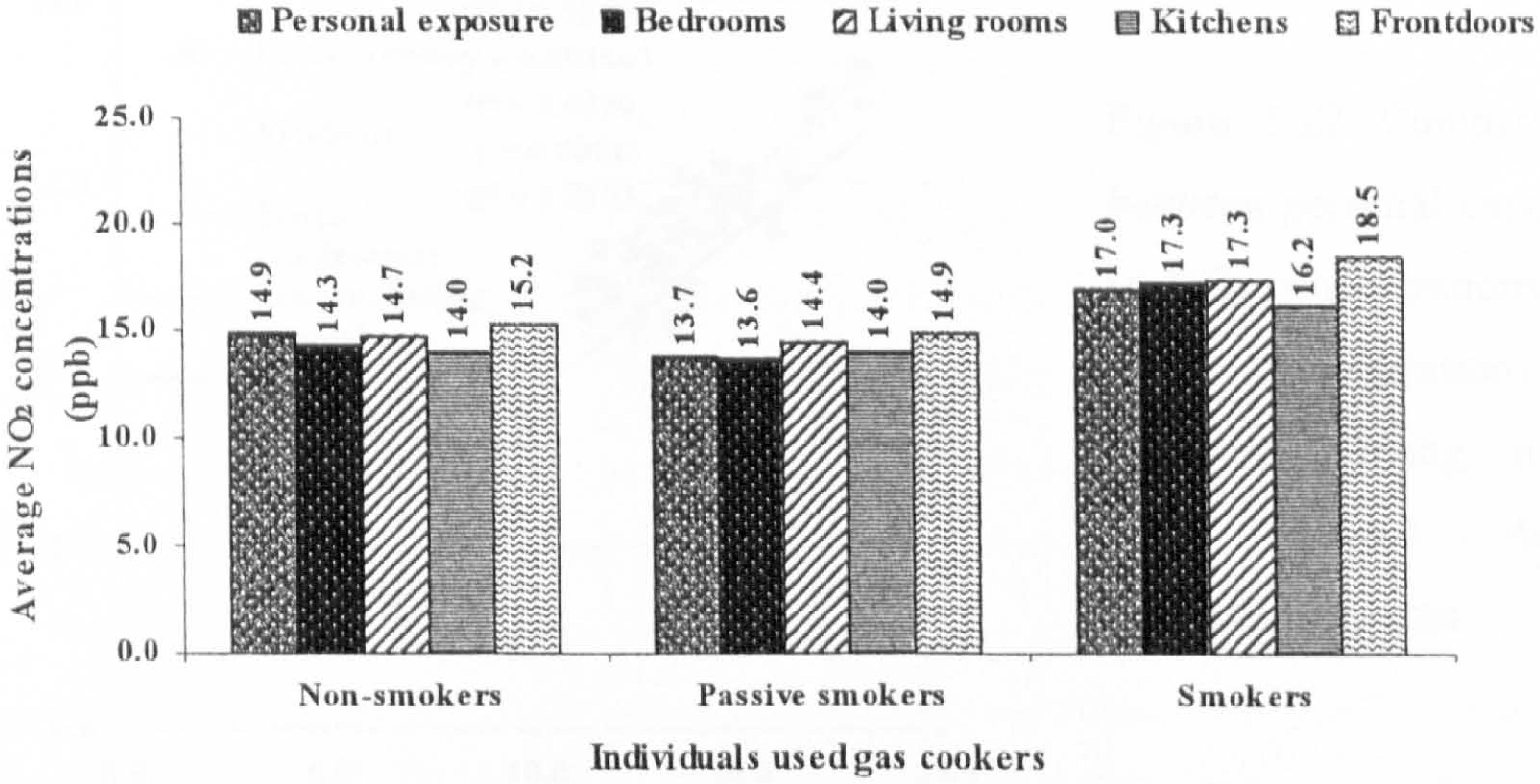


Figure 5.26 Average personal exposure of non-smokers, passive smokers and smokers to NO_2 concentrations and average NO_2 concentrations in microenvironments measured during summer campaign

Table 5.26 Coefficient of correlation (r) results between personal exposure to NO_2 concentrations and NO_2 concentrations in each microenvironment used for summer campaign

	Personal exposure	**Microenvironments**					
		Bedroom	**Living room**	**Kitchen**	**Outdoor**	**Work**	**Car**
Actual measured	1						
Bedroom	**0.86**	1					
Living room	**0.80**	**0.94**	1				
Kitchen	**0.76**	**0.84**	**0.84**	1			
Outdoor	**0.78**	**0.92**	**0.98**	**0.83**	1		
Work	0.03	-0.06	-0.06	-0.08	-0.10	1	
Car	0.04	-0.01	0.06	0.10	-0.02	-0.19	1

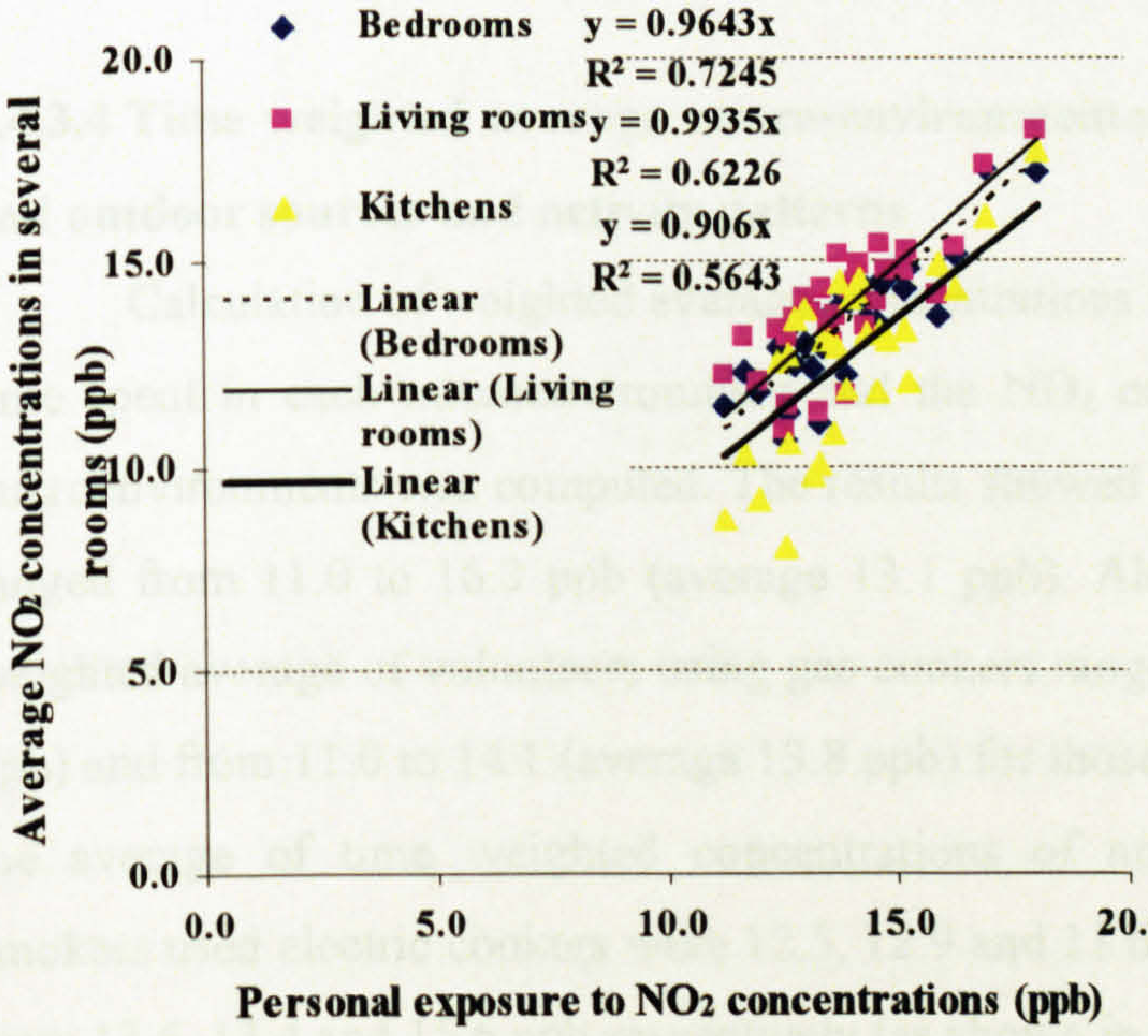


Figure 5.27 Comparisons between personal exposure to NO_2 concentrations and NO_2 concentrations in bedrooms, living rooms and kitchens during summer campaign

Comparisons between outdoors NO_2 concentrations and NO_2 concentrations in bedrooms, living rooms and kitchen are also shown in Figure 5.28. The average NO_2 concentrations in bedrooms, living rooms and kitchens could represent for 83.41%, 95.2% and 66.45 % of the average outdoor NO_2 concentrations. One reason could be possibly due to the windows and/or doors kept opened because of the warm temperatures in summer.

