

Validation of diffusive samplers for nitrogen oxides and applications in various environments

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Remember to breathe. It is after all the secret of life.

Gregory Maguire

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Abstract

The general population is exposed to air pollutants in both indoor and outdoor air, and a wide range of epidemiological and experimental studies have shown that air pollution causes a variety of adverse health effects. To evaluate the health effects from air pollution, it is crucial to assess the concentrations of certain air pollutants. Measurements of these pollutants should be performed at network monitoring stations in urban areas, but it is also of great importance to study the spatial distributions of the pollutants in the environment and to measure personal exposures. To measure the concentration of a pollutant at many sites simultaneously as well as to measure personal exposure requires special monitoring devices that are simple, user-friendly, and accurate. Diffusive samplers fulfil these requirements. One common air pollutant, nitrogen dioxide (NO_2), is often used as a marker for traffic-related air pollution, and this makes measurements of NO_2 with diffusive samplers very important.

This thesis deals with the validation of two different diffusive samplers, the Willems badge and the Ogawa sampler, for measuring NO_2 and nitrogen oxides (NO_x). The Willems badge was validated for NO_2 measurements both in laboratory tests and field tests. The laboratory validation was performed in an exposure chamber where the diffusive samplers were exposed to controlled levels of NO_2 that often occur in ambient air (**paper I**) and at higher concentrations that are common in workplaces (**paper II**). The effect of various factors such as NO_2 concentration, sampling time, relative humidity, and wind velocity on sampling rate was investigated. The sampling rate was 40.0 mL/min for ambient air concentrations and 46.0 mL/min for higher concentrations. No effects of the different factors on sampling rate were found except for a reduced sampling rate at low wind velocity. The results of the laboratory validation were confirmed in field tests in ambient air and with personal measurements in an exposure chamber where the persons were exposed to diesel exhaust. The correlation between diffusive samplers and the chemiluminescence instrument that was used as the reference monitor was good for ambient measurements, and the average ratio between concentrations with diffusive samplers and the reference method was 1.08. The sampling rate for personal sampling was similar to the rate determined in the laboratory study. In conclusion, the Willems badge performs well at wind velocities down to 0.3 m/s, and this makes it suitable for personal measurements but less suitable for measurements in indoor air where the wind velocity is lower.

The Ogawa sampler was validated in field tests in ambient air with the aim to determine the sampling rates for NO_2 and NO_x . At three sites in Umeå and two sites in Malmö, 55 one-week measurements of NO_2 were taken and 47 one-week measurements of NO_x were taken with Ogawa diffusive samplers and co-located

reference chemiluminescence monitors. The effects of some environmental factors were determined by regression analysis. Absolute humidity and temperature were found to have the strongest effect on sampling rate with lower uptake rates at lower absolute humidity and temperature. The sampling rate at temperatures above 0 °C were 8.6 mL/min for NO₂ and 9.9 mL/min for NO_x, and the sampling rates below 0 °C were 6.6 mL/min for NO₂ and 7.2 mL/min for NO_x. NO₂ concentrations that were determined using the manufacturer's protocol were underestimated by 9.1% on average compared to the reference monitor, and greater underestimation (17%) was observed at temperatures below 0 °C. NO_x concentrations, in contrast, were overestimated by 15% on average. The agreement between concentrations measured by the Ogawa sampler and the reference monitor was improved when field-determined sampling rates were used to calculate concentrations.

In a study with the aim of assessing the exposure of the Swedish general population to NO₂ and some carcinogenic substances, both the Willems badge and the Ogawa sampler have been used for personal NO₂ measurements. The surveys take place on a five-year cycle and are conducted in one of five Swedish cities (Göteborg, Umeå, Stockholm, Malmö, or Lindesberg) every year. In each survey, measurements of benzene, 1,3-butadiene, formaldehyde, and NO₂ are conducted on 40 randomly selected people over the course of one week. Each participant fills in activity diaries and answers questions about their home and working life. In the study presented in this thesis, results were available for eight surveys conducted across the five cities. The statistical analysis was based on mixed effects modelling, and this makes it possible to identify determinants of exposure and variability between and within individuals as well as exposure estimations for the general population. In this thesis, the NO₂ part of the study is in focus. The estimated arithmetic mean concentration for the general Swedish population (2000–2008) was 14.1 µg/m³. The exposure level for NO₂ was 11% higher for smokers compared with non-smokers, and the NO₂ exposure levels were higher for people who had gas stoves at home or who were exposed at their place of work. The exposure was lower for those who had oil heating in their houses, and exposures decreased with higher proportions of time spent indoors at home.

Abbreviations

BC	black carbon
CEN	The European Committee for standardisation
CO	carbon monoxide
CO ₂	carbon dioxide
CV	coefficient of variation
D	diffusion coefficient
EPA	The Environmental Protection Agency
ETS	environmental tobacco smoke
FIA	flow injection analysis
IC	ion chromatography
HNO ₂	nitrous acid
HNO ₃	nitric acid
h	hours
IARC	The International Agency for Research on Cancer
J	diffusion flux
kPa	kiloPascal
M	molecular weight
N ₂	nitrogen gas
NO	nitric oxide
NO ₂	nitrogen dioxide

NO ₂ ⁻	nitrite ion
NO _x	nitrogen oxides
PAH	polycyclic aromatic hydrocarbons
PAN	peroxyacetyl nitrate
PM	particulate matter
PM ₁₀	particulate matter with an aerodynamic diameter ≤ 10 μm
PM _{2.5}	particulate matter with an aerodynamic diameter ≤ 2.5 μm
ppb	parts per billion
ppm	parts per million
PTFE	Polytetrafluoroethylene (brand name Teflon)
Rh	relative humidity
RSD	relative standard deviation
S	sampling rate
SO ₂	sulphur dioxide
TEA	triethanolamine
UR	uptake rate = sampling rate
VOC	volatile organic compounds

Enkel sammanfattning på svenska

Luftföroreningar som släpps ut från trafik, uppvärmning och industrier skapar problem framför allt i städer. Befolkningen exponeras för luftföroreningar både inomhus och utomhus, och en lång rad studier har visat att luftföroreningar orsakar negativa hälsoeffekter som hjärt-och kärlsjukdomar, kronisk bronkit, nedsatt lungfunktion och lungcancer. Inom miljömedicin används epidemiologiska studier för att utreda sambanden mellan exponering för miljöfaktorer och sjukdom. För att utvärdera eventuella orsakssamband mellan luftföroreningar och hälsoeffekter, är det viktigt att få ett korrekt mått på exponeringen. Det är omöjligt att mäta alla hundratals luftföroreningar som finns i omgivningsluften. Mätningar av kvävedioxid (NO_2) används därför ofta som en markör för trafikrelaterade luftföroreningar, eftersom det ofta råder ett samband mellan NO_2 och andra trafikavgaser, och för att NO_2 är relativt lätt att mäta. Det instrument som enligt europeisk och svensk standard är referensmetod för mätning av NO_2 är det direktvisande kemiluminiscensinstrumentet. Detta används inom kommunernas mätprogram vid stationära mätpunkter och har många fördelar, men det kräver el, ett varmhållt utrymme och expertis som kan underhålla och kalibrera instrumentet. För att på ett enklare sätt mäta kvävedioxid och kväveoxider (NO_x) kan man använda diffusionsprovtagare; ett litet, lätt, bärbart instrument som bygger på att luften man vill mäta tas upp på ett filter i provtagaren. Filtret analyseras sedan på laboratorium. Fördelen med diffusionsprovtagare är att man kan använda dem på många olika platser samtidigt i en stad och därmed få kunskap om den spatiella variationen av halten. Man kan också använda dem för personburen provtagning och direkt få den personliga exponeringen. För att veta att diffusionsprovtagare mäter korrekt måste de valideras och kalibreras mot referensmetoden och det finns standarder för hur detta ska genomföras. Validering kan ske genom laboratorieförsök eller i fältstudier parallellt med referensinstrumentet, där det senare mäter den "sanna" halten och provtagningshastigheten för provtagaren på så sätt kan bestämmas. Vid validering undersöker man också effekten av olika faktorer som kan påverka mätningen som vind, luftfuktighet, temperatur, koncentration av ämnet och provtagningsstid.

Denna avhandling handlar om validering av två olika diffusionsprovtagare, Willems badge och Ogawaprovtagaren, för mätning av NO_2 och NO_x . Willems badge kan enbart mäta NO_2 och har validerats i laboratorieförsök och i fältstudier i utomhusluft. Den har även validerats för personburen mätning i en exponeringskammare där försökspersonerna exponerades för dieselsavgaser. Provtagningshastigheten bestämdes till 40,0 ml/min för

mätningar i omgivningsmiljö, och 46,0 ml/min för högre koncentrationer som kan påträffas i arbetsmiljö. För Willems badge såg vi att provtagningshastigheten var lägre vid vindhastigheter under 0,3 m/s vilket gör att denna provtagare är mindre lämplig att använda vid mätningar i inomhusluft där luften är stillastående. Den fungerar däremot utmärkt vid mätningar utomhus under 1-7 dagar och för personburen mätning.

Ogawaprovtagaren som kan mäta både NO₂ och NO_x, validerades i fältförsök parallellt med referensinstrument på tre platser i Umeå och på två platser i Malmö. Totalt gjordes 55 veckomätningar av NO₂ och 47 veckomätningar av NO_x. Effekterna av vissa faktorer som kan påverka provtagarens provtagningshastighet bestämdes genom regressionsanalys. Absolut fuktighet och temperatur befanns ha den starkaste effekten på provtagningshastigheten med lägre upptagshastigheter vid lägre absolut fuktighet och temperatur. Provtagningshastigheten vid temperaturer över 0 ° C var 8,6 ml/min för NO₂ och 9,9 ml/min för NO_x och provtagningshastigheten under 0 ° C var 6,6 ml/min för NO₂ och 7,2 ml/min för NO_x. Vid studierna konstaterades också att man får felaktiga resultat om man använder tillverkarens instruktion för uträkning av halter i provet. Denna manual baseras på teoretiska beräkningar, och därför är det viktigt att validera provtagare i den miljö och det klimat där de ska användas. Sammanfattningsvis fungerar Ogawaprovtagaren utmärkt vid mätning utomhus under 7 dagar i ett geografiskt område med kallt klimat. Vid utomhusmätningar ska provtagningshastigheten justeras med avseende på den medeltemperatur som uppmäts vid mätningen.