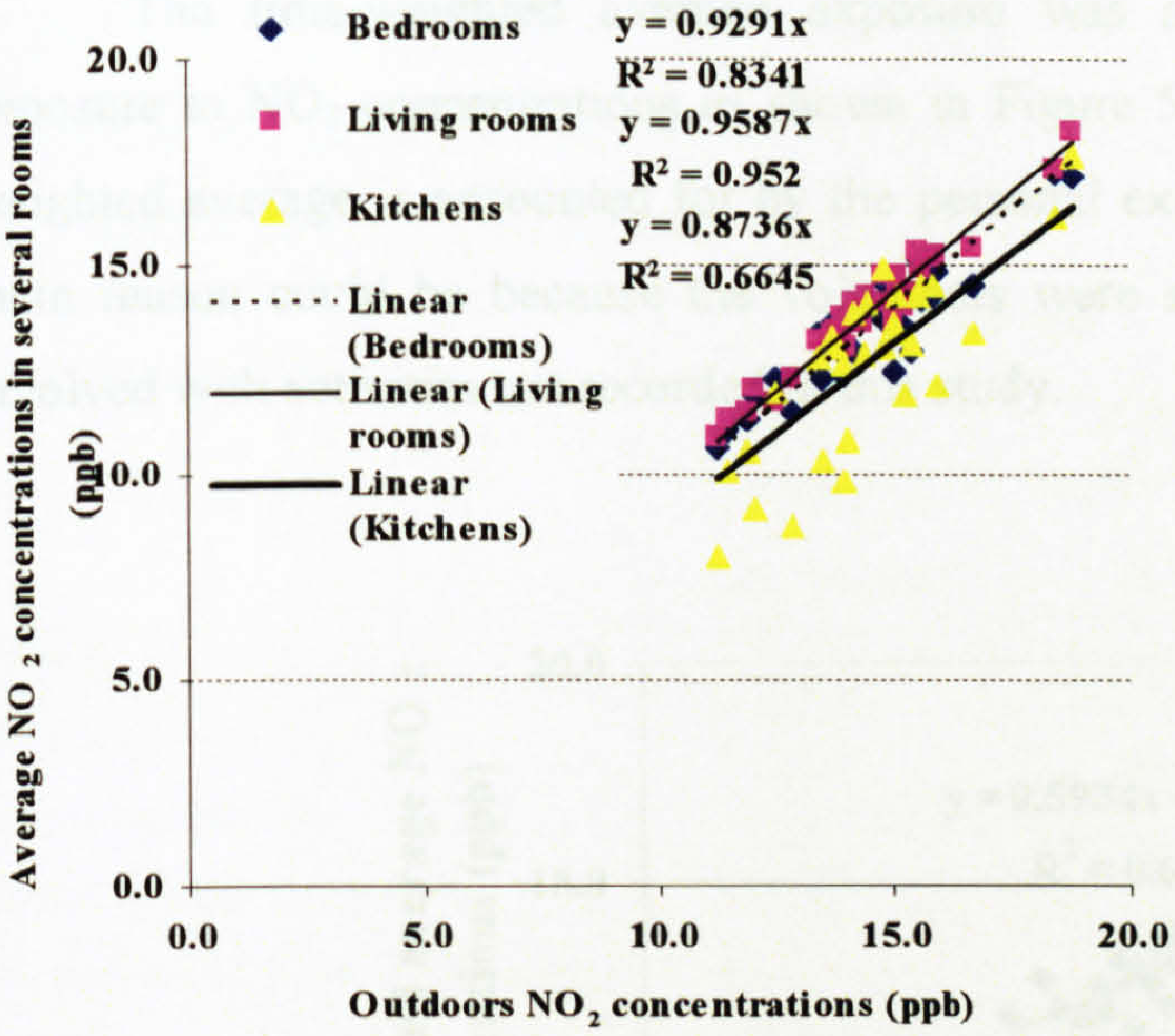


Figure 5.28 Comparisons between average outdoors NO_2 concentrations and average NO_2 concentrations in bedrooms, living rooms and kitchens during summer campaign

5.4.3.4 Time weighted average micro-environmental exposure in relation to indoor and outdoor sources and activity patterns

Calculation of weighted average concentrations from fractional exposures based on time spent in each microenvironment and the NO_2 concentration data measured in the microenvironments was computed. The results showed that overall time weighted average ranged from 11.0 to 16.3 ppb (average 13.1 ppb). Also, the results found that the time weighted average of volunteers using gas cookers ranged from 12.0 to 16.3 (average 12.5 ppb) and from 11.0 to 14.1 (average 13.8 ppb) for those using electric cookers. In addition, the average of time weighted concentrations of non-smokers, passive smokers and smokers used electric cookers were 12.5, 12.9 and 11.6 ppb while those using gas cookers were 13.6, 13.4 and 15.6 ppb respectively (as shown in Table 5.27).

Table 5.27 Time weighted average micro-environmental exposure of volunteers calculated from summer campaign data

	Time weighted average NO_2 concentrations (ppb) (overall ranged from 11.0 to 16.3 , average 13.1 ppb)							
	Electric cookers (average 12.5 ppb)				Gas cookers (average 13.8 ppb)			
	Min.	**Max.**	**Mean**	**Stdev.**	**Min.**	**Max.**	**Mean**	**Stdev.**
Non smokers	11.0	14.1	12.5	0.8	12.0	16.3	13.6	1.2
Passive smokers	11.9	13.5	12.9	0.9	13.2	13.7	13.4	0.2
Smokers	-	-	11.6	-	-	-	15.6	-

The time-weighted average exposure was also plotted against the personal exposure to NO_2 concentrations as shown in Figure 5.29. However, 65.33% of the time weighted average is accounted for by the personal exposure to NO_2 concentrations. The main reason could be because the volunteers were spent more time outside and were involved with activities not recorded in this study.

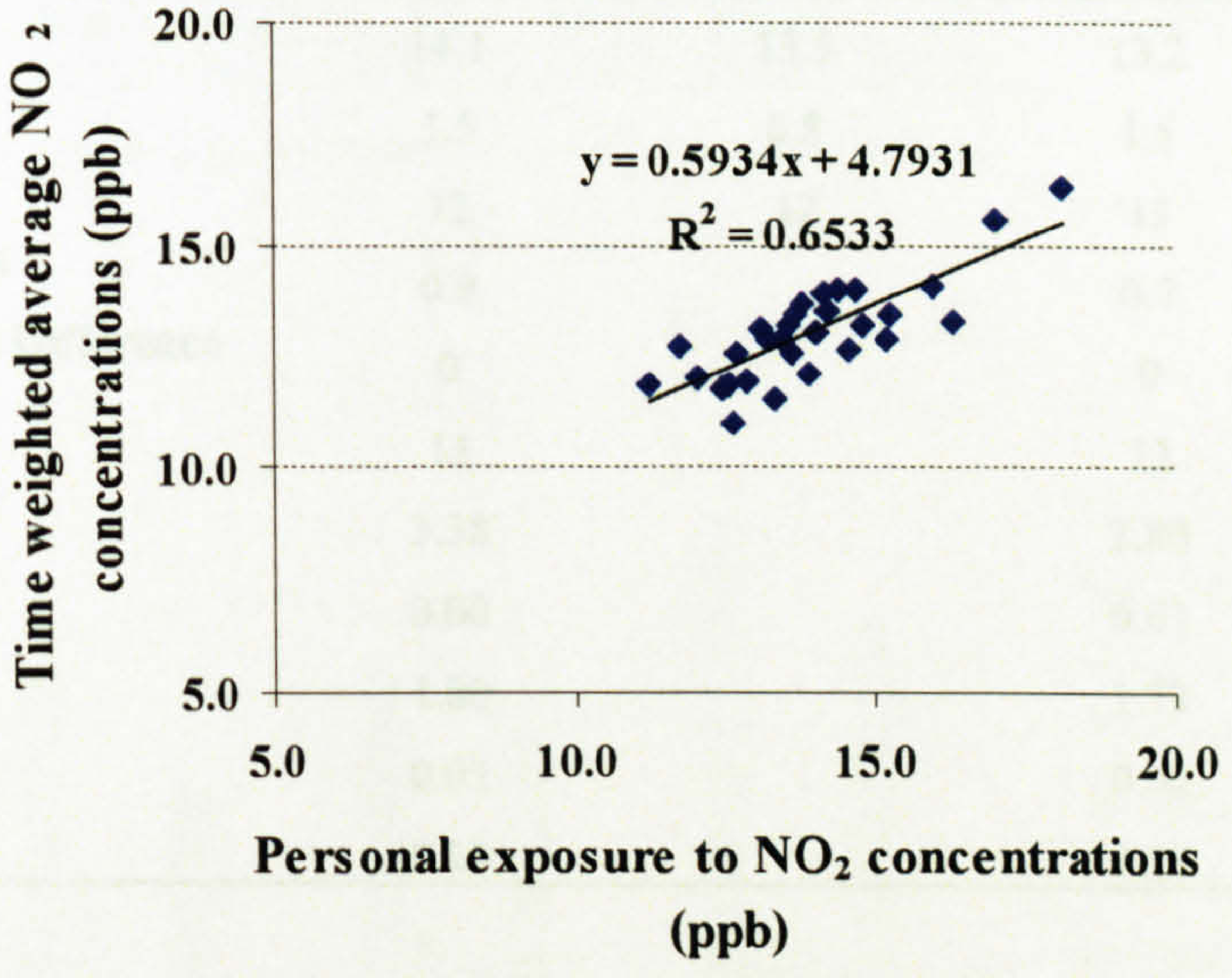


Figure 5.29 Comparisons between the personal exposure to NO_2 and time weighted average micro-environmental exposure used for summer campaign

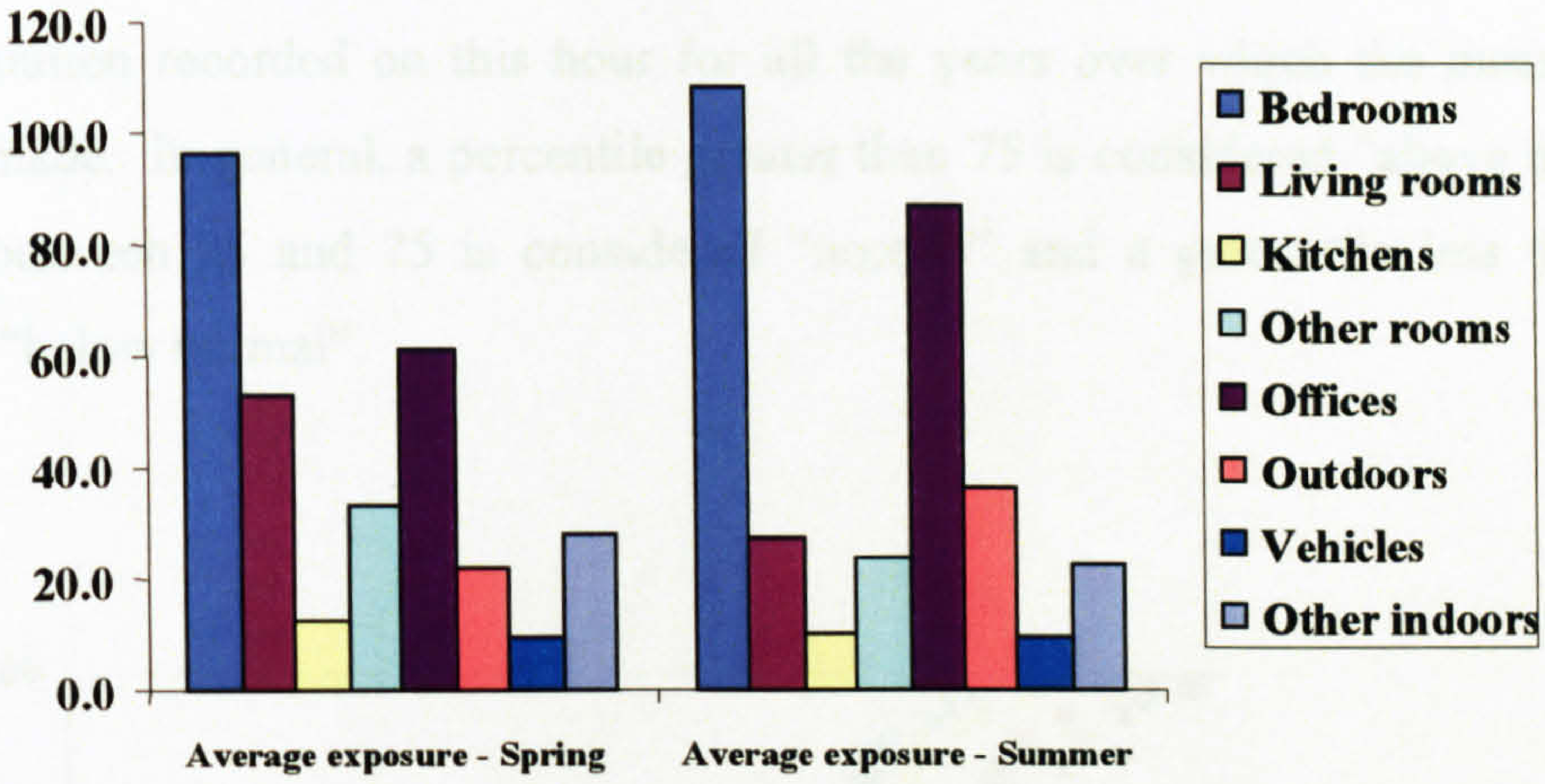
Results from the paired t–test were analysed to find out the difference between two mean data which were the time weighted average and the personal exposure to NO_2 concentrations. The result from the paired t-test ($p\text{-value} < 0.05$) showed that a significant difference was found between the overall time weighted average exposure and the personal exposure to NO_2 concentrations as shows in Table 5.15 (Section 5.2.1.4). Also significant difference was found between the time weighted average exposure of volunteers using gas cookers and their personal exposure. Similarly, a significant difference was found between the time weighted average exposure of individuals using electric cookers and their personal exposure (Table 5.28).

Table 5.28 Paired t-Test between time weighted average micro-environmental exposure and personal exposure to NO_2 concentrations for volunteers using gas cookers and electric cookers from summer campaign.

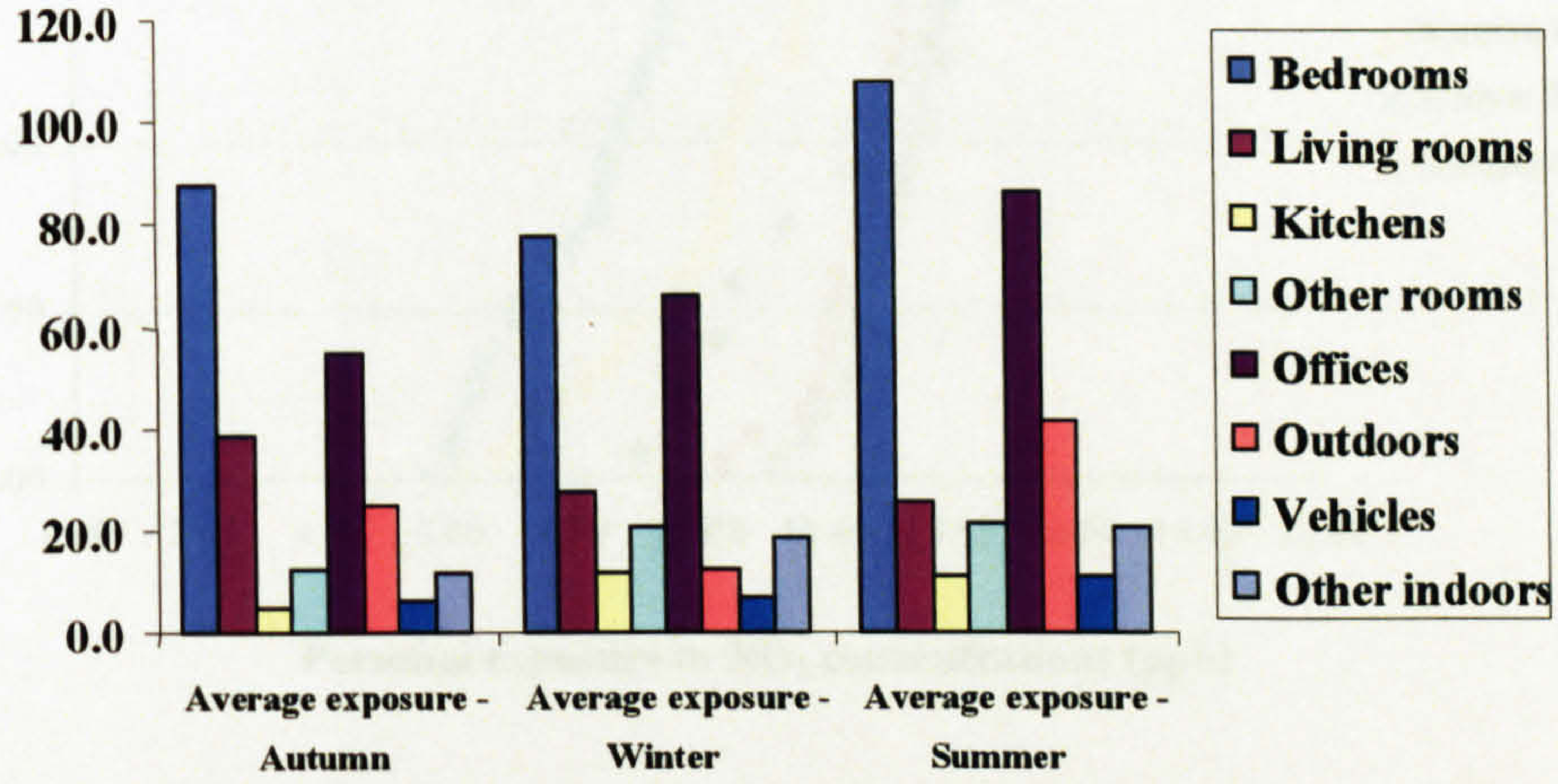
	Gas cookers		Electric cookers	
	Time weighted average NO_2 concentrations	**Personal exposure to NO_2**	**Time weighted average NO_2 concentrations**	**Personal exposure to NO_2**
Mean	14.1	13.5	13.2	12.5
Variance	1.5	0.8	1.5	0.7
Observations	12	12	13	13
Pearson Correlation	0.9		0.7	
Hypothesized Mean Difference	0		0	
Df	11		12	
t Stat	3.38		2.80	
P(T<=t) one-tail	0.00		0.01	
t Critical one-tail	1.80		1.78	
P(T<=t) two-tail	0.01		0.02	
t Critical two-tail	2.20		2.18	