I syfte att bedöma den svenska befolkningens exponering för NO₂ och för några cancerogena ämnen, samt för att identifiera vilka faktorer som påverkar exponeringen genomför Naturvårdsverket varje år en studie i någon av städerna Göteborg, Umeå, Stockholm, Malmö, eller Lindesberg. I varje undersökning görs personburna mätningar av bensen, 1,3-butadien, formaldehyd och NO₂ på 40 slumpmässigt utvalda personer under loppet av en vecka. Både Willems badge och Ogawaprovtagaren har använts för personburna mätningar av NO₂ i studien. Varje deltagare fyller i aktivitetsdagböcker och svarar på frågor om rökvanor, bostadsförhållanden, arbete, tankning av fordon m.m. Studien som presenteras i denna avhandling, sammanfattar resultaten för åtta mätomgångar (2000-2008) i fem städer och i denna avhandling är NO₂- delen av studien i fokus. Den statistiska analysen baserades på mix-effects modellering, som gör det möjligt att identifiera faktorer som påverkar exponering och variabilitet mellan olika individer och inom olika mätningar för en individ. Den möjliggör också uppskattningar av exponering för befolkningen i allmänhet. Medelvärde av NO₂-exponeringen för den allmänna svenska befolkningen

(2000-2008) var 14,1 $\mu\text{g}/\text{m}^3$. Exponeringsnivån för NO_2 var 11% högre för rökare jämfört med icke-rökare, och exponeringen var högre för personer som hade gasspis hemma eller som exponerades på sin arbetsplats. Exponeringen var lägre för dem som hade oljeeldning i sina hus, och exponeringen minskade med högre andel av tid spenderad inomhus hemma. För NO_2 dominerade "mellan-stad-variansen" vilket betyder att den största skillnaden i exponering beror på i vilken stad man bor och skillnaderna i exponeringen inom varje stad är mindre.

List of papers

This thesis is based on the following papers:

- I Hagenbjörk-Gustafsson A, Lindahl R, Levin J-O, Karlsson D. Validation of a diffusive sampler for NO₂. *Journal of Environmental Monitoring*, 1999; 1, 349-352.
- II* Hagenbjörk-Gustafsson A, Lindahl R, Levin J-O, Karlsson D. Validation of the Willems badge diffusive sampler for nitrogen dioxide determinations in occupational environments. *Analyst*, 2002; 127, 163-168.
- III Hagenbjörk-Gustafsson A, Tornevi A, Forsberg B, Eriksson K. Field validation of the Ogawa diffusive sampler for NO₂ and NO_x in a cold climate. *Journal of Environmental Monitoring*, 2010; 12, 1315-1324.
- IV** Hagenbjörk-Gustafsson A, Tornevi A, Andersson E M, Johannesson S, Bellander T, Merritt A-S, Tinnerberg H, Westberg H, Forsberg B, Sallsten G. *Journal of Exposure Science and Environmental Epidemiology*, 2014; 24, 437-443.

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** In *Science for Environment Policy*, 25 September 2014, Time spent in traffic has major effect on personal exposure to cancer-causing chemicals, European Commission DG Environment News Alert Service.

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Background

Air pollution and health effects

Air pollution is comprised of a variable and complex mixture of different substances that can exist in gaseous or particulate form. Many pollutants are linked to each other by chemical processes in the atmosphere and share the same sources ¹. Air pollutants can be emitted directly into the ambient air from a source such as a vehicle exhaust pipe or a chimney, and these are referred to as primary air pollutants. Sulphur dioxide (SO₂), carbon monoxide (CO), nitrogen oxides (NO_x), carbonaceous particles and volatile organic compounds (VOCs) are all examples of primary pollutants produced in combustion processes. Others are formed within the atmosphere itself from chemical reactions of primary pollutants and these are referred to as secondary air pollutants. The most familiar secondary pollutant is ozone, which is formed by reactions involving NO_x and VOCs in the atmosphere ².

Air pollution is defined by the World Health Organization (WHO) as “contamination of the indoor and outdoor environment by any chemical, physical or biological agent that modifies the natural characteristics of the atmosphere”. The US Environmental Protection Agency (EPA) has presented another definition that includes the words human health: “Air pollution is the presence of contaminants in the air that interfere with human health and welfare or produce other harmful environmental effects” ³. There have been a number of notable air pollution episodes all over the world during the 20th century all resulting in an increased number of deaths or hospitalisations. The most famous air pollution disaster occurred in London in 1952 and caused 12 000 estimated extra deaths because of acute or persisting effects of five days of intensive coal smoke and fog ⁴. The word “smog” was coined to describe the polluted condition ⁵. Several studies have since then confirmed the adverse health effects from ambient air pollution ¹ and the WHO estimated ambient air pollution to cause 3.7 million premature deaths worldwide in 2012. The WHO’s International Agency for Research on Cancer (IARC) estimated that 223 000 lung cancer deaths worldwide in 2010 were caused by air pollution ⁶ and they classified outdoor air pollution as carcinogenic to humans (Group 1) in 2013 ⁷. The IARC concluded that there is evidence that exposure to outdoor air pollution causes lung cancer, but they also noted an association between increased risk of bladder cancer and outdoor air pollution.

The particulate matter (PM) component of air pollution was evaluated separately, and was also classified as carcinogenic to humans⁷. For the Swedish population it has been estimated that about 3500 premature deaths per year are related to PM⁸. Humans are affected by polluted environments not only outdoors. Indoor air pollution originating from both outdoor and indoor sources is an important health issue, because people in general spend around 90% of their time indoors. Combustion appliances such as kerosene burners, gas stoves, liquid burners, gas space heaters, and wood burning can cause elevated levels of PM, CO, nitrogen dioxide (NO₂), and polycyclic aromatic hydrocarbons (PAHs) indoors. In developing countries, indoor sources such as combustion of fossil fuels for cooking and heating are likely to contribute more to population exposure than outdoor environments².

People might also be exposed to air pollution at workplaces, both indoors as well as outdoors. People working in environments with motor exhaust emissions, e.g. miners, tunnel workers, and traffic personnel are at higher risk of being exposed. The individual industrial exposure level might be orders of magnitude higher than the exposure of the average general population, but the total number of individuals exposed is limited¹.

Motor vehicles are a major source of urban air pollution and emit hundreds of different compounds. The most abundant of these are large quantities of carbon dioxide (CO₂), CO, NO_x, PM and VOCs such as formaldehyde, benzene, 1,3-butadiene, and acetaldehyde. NO_x and VOCs are also precursors of ozone. Each one of these compounds, together with secondary pollutants produced from these, can cause adverse health effects⁹. The IARC classified diesel engine exhaust as carcinogenic to humans (Group 1) in 2012¹⁰. The latest WHO review on the health aspects of air pollution, REVIHAAP¹, states that there is new scientific information which brings evidence for adverse health effects of PM, NO₂ and ozone even at the lower concentration levels that are commonly present in Europe. Most studies focus on the effects on respiratory and cardiovascular health, but there is growing evidence for a range of other effects. For example, studies have shown that exposure to air pollution during pregnancy is associated with pre-term birth, reduced foetal growth, pre-eclampsia, and spontaneous abortion^{2,11}.

The most measured air pollutant is NO₂, because it is often used as a marker of traffic-related air pollution. The health effects of nitrogen dioxide has however been discussed as nitrogen dioxide correlate well with other air pollutants. Thus, it has been difficult to determine whether the observed health effects originate from nitrogen dioxide *per se*, or if the effects are caused by other constituents in motor vehicle exhausts. There is evidence, from many recent studies, for associations between day-to-day variations in

NO₂ concentrations and variations in mortality, hospital admissions, and respiratory symptoms¹. In many of these studies the effect remains even after adjusting for other pollutants including PM₁₀, PM_{2.5}, and sometimes black carbon¹. Chamber studies also support short-term health effects of NO₂, but at higher concentrations, not commonly found in ambient air. There is clear evidence of airway inflammation and increased airway hyperresponsiveness from NO₂ at concentrations above 1.9 mg/m³^{12, 13}, but the results are less consistent at concentrations between 0.4 mg/m³ and 1.9 mg/m³¹. The long-term effects of NO₂ exposure are more difficult to assess, because no chamber studies exist and the toxicological evidence is limited. However, some new epidemiological studies suggest an association between long-term exposure to NO₂ and cardiovascular and respiratory mortality, and impaired lung function and respiratory symptoms in children¹. In conclusion, the new studies have shown associations between both short-term and long-term exposure of NO₂ and mortality and morbidity. The adverse effects were shown at concentrations that were at or below the current EU limits on exposure¹.

Exposure and exposure assessment

Exposure to an environmental or occupational substance is generally defined as any contact between a substance in an environmental medium (e.g. air, soil, water) and the surface of the human body (e.g. respiratory tract or skin)¹⁴. There are several routes for substances to come into contact with the human body including inhalation through the respiratory system, ingestion through the gastrointestinal system, and absorption through the skin¹⁴. The exposure is quantified by the time of contact and the concentration of the pollutant¹⁵. Human exposure to air pollutants is determined by the concentration of air pollutants in the environment where they spend their time, and by the time spent in such environments. These environments are often referred to as microenvironments.

The total exposure of an individual is the sum of their exposures in multiple microenvironments- such as the indoor home, outdoors, the workplace, in transit, and others (restaurants, shops, indoor sport venues, theatres etc.)- and the time spent in each microenvironment. One way to obtain information on where the individual spends their time is to use questionnaires and time-activity diaries. Together with information on pollutant concentrations in each microenvironment these time-activity diaries can be used to generate detailed exposure profiles¹⁶.

In epidemiological studies, that seek to determine if there is an association between exposure to a specific agent and any health effects, accurate and precise exposure estimates are critical.