5.5 NO_2 exposure in each microenvironment of office workers for various seasons

NO_2 exposure defined here as concentration multiplied by time spent, C_iT_i, in each microenvironment is shown in Figure 5.30. As described in section 5.1 and 5.2, the individuals always spent most of their time indoors especially at home; mainly in their bedrooms or living rooms. Although low NO_2 concentrations were found in these rooms, the individuals spent longer times in these microenvironments and, therefore, the exposure in these microenvironments was high. The highest exposure in all seasons was found in bedrooms, followed by in offices. The low exposure levels were found in kitchens and vehicles. Even though the individuals spent short period of their time in microenvironments with high NO_2 concentrations, the exposures in these microenvironments were not high.



Pilot studies



Campaigns

Figure 5.30 NO_2 exposure (ppb.h) in each microenvironment

5.6 Percentile, personal exposure to NO_2 concentration and time weighted average micro-environmental exposure of office workers for various seasons

A percentile is a value on a scale of one hundred that indicates the percent of a distribution that is equal to or below it. In this study, a variation of the percentile known as the "percent exceedance" is used. It is simply obtained by subtracting the percentile scale value from 100 percent. For example, an average personal exposure to NO_2 concentration at the 75th percentile is the same as an average personal exposure to NO_2 concentration at the 25th percent exceedance. It is also commonly used for hourly NO_2 concentrations. For example, at the 90th percentile the concentration is equal to or greater than 90 percent of the concentration recorded on this hour for all the years over which the measurements have been made. In general, a percentile greater than 75 is considered "above normal", a percentile between 25 and 75 is considered "normal" and a percentile less than 75 is considered "below normal".

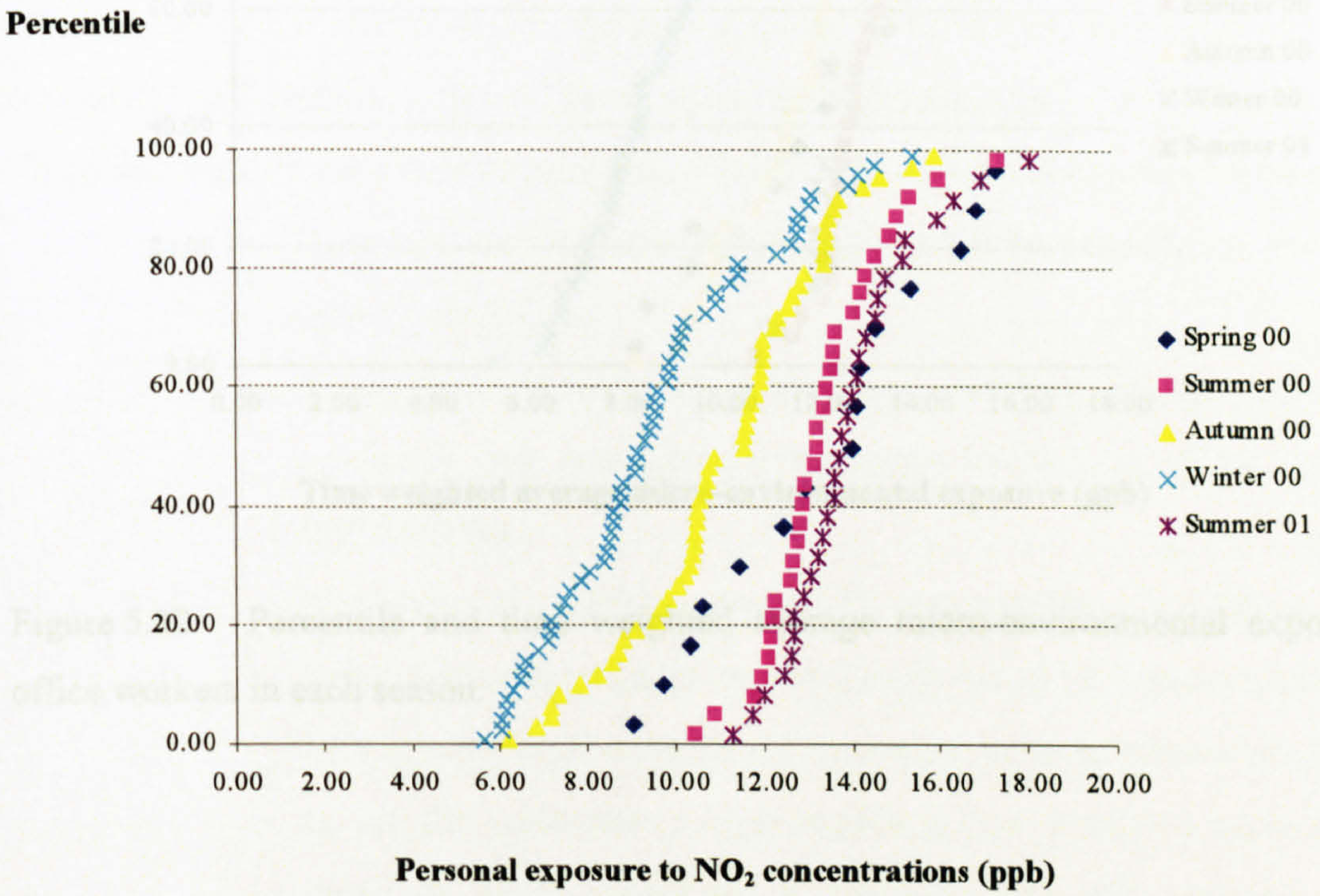


Figure 5.31 Percentile and personal exposure to NO_2 concentration of office workers in each season.

The lowest personal exposure to NO_2 concentrations as well as time weighted average micro-environmental exposure is found in winter 2000. The highest personal exposure to NO_2 concentrations is found in spring 2001 and summer 2000 for the time weighted average micro-environmental exposure as shown in Figure 5.31 and 5.32.