Exposure assessment is the processes of measuring or estimating the concentration, the frequency of exposure and the duration of the exposure to a substance, together with the number of humans who are exposed to the substance. There are different methods of exposure assessment of air pollution and these can be classified as direct and indirect methods ¹⁴. The indirect methods include fixed site measurements of air pollutants or modelled estimates of concentrations. The measurements at fixed sites with ambient air monitors provide accurate measurement data at the point of monitoring. People living in this area are considered to have the same exposure, despite the fact that there is spatial variability of the concentrations within the area, and that these measurement data represent only one of many microenvironments, where people spend their time. Nevertheless, this indirect method is often used to characterize the exposure in environmental epidemiology ¹⁴.

To be certain to capture the subject's total exposure, direct methods as for example personal sampling has certain advantages over the indirect methods described above. For this purpose, personal exposure monitors such as diffusive samplers are useful. These samplers are light-weight devices that are carried by the individual, close to the breathing zone. The concentrations measured by these monitors include contributions from the various microenvironments in which the individual has spent the time during the measurement period. In addition special pollutant-emitting activities carried out by the individual are incorporated into the total exposure measure ¹⁴.

Exposure measurements for large populations are generally extensive. In environmental epidemiology exposure assessment therefore often relies on modelling of exposure, often in conjunction with exposure measurements, which are important either to build or validate a model (e.g. LUR; land use regression models)¹⁴.

Air quality guidelines and regulations

The WHO is the directing and coordinating authority for health within the United Nations system, and it is responsible for setting global norms and standards to minimize adverse health effects. Air quality guidelines were first published in 1987, and revised in 1997 ¹⁷. The last update was launched in 2005 ² and contains revised or retained guideline values for four common air pollutants: PM, ozone, NO₂, and SO₂.

To minimize the adverse health effects of air pollution, legally binding limits for concentrations of outdoor air pollutants are set in the EU by the Air Quality Directives 1999/30/CE, 2004/107/EC, and 2008/50/EC ¹⁸⁻²⁰. In Sweden environmental quality standards were introduced by the government for NO₂/NO_x, SO₂, and lead in 1999. Since then the standards have been updated and completed with standards for some other pollutants such as particulates (PM₁₀ and PM_{2.5}), ozone, benzene, CO, benzo(a)pyrene, cadmium, nickel and arsenic. Most standards are based on the requirements of European Community directives. Some standards have legally binding concentration thresholds that must not be exceeded, while others are target values for which endeavours should be made. The standards are set to protect human health or to protect vegetation and they contain a concentration limit, an average time over which the concentration of the substance is to be measured, and the number (if any) of exceedances allowed per year. The Swedish environmental quality standards are made up of the Air Quality Ordinance (SFS 2010:477) and the Regulations on air quality assessment (NFS 2010:8) ²¹. The standards are valid for outdoor air with the exceptions of workplaces, road tunnels, and tunnels for rail-mounted traffic.

It is not feasible to measure all air pollutants because some substances react very quickly in the atmosphere and are not easily measured. Others on the other hand, are not easily analysed at the laboratory, due to a lack of analytical method. Another issue is that sometimes the pollutant of interest that causes a particular health effect is not known. In epidemiological studies it is not practical to measure all components of the complex traffic air-pollutant mix, so surrogates, such as direct measures of traffic itself, or markers that correlate well with the target pollutant are used as proxies for traffic pollution. NO₂ is one of the most commonly used markers for traffic-related air pollution ⁹.

As there is evidence for adverse health effects of air pollution, it is of great concern to assess the concentrations of certain air pollutants in the air. It is important to gather data, not only from network monitoring stations, but also to study the distribution of certain substances in different microenvironments where humans encounter air pollutants. It is also important to measure the personal exposure of individuals. This requires simple, small, and user-friendly monitoring devices such as passive diffusion samplers that can be used for air sampling in ambient air, in workplaces, and indoors in homes, or for personal measurements ²². Reliable and precise assessment of exposure to air pollutants is crucial, therefore all methods used for measuring concentrations of certain substances in the air must be validated against a reference method, that is specific for each compound.

Since NO₂ often is used as a marker of traffic-related air pollution, reliable measurement methods for this substance are of extra importance.

Aims

The overall aim of this thesis was to validate diffusive samplers for measurements of NO₂ and NO_x.

The specific aims of this thesis were:

- To validate the Willems badge diffusive sampler for measurements of NO₂ in ambient air.
- To validate the Willems badge diffusive sampler for measurements of NO₂ in occupational settings with higher concentrations.
- To validate the Willems badge diffusive sampler for personal measurements of NO₂.
- To validate the Ogawa diffusive sampler for measurements of NO₂ and NO_x in ambient air, within a geographic area with a cold climate.
- To estimate the Swedish population's exposure levels to NO₂ by diffusive personal measurements on randomly selected individuals in five Swedish cities and to identify the determinants of exposure.

Paper I describes the laboratory and field validation of the Willems badge diffusive sampler for NO₂ measurements in ambient air, and **paper II** describes the validation of the Willems badge for measurements of NO₂ at higher concentrations that are common in occupational environments. **Paper III** reports on the evaluation of the Ogawa sampler for measurements of NO₂ and NO_x in ambient air in a cold climate. In **paper IV**, diffusive samplers are used for personal measurements to evaluate determinants of personal exposure to some carcinogenic substances and to NO₂ among the general Swedish population.

Nitrogen oxides

Physical and chemical characterization

The nitrogen oxides present in the greatest concentration in urban and industrial environments, and the ones most measured are nitric oxide, (NO) and NO₂. Of these, the most interesting in terms of human health is NO₂. NO₂ is a strong oxidant and produces one of the major components of acidic precipitation, nitric acid, as it reacts with water. Table 1 shows the physical and chemical characterization of these compounds. Five other nitrogen oxides can be found in ambient air (N₂O, NO₃, N₂O₃, N₂O₄, N₂O₅) but only NO, NO₂, and N₂O can be isolated at room temperature ²³.

Table 1. Physical and chemical characterization of NO₂ and NO

	NO ₂ , Nitrogen dioxide	NO, Nitric oxide or nitrogen monoxide
Molar mass	46 g/mol	30 g/mol
Characterization	Reddish-brown toxic gas with sharp, biting odour. Highly oxidizing and corrosive	Colourless, odourless gas
Boiling point	21.2 °C	-152 °C
Classification:	Very toxic, oxidizing	Toxic, oxidizing

EU directive 67/548/EEC

Measurements of NO and NO₂ are usually given in either ppb (v) (parts per billion by volume, i.e. the volume of gaseous pollutant per 10⁹ volumes of ambient air), ppm (v) (parts per million; 1/10⁶), or in standardized measures such as µg/m³ or mg/m³. The general conversion equation is

$$\mu\text{g}/\text{m}^3 = \left(\frac{(\text{ppb}) \times 12.187 \times M}{273.15 + ^\circ\text{C}} \right) \quad \text{Eq. 1}$$

where M is the molecular weight. An atmospheric pressure of 101.3 kPa is assumed.

Table 2 shows conversion factors from ppb and ppm to µg/m³ and mg/m³ for NO₂ and NO.

Table 2. Conversion factors for NO₂ and NO from ppm/ppb to µg/m³ and mg/m³ at 20 °C

Conversion factors	
ppm/ppb	µg/m ³
1 ppm nitrogen dioxide NO ₂	1913 µg/m ³
1 ppb nitrogen dioxide NO ₂	1.91 µg/m ³
5.2 × 10 ⁻⁴ ppm nitrogen dioxide NO ₂	1 µg/m ³
0.52 ppm nitrogen dioxide NO ₂	1 mg/m ³
<hr/>	
1 ppm nitric oxide NO	1247 µg/m ³
1 ppb nitric oxide NO	1.25 µg/m ³
8.0 × 10 ⁻⁴ ppm nitric oxide NO	1 µg/m ³
0.80 ppm nitric oxide NO	1 mg/m ³

Nitrogen oxides in ambient air

Sources and emissions

On a global scale, the dominant sources of nitrogen oxides in the atmosphere are anthropogenic, with combustion of fossil fuel and biomass burning as the main origins. Emissions from natural sources include lightning, soil release, wildfires, nitrous oxide (N₂O) degradation in the stratosphere and volcanic action²⁴. A total of 90%–95% of the nitrogen oxides are emitted as NO, and 5%-10 % as NO₂²³. At high temperatures, atmospheric nitrogen (N₂) oxidizes to NO, and the higher the temperature the more NO, which is why internal combustion engines are effective at oxidizing N₂ to NO²⁵. Nitrogen is present as an important trace element in some biological molecules such as amines, and this implies that nitrogen is present in both fossil fuels and in biomass. During the combustion process, the organic-bound nitrogen is oxidized to NO. NO reacts quickly in the atmosphere with O₃ and forms NO₂ as a secondary pollutant.

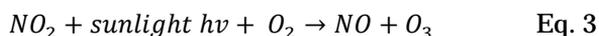
On-road vehicles accounted for 47% of the total emissions of NO_x in Sweden in 2012. Other important sources were energy production, working machines, and industries that accounted for 26%, 16%, and 11%, respectively, of the total emissions in 2012²⁶.

Atmospheric chemistry

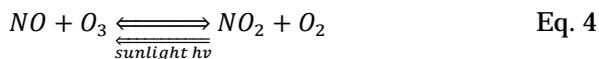
In combustion processes, primarily NO is emitted to the air but it oxidizes very quickly in the atmosphere to NO₂. This reaction is ozone consuming, and this means that ozone disappears, as NO₂ is formed.



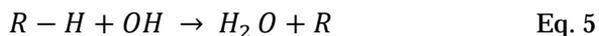
The reaction is rapid and the lifetime of NO is only 1 to 2 minutes, irrespective of season ²⁷. The reaction is driven backwards by the influence of sunlight during the process of photolysis.