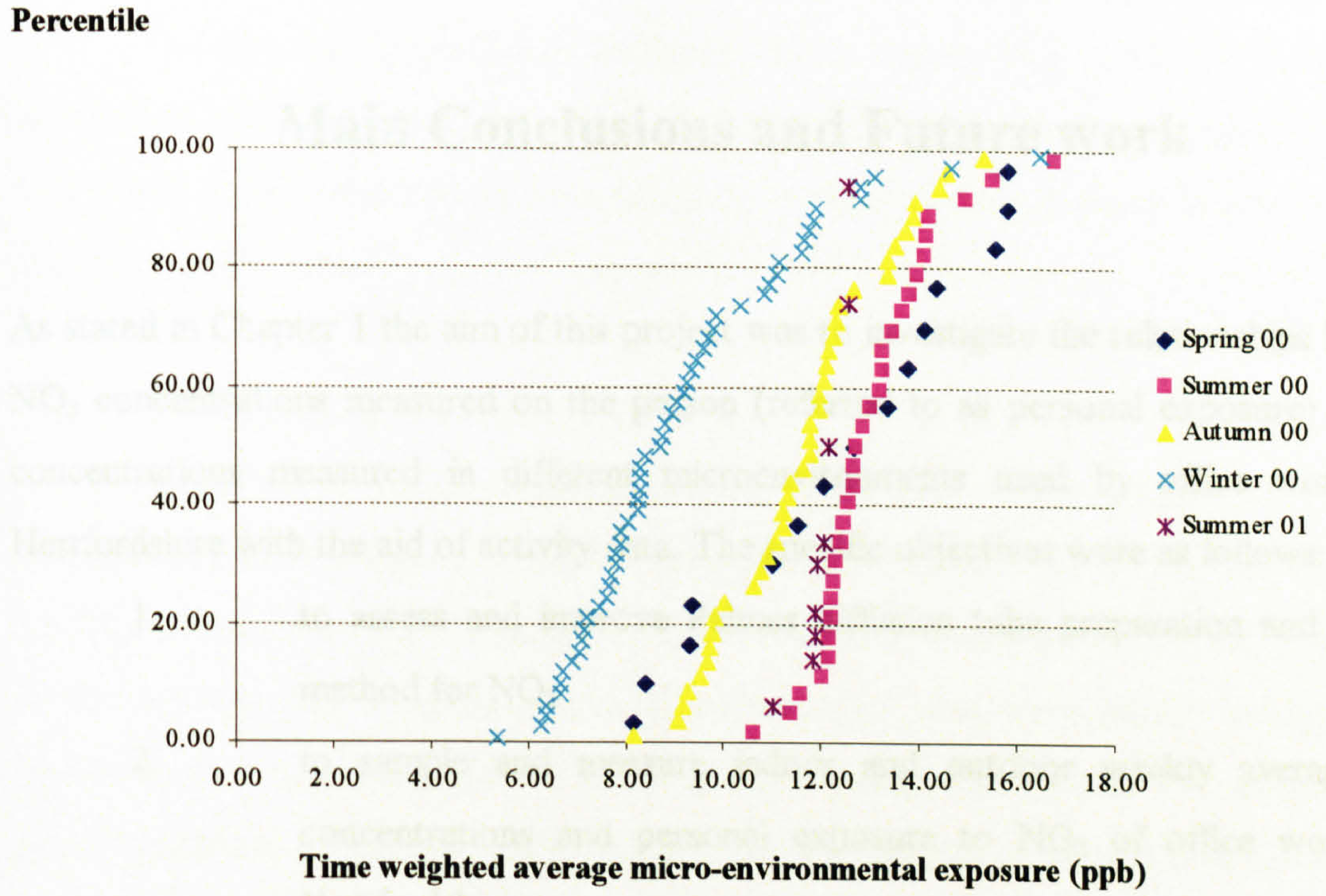


Figure 5.32 Percentile and time weighted average micro-environmental exposure of office workers in each season.

Chapter 6

Main Conclusions and Future work

As stated in Chapter 1 the aim of this project was to investigate the relationships between NO_2 concentrations measured on the person (referred to as personal exposure) and the concentrations measured in different microenvironments used by office workers in Hertfordshire with the aid of activity data. The specific objectives were as follows:

1. to assess and improve Palmes diffusion tube preparation and analysis method for NO_2.
2. to sample and measure indoor and outdoor weekly average NO_2 concentrations and personal exposure to NO_2 of office workers in Hertfordshire.
3. to compare the weekly average NO_2 concentrations in different seasons.
4. to compare and relate the personal exposure to NO_2 to concentrations of NO_2 in microenvironments and time spent in each microenvironment.
5. to test the performance of an empirical time weighted exposure model based on micro-environmental concentrations with personal exposure measurements and activity data.

The main findings are discussed below in relation to these specific objectives.

6.1 Main findings

(i) Improvement of the Palmes sampling method

Palmes diffusion tubes have been used to measure NO_2 concentrations in this project because they are low cost, easy to prepare and deploy and do not require a power supply or complicated maintenance. Large variations can be introduced by simply dipping the sampling mesh into the TEA solution, which has been the normal method of preparation. This work has shown that the amount of TEA deposited onto the mesh should be controlled with a micropipette to give more reliable and reproducible results. Other studies, such as AEA (2001), Bush *et al.* (2001) and Kirby *et al.* (2000), have confirmed this finding.

The preparation method of the Palmes tubes employed in this study showed good agreement with the data from the continuous chemiluminescent method. The two techniques were compared and the resulting correlation was acceptable (r^2=0.8465), as discussed in Chapter 3.

(ii) Questionnaires and activity data

In general, the results from questionnaires of all three campaigns (n = 55, 60 and 30, respectively) showed that all of volunteers lived in urban area in North London (New Barnet) and Hertfordshire such as Hatfield, St.Albans, Hertford, Welwyn Garden City, Potters Bar, Welham Green and Smallford. Most of the houses (95%) were mostly located outside central town areas. Over 92% of the properties had double glazing. The properties had central gas heating system which was used about 4 hr per day in autumn and about 5 hr per day in winter but only used for water heating during the summer campaign period. The central heating/hot water boiler were mostly located in halls, followed by in kitchens and living rooms. The boiler outlet pipes were all located outdoors. No additional boilers were mentioned by the subjects. 37.5%, 38.2% and 43.3 % of the kitchens were equipped with kitchen fans (filter and recirculation) or extractors. The kitchen extract fans were used frequently during cooking and 5-10 minute after cooking.

The questionnaires from all campaigns also reported that individuals shared the properties with at least one person. Almost 45% of the individual were commuters who travelled by cars, buses, trains, undergrounds, and bicycles and also on foot. Over 70% of the individuals' offices were open plan with less than 30% being separate offices. More than 70% of the offices had windows with some offices having only A/C (no windows) and some having both windows and A/C.

(iii) Time activities diaries

The total human exposure to NO_2 is the sum of the exposures in different locations and which is a function of concentrations and the times spent in the environment. Depending on how much time is spent in different micro-environments, in general, the main exposure contributions are from indoor, outdoors and in-transport sources. However, the indoor environments were the major component of the total exposure, because an overwhelming proportion of times were spent indoors. Results from the activity patterns of all campaign studies showed that all volunteers spent more than 80% of their time indoors. These results agreed with other studies such as Quackenboss *et al.*, 1986, which showed that volunteers spent most of their time indoors (> 80%) such as in their houses, offices and other non-smoking and smoking environments (for example public houses, restaurants, cinemas, leisure centres and shopping centres). Over 50% of the time was spent at homes during autumn and winter but less in summer periods, followed by about 30% of the time being spent at the workplace. The individuals spent about 4.8% on average (5.5% in winter and 4.6% in summer) of their time in other non-smoking areas such as in shopping malls and cinemas, and 2.7% on average in other smoking areas such as in restaurants and public houses.

With regard to travelling time, the average total time spent in the traffics was about 45 minutes per day, equivalent to 3.5%, 4.5% and 4.0% in transportations during autumn, winter and summer respectively. The time spent in private transportation (bicycles, motorbikes, cars and taxis) seem to be higher than by public transportation (buses, trains, undergrounds). The average time in transportation was also affected by the density of traffics and the type of transport.

Although, the volunteers spent more than 80% of their time indoors, they spent more of their time outdoors during summer than during spring, autumn and winter. The results showed that the individuals spent 11.9% of their time outdoors during summer but only 4.3% and 4.0% during autumn and winter respectively. These results have similarities to those reported by Quackenboss *et al.* (1986) where the volunteers spent more than 65% of their time at home, 15% was spent outdoors in the summer and 5% in the winter. Also they had spent approximately 4% of their time in motor vehicles, up to 15% at work or school, and approximately 8% in other indoors. Noy *et al.* (1986) reported that the housewives in Wageningen, Netherlands, spent only 5% of their time outdoors during winter.

(iv) Average personal exposure to NO_2 and average NO_2 concentrations in microenvironments

In terms of NO_2 concentrations three conclusions can be drawn.

(a) The average of NO_2 concentrations in all rooms from houses with gas cookers was higher than those houses with electric cookers which is similar to Quackenboss *et al.*, 1982 study.

(b) The average of NO_2 concentrations in kitchens with gas cookers were over two times higher than those with electric cookers, especially in autumn and winter. Similarly to other studies (e.g. Cotterill and Kingham, 1997, Quackenboss *et al.*, 1991, Leaderer *et al.*, 1986, Spengler *et al.*, 1983, Dockery *et al.*, 1981), it was seen that concentrations in kitchens with gas cookers were 2–3 times higher than those with electric cookers. Concerning the indoor sources, using gas cookers with no use of mechanical ventilation, significantly increases exposure to NO_2, which is especially worse in winter as windows are usually kept closed (Cotterill and Kingham, 1997).

(c) The personal exposure to NO_2 concentrations of the individuals living in houses with gas cookers was higher than those who lived in houses with electric cookers.

(v) The relationship between personal exposure to NO_2 concentrations in relation to indoor and outdoor sources and activity patterns

Correlation analysis results during autumn and winter showed that the personal exposure was more closely related to NO_2 concentrations in bedrooms and living rooms then with concentrations in kitchens. Also similar to Quackenboss *et al.* (1982) and Linaker *et al.* (2000) studies, this work found a weak relationship between personal exposures to NO_2 and outdoor concentrations during autumn and winter. However, correlation analysis results showed that a reasonable relationship between personal exposures to NO_2 and outdoor concentrations was found in summer. The relationship between outdoor concentrations and NO_2 concentrations in bedrooms, living rooms and kitchens was also found for the summer period due to increase of ventilation and exchange of air as windows would be more likely to be kept open.

(vi) Time weighted average micro-environmental modelling compared with personal exposure to NO_2 from indoor and outdoor sources

Calculated time weighted average micro-environmental modelling was compared with personal exposure measured from individuals using Paired t–test analysis ($p\text{-value} < 0.05$). The result from the paired t-test confirmed that differences between the time weighted average micro-environmental model predictions and personal exposure to NO_2

concentrations during autumn and winter campaigns were not significant but the differences were significant for the summer campaign due to more outdoors activities and more individuals movements. The results demonstrate the advantage of the simple empirical model as measurements made in indoor micro-environments could be used to as proxies for personal exposure estimation.

Other studies such as EXPOLIS studies (Jantunen, 1999; EXPOLIS, 1999) reported that the time weighted average micro-environmental modelling results were nearly twice lower than the personal exposure to NO_2 concentration measurements. However, in this study, the time weight average was found to have a close agreement with the personal exposure to NO_2 concentration during autumn and winter. This is probably because a longer exposure times was used (a 7-days period or 168 hr) and that NO_2 levels form a larger range of microenvironments (bedrooms, living rooms, kitchens, front doors, workplaces and cars) was investigated in this research. In the other studies the NO_2 data was taken from bedrooms and urban background sites in MACBETH study (Gonzalez-Flesca *et al.*, 2000) and inside (living rooms only) and outside houses and offices for a 2-days (48 hr) exposure time in the EXPOLIS study (Jantunen, 1999; EXPOLIS, 1999).

6.2 Future work

There are several recommendations for future work that have resulted from this project. These include the following:

(i) The survey should be extended to cover areas of different pollution distributions and demographic profiles. For example, London would be a good case study as exposure levels would be expected to vary across the Greater London area. The central area is highly congested whilst the surrounding areas have major routes with heavy traffic including the M25 motorway. Public transport is commonly used in the central areas whereas private car travel is probably higher in the outer regions. The density of building also varies across London. The impact of these parameters on personal exposure would need to be examined in more detail.

(ii) Comparison with other European cities would be interesting for similar reasons to those mentioned in (i). This would demonstrate how the methodology could be transferred to other areas. Furthermore, there is little exposure data in the new member states and hence knowledge and information on air pollution exposure in cities is needed for air quality and health research.

(iii) Projects such as FUMAPEX (http://fumapex.dmi.dk) have employed sophisticated ambient air pollution modelling methods to predict exposure to air pollutants in urban areas. Results from this project have also been analysed by the FUMAPEX team but could not be included in the thesis due to lack of time. It is expected that this collaboration will continue and the data from this project would be used to evaluate and improve exposure models.

(iv) The analysis of data should be continued with deterministic exposure models that take into account indoor and outdoor sources and exchange processes. This project has produced indoor and outdoor datasets on NO_2 which should be of help to examine the performance of such models.

(v) An important step forward would be to relate the current results to traffic and population information. Geographic Information Systems (GIS) would be ideally suited for this purpose and will enable a spatial distribution of exposure to be determined across the region.

(vi) The further personal exposure study should be expanded to look at other air pollutants such as BTX (benzene, toluene and xylenes), PM10 and PM2.5 and also relate the work to their health effects from those pollutants.

(vii) A further study could compare the exposure levels of critical groups in relation to a 'normal or control' group. For example, this could include people suffering from asthma, and also vulnerable people who spend most of their time indoors such as elderly people, babies and their mothers.

(viii) The personal exposure survey could be extended to study other indoors areas such as in public houses, restaurants and follow up seasonal variations in NO_2 concentrations.

(ix) The emphasis of this study was on people living and working in urban and suburban areas. A logical extension of the project would be compare the exposure levels in rural, suburban and urban areas.

6.3 Recommendations for reducing personal exposure to NO_2 from indoor sources

As mentioned in section 6.1 the main exposure contributions can be considered to be arsing from three main categories of sources, namely, indoor, outdoors and in-transport sources. The indoor environments are the major component of the total exposure to NO_2 due to people spending more than 80% of their time indoors. The situations that lead to exposure to high indoor NO_2 concentrations are cigarette smoking, gas cooking and gas heating. Increased ventilation, such as opening windows and doors, operating extract fans of cooker hoods during cooking is important (especially in winter). This along with reducing smoking indoors will lead to lower exposure to NO_2 concentrations. Furthermore, appliances for gas cooking and heating should undergo regular maintenance. In addition, the use of gas cookers to warm the kitchens in winter must be avoided.

People spend 4% (in winter) to 12% (in summer) of their time outdoors and about 4% of their time in transportations and hence these source sectors should also be considered to reduce the total exposure. Therefore, activities such as walking, cycling or driving next to high traffic roads should be avoided as this may lead to exposure to high NO_2 concentrations. People who work in offices or live in residences located near high traffic road should also be cautious of possible high exposure to NO_2 concentrations resulting from traffic, especially in summer, when the windows are usually opened due to warm weather conditions. Again such issues would need to be investigated as part of a detailed future study.

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And also

http://www.hertsdirect.org/yrccouncil/hcc/env/you/raiseaware/quallife/qol/invqol/qol2000/qolairpollution

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Appendix

Protocol & Consent for Participants: Questionnaire, Cooking Time Daily Diary, Total Time-measured for NO_2, and Daily Diary of Time Spent in Various Activities

A Study to Quantify Exposure to Nitrogen Dioxide using Palmes Diffusion Tubes
(Personal exposure to nitrogen dioxide)

Why is this study important?

The Atmospheric Science Research Group (ASRG), at the University of Hertfordshire is conducting an investigation into the levels of nitrogen dioxide people living in an urban, semi-urben and rural area are exposed to, from both indoor and outdoor sources. To achieve this, the group requires volunteer households that are prepared to participate in this study. This information is required to help understand the causes of exposure to nitrogen dioxide.

What is Nitrogen Dioxide and how will it be measured?

Nitrogen dioxide is a gas that is formed in the atmosphere by complex chemical reactions. Studies have shown that there may be a link between levels of nitrogen dioxide and respiratory diseases. The nitrogen dioxide levels will be measured by the use of Palmes diffusion tubes. These are simple devices used to sample nitrogen dioxide gas in air. They consist of 7cm clear plastic tube with one open end (covered with a clear plastic cap when not sampling) and a blue cap placed at the other end housing two wire meshes. The wire mesh is coated with a chemical called Triethanolamine (TEA) which reacts with nitrogen dioxide. The tubes sample the air for typically 7 days after which they will be collected and analysed for nitrogen dioxide levels at the University.

Are these tubes safe and what precautions should I take?

TEA has very low toxicity level and is present in many cosmetic products and thus should not pose any significant health hazard. The tubes do, however, contain small parts such as the caps and wire meshes and consequently they should NOT be placed near children or pets or any other place that is accessible to them. If by any chance a child swallows any part of the tubes you should seek medical advice immediately. Make sure that you give this leaflet to the medical personnel.

Where and how will the sampling be conducted?

The tubes will be placed both inside and outside of the volunteer homes and in office/workplace, at positions agreed upon by the occupants, within the constraints listed below. The tubes will be securely fastened to the wall at a height of 2 meters and will therefore be out of the reach of children and pets. Volunteers will also be required to complete an activity diary for the duration of the study (a week). Tubes will also be fixed to the outermost clothing of volunteers for the duration of the study.

For inside and outside of your home, inside your workplace and inside your car (if have one).

1. Two tubes should be placed vertically at a height of 2 m, the blue cap at the top on the wall:
   - in your bedroom, living room and kitchen
   - outside your home near the front door or the front window of the home

- in your office/workplace
- in your car (if have one)

2. Gently remove the white caps and keep in a safe place. They will be used to cover the tubes after 7 days.
3. Please record the time that you open the tubes. The tubes will be on the wall for a 7-day period.
4. Please record the temperature inside and outside your home everyday.
5. After 7 days, please cover the tubes with the white caps.
6. Please record the time that you cover the tubes with the white caps.