These reactions can be summarized by the following equation



The arrow marked "sunlight hv" indicates that the reaction is driven towards the left at high light intensity, with the production of NO and O₃. The reactions indicate that a photochemical balance between NO and NO₂ is preserved and thus NO and NO₂ are often considered as a group in practice. The sum of NO and NO₂ is customarily referred to as NO_x ²³. During winter, the reaction between NO and O₃, which forms NO₂ occurs 4-10 times faster than the photolysis of NO₂ and the life time of NO₂ during these months is more than 30 minutes ²⁷. Equation 4 indicates that there is no net production of ozone, but that it is rather recycled ²³. To get a net production of ozone, NO has to be converted to NO₂ without consuming ozone during the process. This can be achieved when reactions with organic compounds are involved. For a general organic compound R-H where R = CH₃, CH₂CH₃, CHO, etc., the principal reactions are as follows:



RO₂ provides a pathway to oxidize NO without destroying ozone—unlike the reaction in Equation 4—and this results in a net production of ozone ²³.

Nitrogen dioxide is an important trace gas in the atmosphere as, in the presence of ultraviolet light and hydrocarbons, it is the main source of a variety of secondary air pollutants as e.g. ozone, nitrates and therefore also contributes to fine particle mass ². Peroxyacyl nitrates such as peroxyacetyl nitrate (PAN), are powerful respiratory and eye irritants that are present in photochemical smog. These secondary air pollutants and strong oxidants are produced from the oxidation of aldehydes and other VOCs in the presence of NO₂ and sunlight, (Figure 1) ²⁸. In large industrialized cities, the concentration of photochemical oxidants such as ozone, aldehydes, and PAN

can increase dramatically during unfavourable meteorological conditions. This *smog*, a photochemical oxidant smog, is found predominantly in large cities with a large amount of motor vehicles and a warm, sunny, dry climate³.

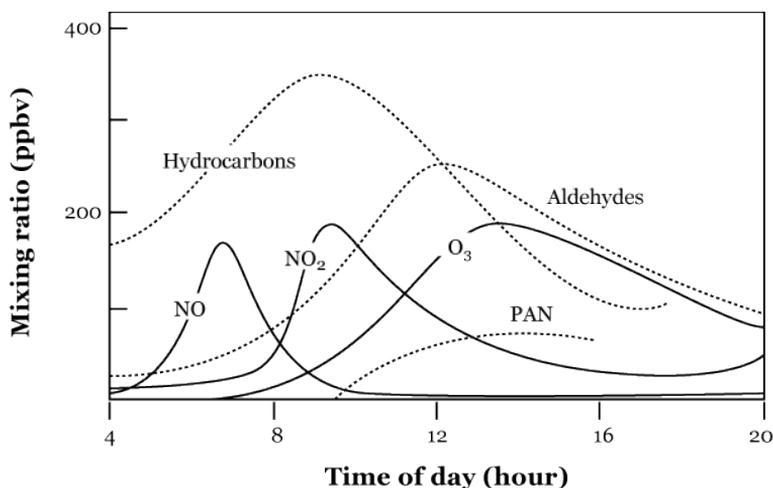


Figure 1. Photochemical production of oxidants during an air pollution episode in Los Angeles.

In summary the concentrations of NO and NO₂ in ambient air are much dependent on their distance from the local sources, the intensity of sunlight and the ozone concentration.

Concentrations in ambient air and regulations

The major source of NO₂ and NO in urban areas is motor vehicle traffic. A major part (90%–95%) of the NO_x emitted from vehicles is NO, while a small part is emitted directly as NO₂. Diesel vehicles emit larger amounts of NO_x compared to petrol vehicles. NO_x emissions show a typical diurnal pattern with high concentrations during morning and afternoon rush hours. The concentrations are typically higher in winter than in summer due to heating and meteorological conditions (inversions).

Europe

The European air quality limits on ambient concentrations of NO₂ are shown in Table 3. The annual limit value for NO₂ is 40 µg/m³ and this was exceeded at 42% of the traffic sites in 2011 with a maximum annual mean of 103 µg/m³
29.

Table 3. European and Swedish air quality limits for NO₂.

Objective	Averaging period	Limit value (µg/m ³)		Number of allowed exceedances (times/year)	
		Europe	Sweden	Europe	Sweden
Human health	1 hour		90		175
Human health	24 hours	200	60	18	7
Human health	1 year	40	40		

Examples of mean annual NO₂ concentrations at various fixed monitoring stations, in some European cities during 2012, are shown in Figure 2.

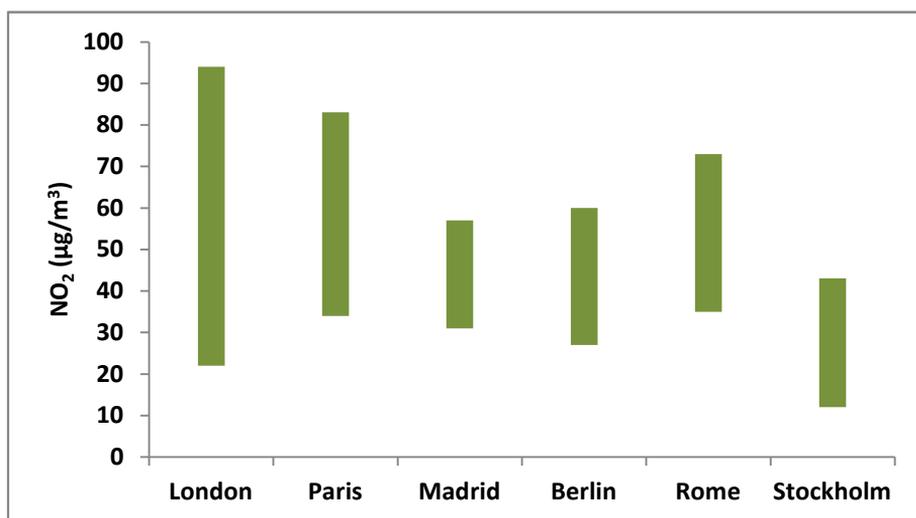


Figure 2. Annual mean NO₂ concentration ranges measured at various fixed monitoring stations (urban background and traffic sites) in London, Paris, Madrid, Berlin, Rome, and Stockholm in 2012³⁰.

Sweden

The Swedish air quality limits for NO₂ are shown in Table 3. The one-hour limit value of 90 µg/m³ must not be exceeded more than 175 times per year. This limit value was exceeded more than allowed at 6 sites in five Swedish cities during 2012³¹. It is interesting to note that two of these sites represent

middle-sized cities in the north of Sweden (Sundsvall and Umeå) while, more expectedly, four of these sites are situated in the three biggest cities of Stockholm, Göteborg, and Malmö. The 24-hour limit value, allowed to be exceeded seven times a year, was exceeded at 11 sites in seven cities in 2012. Three of these cities represent middle-sized to smaller cities in the north of Sweden (Skellefteå, Sundsvall and Umeå). The reason for the limit value being exceeded in smaller to middle-sized cities in northern Sweden is probably due to climate, with colder winters compared to southern Sweden. The increase in wood burning and periods of inversion at low temperature, also contribute to higher concentrations of pollutants. Figure 3 shows the mean monthly temperature and concentration of NO₂ at a background station in Göteborg, over the course of nine years. It is clearly shown in the figure that the concentration of NO₂ depends on the temperature and that the concentration is high at low temperatures and vice versa.

The mean annual concentration of NO₂ at street level in 10 Swedish cities ranged from 25 µg/m³ to 49 µg/m³ in 2012, and the annual limit value was exceeded at two sites in the biggest Swedish cities of Stockholm and Göteborg. The same year, the annual mean NO₂ concentration ranged from 0.5 µg/m³ to 4.5 µg/m³ at 13 regional background sites ³².

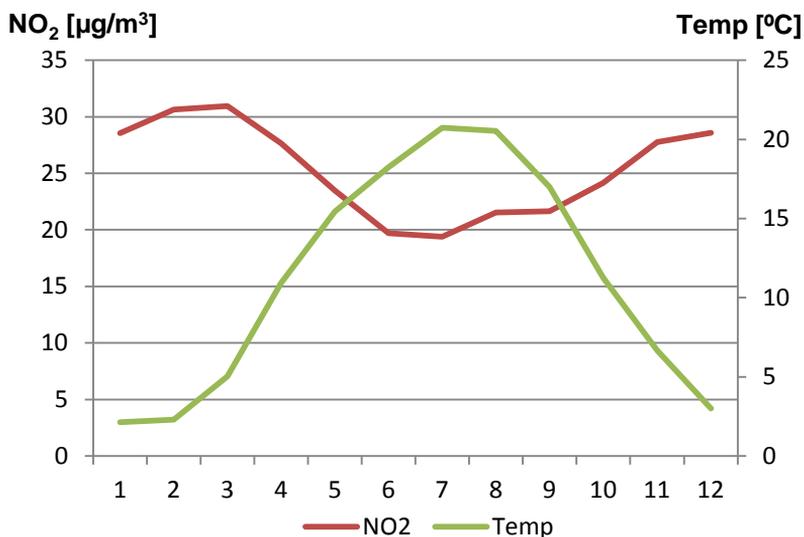


Figure 3. Mean NO₂ concentrations and mean temperatures over the course of nine years (month 1–12) at a background station in Göteborg, Sweden.

Spatial distribution

The concentrations of NO₂ vary between rural, urban background and traffic areas. The highest concentrations of NO₂ are found near the source and at traffic sites. The concentration decreases at urban background sites and is lowest at regional background sites ²⁹. Gilbert et al. (2003) reported on decreasing concentrations of NO₂ with increasing distance from a busy highway, and the concentration was higher downwind than upwind ³³. Another study showed that the concentrations of NO₂ on the upwind side drop off to background levels within 200 meters, whereas on the downwind side, the concentrations do not reach background levels until 300-500 meters ³⁴. Gilbert et al. (2003), also found that the greatest decrease in NO₂ concentration occurred in the first 200 meters, but in downwind directions the concentrations did not reach background levels until 1400 meters ³³.

In Umeå, the NO₂ concentrations are measured with diffusive samplers over the course of one week two to three times a year at about 40 sites. Figure 4 shows the mean concentration of NO₂ at 23 of these sites (with 10 measurement occasions) from 2009 to 2014. The highest concentrations were found at traffic sites, such as Västra Esplanaden, where the mean concentration over these years was almost 60 µg/m³. At a rural site (Baggböle), the mean NO₂ concentration was about 4 µg/m³.

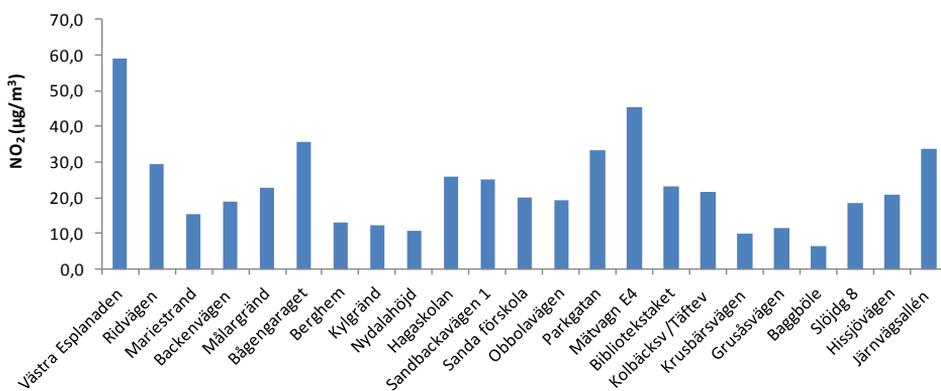


Figure 4. The spatial distribution of NO₂ concentrations in Umeå, Sweden. The mean concentrations of NO₂ measured with diffusive samplers during one-week measurements on ten occasions between 2009 and 2014.

Trends in emissions

From 1990 to 2012 the emissions of NO_x in Sweden were reduced by about 50% (from 270,000 tons to 131,000 tons). The reduction in NO_x emissions is explicitly seen at a roof urban background station in Stockholm, where the mean annual NO_x concentration was reduced from 40 µg/m³ in 1990, to 20 µg/m³ in 2004³⁵. Even though the NO_x emissions have decreased in urban areas in Western Europe since 1990, the levels of NO₂ have not decreased at the same rate as the NO_x concentrations^{36, 37}. In fact the NO₂ share of NO_x has increased markedly. Carslaw et al. (2005) reported that the NO₂/NO_x emission ratio at roadside sites in London increased from 5–6 vol % in 1997 to about 17 vol % in 2003³⁸. In Stockholm, a similar pattern could be seen at two traffic sites where the NO₂/NO_x ratio increased from 10%–15 % in 1990 to about 25%–35% in 2004³⁵.

The potential causes of these increasing NO₂/NO_x emission ratios are related to the proportion of NO_x emitted directly as NO₂ (the primary NO₂ fraction) from vehicle exhausts. For petrol-fuelled vehicles the primary NO₂ fraction is less than 5%, whereas for diesel-fuelled vehicles, with no exhaust after-treatment system, this fraction is about 10%–12%³⁹. Particularly under low engine load conditions, which are common in urban traffic areas, diesel-powered vehicles emit more NO₂³⁸. The increasing proportion of diesel-engine vehicles in Sweden and in Europe will, therefore, have a significant impact upon the ambient NO₂ concentrations, especially at road-side locations. In Sweden, 80% of the heavy-duty vehicles and 17% of the passenger cars were diesel-powered in 2011⁴⁰. Another cause of increasing NO₂/NO_x emission ratios is the exhaust treatment technology such as particle filters and oxidation catalysts in diesel cars. Some of the particulate filters are based on the oxidation of NO to NO₂ to achieve the catalytic action, and this leads to higher direct emission of NO₂, with ratios up to 60% of the primary NO_x emissions being in the form of NO₂ for some new passenger car technologies³⁹.

Nitrogen oxides in occupational environments

Sources and concentrations

Occupational exposure to NO_x most often occurs in occupations where the workers are exposed to motor exhausts, especially miners, tunnel workers, vehicle drivers, bus garage workers, street workers, etc. who have higher risk of short-term exposure to NO_x⁴¹. The highest exposure is reported from tunnel-construction workers, fire fighters and miners using diesel-powered equipment (Table 4).

Table 4. Some workplaces with measured NO₂ and NO exposure.

Workplace/occupation	Country/city	Component measured	Mean concentration (range) mg/m³	Reference
Tunnel construction workers	Norway	NO ₂	1.5 (0.06–5.5)	AoH 2003:16, ⁴¹
Diesel engine drivers (coal mine)	Germany	NO ₂	0.4	Dahmann 2009, ⁴²
Diesel engine drivers (coal mine)	Germany	NO	1.7	Dahmann 2009, ⁴²
Blasting specialists, mine	Germany	NO ₂	0.027	Dahmann 2009, ⁴²
Miners (non-metal mine)	USA	NO	(0.25–1.9)	Coble 2010, ⁴³
Miners (non-metal mine)	USA	NO ₂	(0.19–1.2)	Coble 2010, ⁴³
Miners (iron ore mine)	Sweden	NO ₂	0.28 (0.05–0.68)	Ådelroth 2006, ⁴⁴
Taxi drivers	Sweden	NO ₂	0.048	Lewné, 2006, ⁴⁵
Lorry drivers	Sweden	NO ₂	0.068	Lewné, 2006, ⁴⁵
Taxis	Paris	NO ₂	0.14	Zagury, 2000, ⁴⁶
Several occupational groups	Sweden	NO ₂	0.11	Lewné, 2011, ⁴⁷
Tunnel construction workers	Sweden	NO ₂	0.35	Lewné, 2011, ⁴⁷
Bus depot workers	Sweden	NO ₂	0.19	Lewné, 2011, ⁴⁷
Shoe stalls	Korea/Seoul	NO ₂	0.11	Bae, 2004, ⁴⁸
Fire fighters	Spain	NO ₂	(0.019–4.8)	Miranda, 2012 ⁴⁹
Farm silos		NO	(3.7–775)	AoH 2008;42:3 ⁵⁰
Kitchen with gas stoves	Brazil	NO ₂	(0.029–0.19)	Arbex, 2007 ⁵¹

High occupational short-term exposures can occur especially when working in confined rooms with insufficient ventilation. Arc welders, silo workers, and miners working with blasting are at particularly high risk. The personal exposure to NO₂ as a marker of occupational exposure to diesel exhaust was investigated in a Swedish study, and the workers included in the study were divided into several occupational groups based on job characteristics. Accordingly, the highest NO₂ exposures in the study were found in workers exposed to diesel exhaust indoors (Table 4) ⁴⁷.

People working in outdoor urban environments, such traffic police officers, and street cleaners or in indoor environments near busy roads, such as roadside storekeepers, parking garage attendants, service station attendants, etc. might also be occupationally exposed to air pollutants from traffic exhausts ⁴⁸. Other occupations at risk are fire fighters, personnel working with explosives, and personnel in combat situations due to the formation of NO_x in combustion processes. Agricultural workers might be exposed to high levels of NO₂ formed during anaerobic fermentation processes of crops in tightly sealed silos (silo filler's disease). Toxic levels of NO₂ peak 48–72 hours after filling the silo but can persist for up to one month ⁵².

Gas stoves are a major contributor to indoor NO₂ exposure, and professional cooks might therefore, be exposed to elevated levels of NO₂. High concentrations of NO₂ have also been found in ice-skating rinks with exhaust from ice resurfacing machines in combination with poor ventilation ⁵³.

The present Swedish 8-hour occupational threshold is 2 mg/m³ if the source is exhaust emissions and 4 mg/m³ otherwise.

Measurements of nitrogen oxides

Sampling techniques

Active sampling—The chemiluminescence monitor

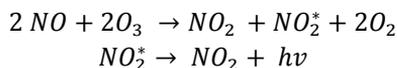
According to the Ambient Air Quality Directive 2008/50/EC, the reference method for measurement of NO₂ and NO_x is the chemiluminescence method as described in EN 14211:2012 “Ambient air quality. Standard method for the measurement of the concentration of nitrogen dioxide and nitrogen monoxide by chemiluminescence”⁵⁴.

The chemiluminescence monitor is widely used for continuous monitoring of NO₂ and NO_x at network stations. The instrument provides on-line measurement data, with high time resolution (minutes). The main strengths and weaknesses of the method are shown in Table 5.

Table 5. Summary of the advantages and disadvantages of two different sampling techniques for NO₂/NO_x measurements

Technique	Advantages	Disadvantages
Chemiluminescence	The reference method Accurate	Needs electricity Needs temperature-controlled trailer with data connection
	Sensitive Real-time data	High cost Needs calibration and expertise maintenance
	High time resolution, <1 h	Data loss due to malfunction
Diffusive samplers	Small Portable Easy to deploy Low capital and operating cost	No real-time measurement
	No need for pumps or electricity Makes it possible to perform surveys over wide geographical areas to get spatial variation Unobtrusive Good for personal sampling No data loss	Gives the weight average concentration over the measurement period Low time resolution of 24 hours-7 days Needs laboratory analysis

The principle of the chemiluminescence technique for NO_x measurements is based on the following reaction between NO and ozone:



where $h\nu$ represents the emitted light.

Sampling of gas is made by passing the gas to a reaction chamber in the monitor where the gas reacts with ozone. The emitted photons (chemiluminescence) from the excited NO₂ molecule are counted in a photomultiplier and transformed into an electric signal proportional to the amount of NO in the sample.

The chemiluminescence monitors do not measure concentrations of NO₂ directly in the air sample. NO₂ must first be reduced to NO in a converter before passing the ambient airstream to the reaction chamber. The monitor typically alternates between two states, one that samples and measures the concentration of NO in the ambient air directly, and one that measures the sum of NO and NO₂ (NO_x) by passing the air sample over a converter that converts NO₂ to NO. The difference of the two values is reported as the NO₂ concentration⁵⁵. Advanced monitors such as the Eco Physics CLD 700 that was used in **paper I, II, and III** have dual-chambers. The inlet gas is divided into two equal gas streams; one passes through the converter to the NO_x chamber and the other gas stream passes directly to the NO chamber. This allows NO and NO_x to be determined continuously (Figure 5). Most chemiluminescence monitors use a molybdenum converter in which NO₂ is converted to NO using molybdenum surfaces heated to 300°C–350 °C.