For your outermost clothing:

1. Please fix the tubes, vertically, on your coat, the blue cap always at the top. Try to fix the tubes near the breathing zone, 1-1.5 ft around your nose.
2. Gently remove the white caps and keep in the safe place. They will be used to cover the tubes after 7 days.
3. Please record the time that you open the tubes.
4. The tube should be kept near your breathing zone for a 7-day period.
5. Please record your activity pattern in the diary provided.
6. Please do not let the tubes come into contact with water. Do not take them into a bathroom when you take a bath or a shower.
7. Please put the tubes on the bedside table near your bed when you sleep. Moreover, please keep them far away from a fan, heater, radiator and opened window when at the side of your bed.
8. After 7 days, please cover the tubes with the white caps.
9. Please record the time that you cover the tubes with the white caps.

Important points to remember

1. All tubes are to be used by adults only.
2. The tubes should be not left within the reach of children or animals.
3. Only the white caps should be removed, the blue caps should not be removed
4. If the meshes or the blue cap comes into contact with the mouth, wash down with plenty of fluids, preferably milk (advice obtained from the National Poisons Line). If contact with skin occurs, wash with water for a minimum of 15 minutes. If you concerned seek medical advice and give this leaflet to then medical personnel. In either case, please contact a member of staff on one of the numbers given below.

Miss Chiraporn Kornartit	Miss Anna Tod
(Research Student)	(Researcher of ASRG)
Tel: 01707 285232 (ext:5232)	Tel: 01707 286278 (ext:3278)
Fax: 01707 285258	Fax: 01707 285258
E-mail: c.kornartit@herts.ac.uk	E-mail: a.m.tod@herts.ac.uk

Who should I contact for more information?

This project is managed by Prof Ranjeet S Sokhi who is the Head of ASRG. For further information please contact Chiraporn Kornartit, Anna Tod, or:

Prof Ranjeet S Sokhi	Dr Agneta Burton
Tel: 01707 284520 (ext:4520)	Tel: 01707 284517 (ext:4517)
Fax: 01707 285258	Fax: 01707 285258
E-mail: r.s.sokhi@herts.ac.uk	E-mail: m.a.burton@herts.ac.uk

Reference number: ASRG/....................

Dear ....

You have been provided with the following:

- 14 x tubes labelled P, B, L, K, F, W and C* - 1 x personal tube holder
- 1 x daily diary - 1 x questionnaire - 1 x cooking-time report

***Note:** P = personal' tubes, B = bedroom' tubes,
L = living room, K = kitchen' tubes,
F = front door' tubes (outside your home) W = workplace' tubes,
C = Car

Please read the following instructions carefully.

Location and exposure of tubes:

Tube P

1. The tubes in the holder should be attached vertically to your outermost clothing with the blue caps at the top. Please try to ensure that the tubes and holder are positioned within your breathing zone, 1-1.5 feet around your nose.
2. Gently remove the clear caps and keep in a safe place. They will be needed to be replaced on the tubes after 7 days. Do not remove the blue caps.
3. The tubes should be kept in this position for 7 days.
4. Please record your daily activity in the diary provided.
5. Do not take the tubes into the bathroom when you take a bath or shower.
6. When sleeping, place the tubes near to your bedside, away from any fans, heaters, radiators or draughts.
7. When participation in any sport or activity that could pose as a hazard when wearing the tubes, please remove the tubes from your dress.

Tube B & L

1. The tubes in the holder should be placed vertically at a height of 2 metres from the floor in your bedroom & living room outermost with the blue caps at the top using some bluetak provide back of the holder.
2. Please position the tubes as far away as possible from any fans, heaters, radiators, opened windows or doors.
3. Gently remove the clear caps and keep in the safe place. They will be needed to be replaced on the tubes after 7 days.

Tube K

1. The tubes in the holder should be placed vertically at a height of 2 metres from the floor in your kitchen outermost with the blue caps at the top using some bluetak provide back of the holder.

2. Please position the tubes as far away as possible from any cookers, fans, heaters, radiators, opened windows or doors.
3. Gently remove the clear caps and keep in the safe place. They will be needed to be replaced on the tubes after 7 days.

Tube F

1. The tubes in the holder should be placed vertically at a height of 2 metres from the floor outside your house outermost with the blue caps at the top using some bluetak provide back of the holder.
2. Gently remove the clear caps and keep in the safe place. They will be needed to be replaced on the tubes after 7 days.

Tube W

1. The tubes in the holder should be placed in your office at a height of 2 metres from the floor. If this is not possible, the tubes can be secured to any shelving, filing cabinets or office furniture, which is at least 2 metres high.
2. Please ensure that the tubes are not in a position where it will be knocked or moved, and is as far away as possible from any source of heating, open doors or windows.
3. Gently remove the clear caps and keep in the safe place. They will be needed to be replaced on the tubes after 7 days.

Tube C

1. The tubes in the holder should be placed in your car. Please ensure that the tubes are not in a position where it will be knocked or moved, and is as far away as possible from any source of heating & open windows.
2. Gently remove the clear caps and keep in the safe place. They will be needed to be replaced on the tubes after 7 days.

Important notices:

- Please do not remove the blue caps.
- Please record time that you open the tubes.
- After 7 days, please re-cap the tubes with the white caps and record time that you re-cap the tubes. Please ensure that all caps are securely replaced on the tubes
- All the tubes, a daily diary, a cooking-time report and a questionnaire will be collected from you for subsequent analysis.

If you have any problems during the week's exposure, please contact:

Chiraporn Kornartit (Research student)	Anna Tod (ASRG Researcher)
Tel: 01707 285232 (ext.5232)	Tel: 01707 286278 (ext.3278)
Prof Ranjeet Sokhi (Supervisor)	Dr Agneta Burton (Supervisor)
Tel: 01707 284520 (ext.4520)	Tel: 01707 284517 (ext.4517)

Please keep these instructions as well as the originally signed protocol safe and to hand.

This has been previously approved

Faculty Protocol Number NS10/2/99U

Reference number: ASRG/....................

Consent to Participate in:
Research Project Involving Personal Exposure to NO_2 and Comparison of Indoor & Outdoor NO_2 Concentrations Using Diffusion Tubes and Questionnaire on Activity Patterns

I ______________________________ give my consent to taking part in this study, as outlined in the instructions and details given to me. I understand what is expected and what precautions I should take to avoid any accidents with the tubes.

I understand that I have the right to withdraw from the study at any time, without giving any reasons, and that all information I give in the questionnaire and daily diary will be dealt with in the strictest of confidence. I have also spoken to the appropriate people within my place of work (if appropriate), and have been given consent from them to place the tubes within my office.

I also understand that the information that I provide may be stored on a computer for research purposes.

Signed .... Date ....

Contact details: Home ....

.... Postcode ....

Tel: ( ) ....

Office ....

.... Postcode ....

Tel: ( ) ....

Reference number: ASRG/....................

Research Project Investigating Personal Exposure to NO_2 from Indoor & Outdoor Sources: Questionnaire on Activity Patterns

This questionnaire should take about 30 minutes to complete

I. Your personal details

1. Male/Female *(Delete as appropriate)*

2. Your age

[ ] <18 [ ] 18 – 25 [ ] 26 – 30 [ ] 31 – 35
[ ] 36 – 40 [ ] 41 – 45 [ ] 46 – 50 [ ] 51 – 55
[ ] 56 – 60 [ ] 60+

3. Do you smoke (e.g.cigarettes, cigars, pipe tobacco)?

[ ] Yes [ ] No

II. Household

4. How many people of each age range listed below live in the household, including yourself? *(Please write a NUMBER for each age category.)*

[ ] <18 [ ] 18 – 25 [ ] 26 – 30 [ ] 31 – 35
[ ] 36 – 40 [ ] 41 – 45 [ ] 46 – 50 [ ] 51 – 55
[ ] 56 – 60 [ ] 60+

5. Does anybody else smoke inside your house?

[ ] Yes [ ] No

6. What type of home do you live in? *(Please tick one box.)*

[ ] Purpose built flat
[ ] Conversion flat
[ ] Centre terrace house
[ ] End terrace house
[ ] Semi-detached house
[ ] Detached house
[ ] Bungalow
[ ] Other

7. How would you describe the location of your home? *(Please tick one box.)*

[ ] A rural area with no other homes, or only a few homes, close by village in a rural area
[ ] A suburban street with large gardens
[ ] A street in a town with no gardens, or with small gardens

[ ] A city centre with density packed housing

8. What type of road is your home located on? *(Please tick one box.)*

[ ] Mail dual carriageway

[ ] Main single carriageway

[ ] Main Estate road

[ ] Minor single carriageway

[ ] Minor Estate road

[ ] Country road

9. How close are the following roads to your home? *(Please tick all that apply.)*

Motorway	[ ] < 0.5 mile	[ ] 0.5 - 1 mile	[ ] > 1 mile
Dual carriageway	[ ] < 0.5 mile	[ ] 0.5 - 1 mile	[ ] > 1 mile
Main A road	[ ] < 0.5 mile	[ ] 0.5 - 1 mile	[ ] > 1 mile
Main B road	[ ] < 0.5 mile	[ ] 0.5 - 1 mile	[ ] > 1 mile

10. Which type of glazing does your home have? *(Please tick one box.)*

[ ] Double glazing

[ ] Secondary double glazing

[ ] Single glazing

[ ] Mixed

III. Car

11. Does your household own a car?

[ ] Yes [ ] No If No, go to Question 17.