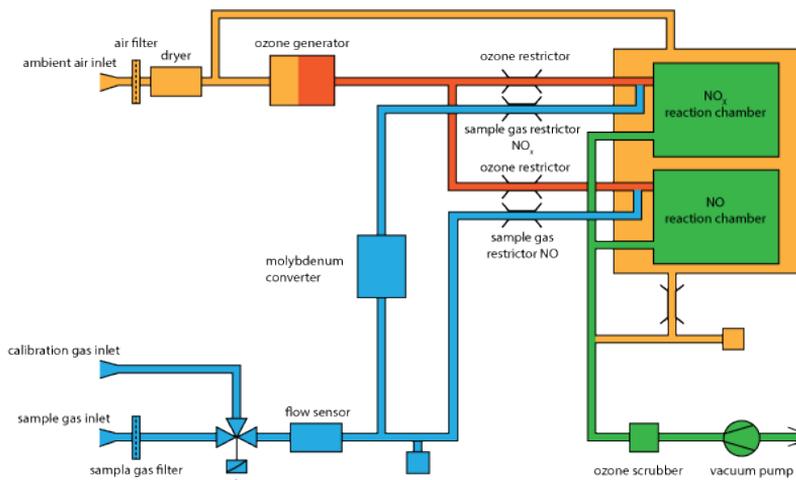


Figure 5. Flow diagram of an Eco physics CLD 700 chemiluminescence monitor, used in **paper I, II, and III.**

Interference

Two forms of interference can occur in the chemiluminescence monitor. Quenching causes a reduction of the signal of the instrument due to collision between excited NO_2^* molecules and other molecules in the reaction chamber. H_2O , CO_2 , N_2 , and O_2 , which are the main components of air, are the molecules most likely to cause quenching. Humidity might give rise to a significant effect⁵⁶. Permeation dryers at the sample inlet may prevent quenching effects.

The most significant problem with chemiluminescence monitors is their inability to specifically and directly detect NO_2 ⁵⁷. Other gas-phase nitrogen containing molecules such as nitric acid (HNO_3), nitrous acid (HNO_2), PAN, and alkyl nitrates are converted to NO in the NO-to- NO_2 converter and, therefore, can be reported as NO_2 by the NO_x monitor⁵⁸. Of these compounds, PAN, HNO_3 , and HNO_2 are believed to significantly contribute to interference. PAN can be found in large quantities in big cities, and thus interference might be a particular problem in these areas. In a study in Mexico City with the aim of evaluating the chemiluminescence reference method, however, PAN was not considered to contribute significantly to the interference in the study, because of low ambient concentrations⁵⁷. Probably the concentration of PAN is low also in Sweden, and the interference from PAN is likely to be very small. The primary interfering species in that study

were found to be gas-phase HNO₃ and alkyl nitrates formed from photochemical reactions, and these accounted for up to 50% of the ambient NO₂ concentrations ⁵⁷.

Diffusive sampling

In contrast to active methods, diffusive sampling does not need electricity or a pump to measure pollutants. The technique is based on the diffusion of gas molecules from the sampled medium, such as the air, to the collection medium (the sampling filter). The main advantage with diffusive samplers is that they are small, lightweight, and unobtrusive and, therefore, more readily acceptable for study participants, easy deployed, and cost-effective (Table 5).

Theory

The first diffusive sampler and the underlying mathematical factors for the estimation of sampling rates in a diffusive sampler were first introduced by Palmes and Gunnison in 1973 ⁵⁹. The primary mechanism behind diffusive sampling is the passive flow according to Fick's first law of diffusion of analyte molecules from the sampling medium through the sampler tube/sampler badge to a sampling filter in the diffusive sampler. Fick's law states that molecules diffuse from regions of high concentration to regions of low concentrations. The rate of diffusion or diffusion flux (J) of an analyte is dependent on the molecular diffusion coefficient D, over a sampling area A, and the concentration gradient $\frac{\partial c}{\partial x}$ of the analyte:

$$J = -D \times A \times \frac{\partial c}{\partial x} \quad \text{Eq. 8}$$

The theoretical sampling rate of a diffusive sampler with a cross sectional area A, can be calculated by

$$J = \frac{m}{t} = DA \times \frac{C - C_0}{L} \quad \text{Eq. 9}$$

where m = the mass transported, t = time, C = concentration, and L = the diffusion path length of the sampler. If we assume that C₀ = 0, i.e. the concentration on the collector surface is zero, then the sampling rate (S) (or the uptake rate, UR) can be calculated:

$$S = \frac{m}{C \times t} \quad \text{Eq. 10}$$

To calculate the concentration of NO₂ in a sample the following equation is used:

$$C_{NO_2} = \frac{m_s - m_b}{t \times S} \times 10^6 \quad \text{Eq. 11}$$

where

C_{NO₂} = the concentration of NO₂ in µg/m³,

m_s = mass of NO₂ in the sample in µg,

m_b = mass of NO₂ in the blank in µg,

t = sampling time in minutes, and

S = sampling rate in cm³/min (or mL/min).

Fick's law can be applied in determining the theoretical sampling rate for a NO₂ diffusive sampler under the following assumptions: ideal, steady state conditions; the collection medium is a perfect sink; the molecular diffusion coefficient for NO₂ in air is known; the concentration at the entrance of the tube is maintained at a constant level; and there is no adsorption or absorption by the tube walls. If all of these conditions are met, or are sufficiently good such that the error introduced is small, then the absolute sampling rate of the sampler is given by the geometry of the sampler (the diffusion path length and the cross-sectional area). In this case, the sampler does not need to be validated ²². In actual sampling in outdoor environments, however, there will most likely be deviations from ideal conditions, and this means that validation of the sampler is necessary ²².

The theoretical sampling rate of a sampler as shown in Eq. 9 is dependent on the diffusion path length and the cross-sectional area of the diffusive sampler. Modifications of the sampler geometry by increasing the cross-sectional area and/or decreasing the diffusion path length will result in a

higher sampling rate that has the advantage of producing shorter time-weighted averages.

Sorbent

The sampling filter in a diffusive sampler can be coated with a chemical sorbent that reacts with the substance being measured. The most common sorbent used in diffusive samplers for NO₂ is triethanolamine (C₂H₄OH)₃N (TEA). TEA is a hygroscopic liquid with a melting point of 21.6°C, and it has high capacity to trap NO₂ from the air sample²². NO₂ reacts with TEA to form nitrite ions (NO₂⁻) as follows:



The collected NO₂⁻ on the sampling filter is extracted in water and analysed either with a colorimetric method and spectrophotometric detection, or with ion chromatography (IC) and conductivity detection.

Interference

In addition to reacting with NO₂ on the sampling filter, TEA can also react with other compounds to form NO₂⁻ ions. PAN and HNO₂ are the two most important potential substances to give positive interference²². Laboratory tests at high concentrations of PAN (500 ppb) have shown that TEA-coated filters collected PAN. A part of the delivered PAN, 15%-25 %, was converted to NO₂⁻, and the remainder was NO₃⁻. The interference from HNO₂ was showed to be negligible⁶⁰. In Sweden, PAN concentrations are low, and the interference from PAN is likely to be very small. The substances yielding possible positive interference in a diffusive sampler also cause possible positive interference in the chemiluminescence NO_x monitor with thermal conversion of NO₂ to NO in the converter. This positive interference will therefore not be identified when comparing diffusive samplers with reference monitors.

Chemiluminescence monitors versus diffusive samplers

Chemiluminescence monitors have numerous advantages. They offer real-time data with short time resolution and high sensitivity (Table 5). They are ideal for NO₂ and NO_x measurements at fixed monitoring stations to measure adherence to the national ambient air quality guidelines based on short averaging times (1 hour and 24 hours). In addition, they are able to provide detailed measurements of fluctuations in the concentrations of the

pollutants. However, there are drawbacks to these systems. The monitors are heavy and expensive and the operating costs are high due to the need for electrical power, temperature controlled trailer complete with data connection, and operators to daily oversee the sampling, calibration and repair.

The main advantages with diffusive samplers are that they are small, easy to deploy, portable, inexpensive, and require no electricity (Table 5). Diffusive sampling is in general less labour intensive and less costly than active sampling. This enables measurements in ambient air at remote sites and at many sites in a city simultaneously to provide information of the spatial and temporal variation of NO₂ concentrations. The diffusive samplers are very useful in taking indicative measurements with lower quality requirements and for mapping NO₂ concentrations. The European daughter directives 1999/30/EC and 2002/3/EC state that indicative methods can be used for NO₂ measurements in lowly polluted areas as long as they meet the data quality objective for uncertainty (precision and bias) of 25% ⁶¹. For measurements taken at fixed sites either continuously or by random sampling the data quality objective for uncertainty is 15% ¹⁸. Diffusive samplers are also valuable for exposure assessment in epidemiological studies, especially in long-term studies where knowledge about the spatial distribution of the pollutant is essential. To capture small-area variation in NO₂ concentrations, diffusive samplers are also invaluable, when building and validating a land use regression model (LUR model) used for exposure assessment purposes ^{34, 62}. An additional benefit of using diffusive samplers is that there is no data loss during sampling periods. With chemiluminescence monitors there are inevitably periods of data loss experienced due to malfunction of the monitor. Another important advantage of diffusive samplers is their ability to be used for personal exposure monitoring.

The main limitations of diffusive samplers are their lower sampling rate compared to active methods, and they therefore require longer sampling durations of 24 hours or more. Their low time resolution and the fact that they give a weighted average over the sampling time, make diffusive samplers less appropriate to use for measurements aimed at ensuring adherence to short-term air quality guidelines.

Examples of diffusive samplers for NO₂

Depending on the design, diffusive samplers are in general classified into three types: tube-type samplers, badge-type samplers and radial-type samplers (Figure 6). The tube-type samplers typically have long, axial diffusion length and a small cross-sectional area that results in relatively low sampling rates. The badge-type samplers have shorter diffusion path lengths and a greater cross-sectional area and thus typically have higher sampling rates than tube-type samplers (i.e. 50 mL/min rather than 50 mL/h) ⁶³. The radial diffusive sampler has a cylindrical diffusive surface, and the pollutant diffuses through a membrane to a cylindrical cartridge where it is trapped.

The first sampler developed for monitoring of NO₂ was the Palmes tube, that was developed for measurements in occupational settings, especially in underground mines ⁶⁴. A variety of samplers of different designs for NO₂ measurements have been evaluated since the first sampler was introduced (Table 6). Most of the modifications have been aimed at increasing the sampling rates or reducing the effects of meteorological conditions (e.g. wind speed, temperature and humidity), or increasing the sensitivity of analysis ⁶⁵.

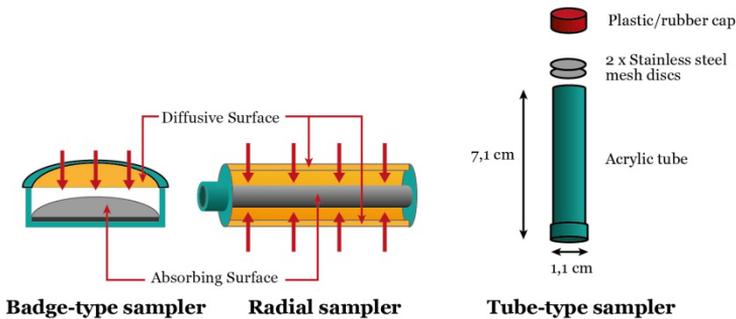


Figure 6. Badge-type, radial and tube-type sampler

Table 6. Examples of some diffusive samplers for measurements of NO₂ ^{65, 66}.

Diffusive sampler	Dimensions (diffusion length x diffusion area)	Absorbent	Sampling rate (mL/min)		NO _x measurements
			Manufacturer	Experimental	
Tube-type					
Palmes tube (Gradko sampler)	7.1 cm x 0.95 cm ²	TEA	1.2	1.2	no
Analyst sampler	2.54 cm x 3.27 cm ²	Na ₂ CO ₃ + C ₃ H ₅ (OH) ₃	12.3	11.7	yes
Passam sampler tube-type	7.4 cm x 0.75 cm ²	TEA	0.85	0.87	no
Badge-type					
Yanagisawa filter badge	1.0 cm x 20 cm ²	TEA	N R	N R	no
Passam sampler badge-type	2.0 cm x 4.15 cm ²	TEA	15.5	N R	no
IVL sampler	1.0 cm x 3.14 cm ²	NaI/NaOH	29	N R	no
Willems badge	0.6 cm x 6.16 cm ²	TEA	N R	40 /46	no
Ogawa sampler	0.6 cm x 0.79 cm ²	TEA	12.1	8.6	yes
Radial-type					
Radiello® sampler	1.8 cm x 2.0 cm ²	TEA	31.5	N R	no

TEA=Triethanolamine ; N R= not reported;

The Willems badge, (**paper I, II, and IV**) was initially developed at the Wageningen Agriculture University, in the Netherlands, for ammonia measurements and later adopted for measurements of NO₂ ^{67, 68}. The function of the Willems badge was improved from the first design by adding a Teflon draught shield and a longer diffusion length inside the sampler. This resulted in decreased influence from wind ⁶⁹. The sampler consists of a cylindrical polystyrene body (10 mm deep by 28 mm in diameter) with a glass fibre absorption filter at the bottom of the badge (Figure 7).

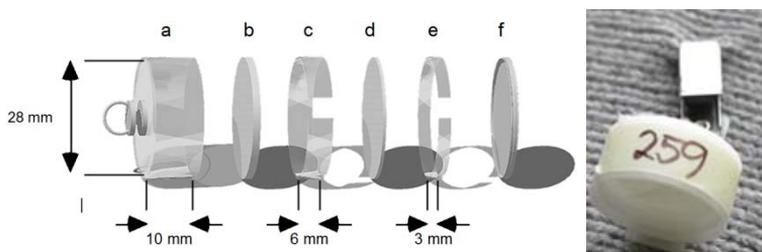


Figure 7. The Willems badge. Left: Schematic view. a) Polystyrene sampler base. b) Sampling filter. c) Spacer ring. d) Teflon filter. e) Fixation ring. f) Polyethylene cap. Right: Sampler with clip for indoor use and personal measurements.

The filter is coated with TEA as a collection medium for NO₂. A 6 mm spacer ring separates the sampling filter from a Teflon membrane and this creates a turbulence-free space in the sampler where diffusion of NO₂ from the

surrounding air to the sampling filter occurs. The Teflon membrane is secured by a 3 mm fixation ring, and the sampler is closed by an airtight cap when not sampling. The sampler is mounted with the open side down, and it is protected in a weather shelter for taking ambient air measurements.

The sampler was used in the PEACE (Pollution Effects on Asthmatic Children in Europe) study for measurements of NO_2 concentrations inside and outside the homes of asthmatic children in nine European countries ⁷⁰. The Willems badge was also used for personal NO_2 exposure assessment of individuals working in office buildings in Sweden ⁷¹ and for ambient NO_2 and NH_4 measurements in Canada ^{72 73}.

The Ogawa diffusive sampler (Ogawa & Company, Pompano beach, FL, USA), (**paper III** and **IV**) was initially designed in Japan 1986 for simultaneously measurements of NO_2 , NO and NO_x and it was later adopted for ozone measurements as the Harvard ozone passive sampler ⁷⁴. The sampler consists of a cylindrical body (2 cm in diameter \times 3 cm deep) and has a two-ended design, consisting of two chambers, that both holds one pre-coated sampling filter between two stainless steel screens (Figure 8 and 9). The sampling filter consists of cellulose fibre ⁶⁶. A patented diffuser end cap made of Teflon, with 25 holes (0.2 mm in diameter) secures the filters and screens. The two-ended design enables measurements of NO_2 and NO_x simultaneously by using different sampling filters. The NO_2 filter is coated with TEA and the NO_x filter is coated with a mixture of TEA and PTIO (2-phenyl-4,4,5,5-tetramethylimidazoline-1-oxyl-3-oxide) that is added to oxidize NO to NO_2 . The concentration of NO in the air sample is calculated as the difference between the measured NO_x concentration and the measured NO_2 concentration ⁷⁵.

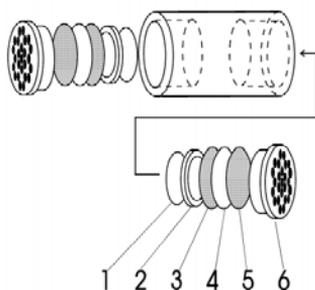


Figure 8. The Ogawa sampler. Each chamber consists of 1) a solid pad, 2) a pad retaining ring, 3) a stainless steel screen, 4) a coated sampling filter, 5) a second stainless steel screen, and 6) a diffuser end cap.

The Ogawa sampler has been widely used for measurements and field evaluations in warmer climates in Texas ⁷⁶⁻⁷⁸ and in California ^{79 80} and for field comparisons in the summertime in Michigan ⁸¹ and in the Californian mountains ⁸².



Figure 9. The Ogawa sampler with sampler clip for indoor use to the left, and with a weather shelter to the right.

In a review with the aim of drafting a proposal for methods for monitoring NO₂ in ambient air with diffusive samplers in the EU, five samplers were described and among them was the Ogawa sampler ⁶⁶. The conclusion concerning the Ogawa sampler was that the comparability of sampler results to those obtained with reference monitors was good, with average ratios from 0.90-1.07. The authors of the review used an extensive dataset⁷⁸ with parallel measurements of Ogawa samplers and the reference method for one year at six locations in El Paso, Texas to evaluate the equivalence of the sampler. The sampler was found to pass the uncertainty requirement for indicative measurements. It might also have passed the criterion for fixed measurements (expanded uncertainty of max 15 %) after correcting the sampling rate. It was also concluded, however, that the El Paso study was performed under conditions that were not typical for the EU⁶⁶.

The Willems badge sampler has a greater cross-sectional area and shorter path length and, therefore, a higher sampling rate (40 mL/min in **paper I** and 46 mL/min in **paper II**) than the Ogawa sampler. However, the Willems badge is not commercially available and can only measure NO₂. With its two-ended design, the Ogawa sampler has the capability of measuring both NO₂ and NO_x simultaneously. The experimentally determined sampling rates for NO₂ and NO_x in **paper III** at temperatures above 0°C were 8.6 mL/min and 9.9 mL/min, respectively.

Validation of diffusive samplers for measurements of NO₂/NO_x

Standard protocol for the validation of diffusive samplers

Accurate and reliable measurement methods are important for obtaining correct exposure assessments for air pollution surveys and epidemiological studies. It is of great importance, therefore, for diffusive samplers to be validated in parallel to the reference method, and it is important to validate diffusive samplers in the specific environment (temperature, wind speed, and relative humidity) and at the concentration levels that they are intended to be used.

Various factors can affect the sampling rate of diffusive samplers, including wind speed, temperature, humidity, sample concentration, and sampling time. Protocols for determining sampler performance were developed by Brown in 1984⁸³. The European Committee for Standardization (CEN) adopted a protocol in 1995 for diffusive sampler testing in workplace atmospheres called “Workplace atmospheres–Diffusive samplers for the determination of gases and vapours–Requirement and test methods”⁸⁴. CEN protocols for the test of diffusive samplers for measurements in ambient air were published in 2002/2003⁸⁵⁻⁸⁷. These protocols describe the test procedure to be used in the laboratory to determine the sampling rate and to examine factors that might affect the sampling rate of the sampler such as the concentration of the pollutant, exposure time, relative humidity, temperature and wind speed. The experiments are ideally performed at two levels with all factors set at low or at high levels in a full multifactorial test. Other tests described in the protocol include desorption efficiency, storage of the sampler, shelf life, sampler leak tests, determination of the blank value, and confirmation of the laboratory results in field tests. The conditions in outdoor ambient air differ substantially from the controlled conditions of laboratory studies in terms of fluctuating wind speeds, pollutant concentrations, temperatures, the presence of other air pollutants etc. Therefore the full validation of a diffusive sampler requires field tests to confirm the results of the laboratory validation. Field tests of diffusive samplers must be carried out in the environmental conditions where they are supposed to be used. When diffusive samplers are intended to be used for stationary measurements in workplaces, field tests of the sampler should be performed in industrial environments where interfering substances are likely to be found. Personal sampling with diffusive samplers should be preceded by an evaluation with personal measurements with diffusive samplers and the reference method in parallel.