12. Which type of fuel does your car use?

[ ] Unleaded petrol

[ ] Leaded petrol

[ ] Diesel

[ ] Other *(Please specify.)*..............

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13. Where do you park your car?

[ ] In a garage

[ ] On a road/street

[ ] In a car park

[ ] Other *(Please specify.)*..............

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If Not IN THE GARAGE, go to Question 17.

14. Which of the following best describes your garage(s)? *(Please tick all that apply.)*

[ ] Attached to my home

[ ] An integral part of my home (e.g. under a bedroom)

[ ] Detached from my home If DETACHED, go to Question 17.

15. Is there an internal door joining your home and your garage?

[ ] Yes [ ] No If No, go to Question 17.

16. Which room has a door to the garage?

[ ] Hall [ ] Utility room [ ] Living room

[ ] Kitchen [ ] Other *(Please specify)*........................

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IV. Heating systems

17. Do you have a central heating system? (not including electric storage heaters.)

[ ] Yes [ ] No (If No, go to Question 21.)

18. Do you use it at this time of year?

[ ] Yes [ ] No (If No, go to Question 21.)

19. What type of central heating system do you have?

[ ] Central heating with radiators [ ] Warm air central heating

[ ] Floor or ceiling heating

20. What fuel do you use for your central heating?

[ ] Natural gas [ ] Electricity [ ] Bottled gas

[ ] Coal/coke/solid fuel [ ] Paraffin [ ] Wood

[ ] Oil [ ] Other *(Please specify.)*..............

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21. Do you use any additional type of heaters at this time of year?

[ ] Yes [ ] No

If Yes, what type of heater do you use?

[ ] Electric heater [ ]Radiator

[ ] Warm air heater [ ] Other *(Please specify.)*..............

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22. Where is the central heating boiler *(If you have one)*?

[ ] Most used living room [ ] Another living room

[ ] Main bedroom [ ] Other bedroom

[ ] Kitchen [ ] Hall/landing

[ ] Bathroom [ ] Other *(Please specify.)*........................

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[ ] Do not have. (If Do not have, go to Question 27.)

23. Do you use the central heating boiler to provide hot water?

[ ] Yes [ ] No

24. Does the boiler have any of the following?

[ ] A balanced flue through the wall to outside [ ] A chimney

[ ] Another ventilated flue [ ] Do not know

25. Do you have any other heating boilers?

[ ] Yes *(Please specify.)*................................ [ ] No

If Yes, in which rooms are these boilers located?

[ ] Most used living room [ ] Another living room

[ ] Main bedroom [ ] Other bedroom

[ ] Kitchen [ ] Hall/landing

[ ] Bathroom [ ] Other (Please specify.)........................

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26. Do you use any of the following in your home at this time? *(Please tick all that apply.)*

[ ] Gas instantaneous water heater, e.g. Ascot

[ ] Gas fired back boiler (not central heating)

[ ] Solid fuel back boiler (not central heating)

V. Cooking and cooking fuels

27. What is the main fuel for each part of your gas cooker? *(Please tick one box in each column.)*

	Hob	Grill	Oven
Natural Gas	[ ]	[ ]	[ ]
Electricity	[ ]	[ ]	[ ]
Do not know	[ ]	[ ]	[ ]

28. Which of the following best describes the grill? *(Please tick one box.)*

[ ] High level grill [ ] Grill within an oven

[ ] Low level grill [ ] No grill

29. Does the cooker have any pilot lights that are continuously alight?

[ ] Yes [ ] No [ ] Do not know

30. Does anyone in the household ever use a cooker, when not cooking, to heat the kitchen (or any part of the home) at this time of year? *(Please tick one box.)*

[ ] Often [ ] Sometime

[ ] Rarely [ ] Never

31. Do you use an Aga/Rayburn type cooker?

[ ] Yes [ ] No (If No, go to Question 33.)

32. What fuel does your Aga/Rayburn type cooker use?

[ ] Natural gas [ ] Electricity

[ ] Bottled gas [ ] Coal/coke/solid fuel

[ ] Oil [ ] Other *(Please specify.)*..............

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VI. Ventilation

33. Is there an external door in the kitchen? *(Please tick one box.)*

[ ] Yes [ ] No

34. Is the kitchen door to the outside draught-proofed?

[ ] Yes [ ] No [ ] Do not know

35. Is the kitchen separate from the rest of the house or open plan*?

*(*Open plan means that the kitchen cannot be isolated from the living room or the rest of the house by a door, a beaded curtain or a louvered door.)*

[ ] Separate [ ] Open plan

36. Do you use a cooker hood (which is extract air to the outside but NOT which only filter the air and return it to the kitchen) in the kitchen? *(Please tick one box.)*

[ ] Yes [ ] No [ ] Do not have it

37. Do you use an extract fan in the kitchen?

[ ] Yes [ ] No [ ] Do not have it

38. Do you open any windows in the kitchen during cooking?

[ ] Often [ ] Sometime [ ] Rarely

[ ] Never [ ] Do not have them

VII. Workplace arrangement

39. Which of the following best describes your office? *(Please tick all that apply.)*

[ ] Separate office [ ] Open plan*

*(*Open plan means that your table cannot be isolated from another or other staff by a wall.)*

40. How close are the following roads to your office? *(Please tick all that apply.)*

Motorway	[ ] < 0.5 mile	[ ] 0.5-1 mile	[ ] > 1 mile
Dual carriageway	[ ] < 0.5 mile	[ ] 0.5-1 mile	[ ] > 1 mile
Main A road	[ ] < 0.5 mile	[ ] 0.5-1 mile	[ ] > 1 mile
Main B road	[ ] < 0.5 mile	[ ] 0.5-1 mile	[ ] > 1 mile

41. Do anyone smoke in your office?

[ ] Yes [ ] No

Thank you for completing this questionnaire.

Reference number: ASRG/....................

Cooking Time Daily Diary

__Please complete this form by putting ALL TIME that the GAS COOKER was used by ALL MEMBERS in your household (min. or hr.) during an experiment period.__
This should not take more that 5 minutes each day.

	GAS COOKER		AGA/RAYBURN	
DATE	**TIME by YOURSELF** *(min. or hr.)*	**TIME by OTHER MEMBERS** *(min. or hr.)*	**TIME by YOURSELF** *(min. or hr.)*	**TIME by OTHER MEMBERS** *(min. or hr.)*
MON.				
TUE.				
WED.				
THU.				
FRI.				
SAT.				
SUN.				

Thank you for completing this form.

Reference number: ASRG/....................

Total Time-measured for NO_2

Please record time that you open all tubes and time that you recap the tubes.

Start measuring NO_2 concentrations (opened tubes)

Personal	Bedroom	Living room	Kitchen	Front door	Office	Car (If have one)

Stop measuring NO_2 concentrations (closed tubes)

Personal	Bedroom	Living room	Kitchen	Front door	Office	Car (If have one)

Reference number: ....

Daily Diary of Time Spent in Various Activities for those Assisting in Personal Sampling of NO_2 Palmes Diffusion Tubes

Please complete this form by indicating the times that you spend on each of your main activities every day during the experiment period.
This should not take more that 10 minutes each day.

Places Date	At HOME			In OFFICE/ At WORK	Other nonsmoking INDOORS	Other smoking INDOORS	OUTDOORS	In any VEHICLES	TRAFFICS (Heavy, medium, light)
	Bedroom	**Living room**	**Kitchen**						
Example:	*9 hr*	*3 hr*	*10 min*	*8 hr*	*1 hr* *(shopping mall)* *1 hr* *(friend's house)*	*1 hr* *(pup)*	*30 min.* *(walking, main road, light traffic)*	*50 min.* *(bus)* *30 min.* *(car)*	*heavy traffics* *heavy traffics*
MON									
TUES									
WED									
THUR									
FRI									
SAT									
SUN									

Thank you for completing this personal daily diary.