The validation of a diffusive sampler includes the estimation of the precision and the accuracy of the sampler. Accuracy (A, as a percentage), is the closeness of the measurement results to the “true” value, in this case the concentration obtained with the reference chemiluminescence monitor.

$$A = \frac{C(\text{diffusive sampler}) - C(\text{ref instrument})}{C(\text{ref instrument})} \times 100 \quad \text{Eq. 12}$$

where $C_{(\text{diffusive sampler})}$ is the mean concentration measured by the diffusive sampler using the experimentally determined sampling rate and $C_{(\text{ref instrument})}$ is the mean “true” concentration measured by the reference monitor.

The precision is the degree of variability of the measurement results and can be expressed by the coefficient of variation (CV) or the relative standard deviation (RSD) of a series of replicate measurements

$$CV = \frac{s}{X} \times 100 \quad \text{Eq. 13}$$

where s is the standard deviation of the replicates and X is the mean of the replicates. The CV and RSD are expressed as percentages.

To ensure that the diffusive sampler works correctly, and on the same level as the reference instrument, the value of the measures accuracy and precision should be as small as possible.

Laboratory validation of diffusive samplers for NO₂ measurements

The full laboratory validation of diffusive samplers according to the standard protocol requires special laboratory facilities. A dynamic system for generating a known concentration of the test gas in air is used, and the stable atmosphere of the test gas is passed through an exposure chamber of inert material (glass, PTFE or stainless steel). The concentration and the flow of the test gas to the chamber as well as the relative humidity and temperature in the chamber have to be variable and controlled. The concentration of the generated gas mixture must be verified by a reference method or by a method that can be demonstrated to give results equivalent to the reference method ⁸⁵. The diffusive samplers are deployed in the exposure chamber (Figure 10) during the validation experiment, and a chemiluminescence instrument monitors the actual concentration in the chamber concurrently. After the exposure the diffusive sampler filters are analysed in the laboratory.

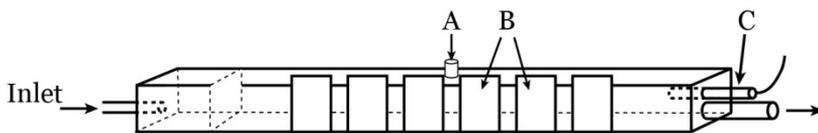


Fig 10. Exposure chamber for testing diffusive samplers. A–Port for chemiluminescence monitor probe; B–Removable doors; C–Probe for relative humidity measurement.

The Willems badge

Since the Willems badge is not commercially available, the sampler parts that are reusable were produced at the Umeå University mechanics and electronic workshop (UNIMEG). The filters were punched from sheets of Whatman glass fibre sheets. The filters were boiled in water for a few minutes, rinsed in acetone, dried, and then coated in a solution of TEA and acetone and dried in a vacuum desiccator. The samplers were assembled directly after drying the coated filters, and loaded samplers were stored in a refrigerator (+8 °C) before use (**paper I and II**).

For ambient air measurements, the samplers were deployed on lampposts or on other suitable poles at about 2.5 m off the ground. The samplers were attached to an aluminium plate or inside a plastic pot to be protected from rain and snow. For personal measurements, the samplers were attached at the shoulder and close to the breathing zone. For indoor measurements, the samplers were deployed at a height of about 1.5 m above the floor and in locations away from vertically moving air from ventilation, windows, and lamps. The samplers were always exposed with the open end facing downwards.

Sampling with the Willems badge was started by removing the cap, and sampling was stopped by recapping the sampler. After exposure, the samplers were stored in plastic bags in a refrigerator before analysis (**paper I and II**).

The Ogawa sampler

The commercially available Ogawa sampler parts, that are reusable, as well as coated NO₂ and NO_x filters were purchased from Ogawa & Company, USA. The samplers were loaded at the laboratory and placed in an airtight zipped

plastic bag. Before and after exposure the samplers were stored in a refrigerator (+ 8°C). The measurement was started by taking the sampler from the zipped bag, and the measurement was ended by putting the sampler back and resealing the bag. For ambient air measurements the sampler was attached to a 30 cm long aluminium holder to allow free airflow around the sampler (Figure 11). The sampler was protected from rain by an Ogawa shelter as described by the manufacturer, and the samplers were deployed as described above for the Willems badge. (**paper III**).



Figure 11. Measurement of ambient air with Ogawa samplers under weather shelters.

Analysis of NO₂/NO_x

All samples were extracted before analysis by transferring each filter to a vial, and adding 5 mL of the extraction solution. For the Willems badge samples in **paper I and II**, the extraction solution consisted of 0.005 M NaOH. The vials were shaken for 30 minutes and centrifuged for 10 minutes. For the Ogawa samplers (**paper III, and IV**), the filters were extracted in ultra-pure water followed by sonication for 10 minutes and filtered through an IC syringe filter. After extraction, NO₂⁻ was detected by either spectrophotometric analysis or IC analysis.

Spectrophotometric analysis

Colorimetric methods are commonly used to determine the concentration of the trapped NO₂⁻ on the filters. The method is based on the reaction between acidified sulphanilamide and NEDA (Saltzman reagent)⁸⁸ with NO₂ to form

a coloured solution. The intensity of the colour is determined by spectrophotometric analysis at 540 nm. The colorimetric method was performed by the flow injection technique (FIA), described in detail in **paper I**. The limit of detection (LOD) of the spectrophotometric method (defined as three times the mean standard deviation for the NO_2^- mass on filters of 24 samples of low concentration) was determined to be $4 \mu\text{g}/\text{m}^3$ over 24 hours (**paper I**).

Ion chromatography

Low concentrations of NO_2^- on the sample filters can be determined by ion chromatography. By using this method the detection limit can be decreased by orders of magnitude ⁸⁹.

The two methods for determination of NO_2^- concentrations on filters—the colorimetric method and the IC-method—were compared in **paper II** in which the analytical instrumentation of the ion chromatograph is described in detail. The methods showed almost identical results (Figure 12). The sensitivity was lowered by a factor 5 with IC, and the LOD was $0.75 \mu\text{g}/\text{m}^3$ for a 24-hour exposure (**paper II**). The day-to-day reproducibility, expressed as the CV of the concentration in the lowest control sample in eight runs during different days, was 1.6%. The repeatability of the method determined as the mean CV of a control sample run in six replicates at two different occasions was 1.5% (**paper II**). Henceforth, the IC method was chosen for the analysis of NO_2 and NO_x .

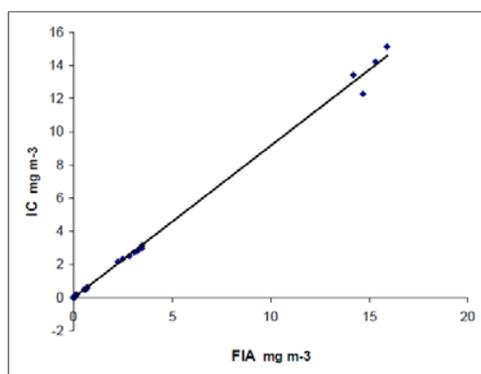


Figure 12. The relationship between the NO_2^- -concentration measured by IC and the spectrophotometric analysis for 33 samples ($r=0.99$).

The analysis of NO₂ with Ogawa samplers was performed by IC on a new system described in **paper III**. The detection limits (defined as three times the mean standard deviation for the NO₂⁻ mass on ten blank filters) for 24 hours sampling of NO₂ and NO_x were 0.57 µg/m³ and 1.17 µg/m³, respectively. The limits of quantification, LOQ, (defined as ten times the mean standard deviation for the NO₂⁻ mass on filters of ten blank samples) were 1.9 µg/m³ and 3.9 µg/m³ respectively for 24 hours sampling of NO₂ and NO_x (**paper III**).

For all analyses described in **papers I–IV**, the amount of NO₂ in the sample was quantified by using an external standard method. At least two field blank and two laboratory blank samples were run together with the measurement samples in each run. The NO₂⁻ concentrations in the blank samples in each run were subtracted from the concentration in the sample. For quality control, known samples of two NO₂⁻ concentrations (control samples) were run together with the samples in each run. All samples (**papers I–IV**) with concentrations below the LOD were assigned a concentration corresponding to LOD/2.

Laboratory validation of the Willems badge for NO₂ measurements

The laboratory validation studies of the Willems badge diffusive sampler are summarized in **papers I** and **II**. The performance of the sampler for measurements in ambient air is described in **paper I**, and the performance for measurements at higher concentrations that are common in occupational environments is described in **paper II**. The validation studies differ in concentrations and in exposure time. For measurements in ambient air with relatively lower concentrations in these environments, longer exposure times are needed. The sampler must, therefore, be tested under these conditions. The overall aim of the studies was to experimentally determine the sampling rate in laboratory studies and to confirm the results in field studies.

An atmosphere of NO₂ gas was generated by mixing NO₂ gas from a gas cylinder with clean, humidified air in an exposure chamber. The airflow through the chamber was 40 L/min, and this resulted in an air velocity of 0.3 m/s. The relative humidity was 20% or 80%. An ECO Physics CLD 700 AL chemiluminescence monitor was used as the reference method.

The sampling rate of the Willems badge was determined by a seven-run multifactorial test with NO₂ concentrations in the range of 5–150 µg/m³ (**paper I**). Sampling was performed for 1–7 days with a relative humidity of 20% or 80%. The influence of sampling time, NO₂ concentration, and

relative humidity on the sampling rate was evaluated statistically with the SIMCA software ⁹⁰. The effect of wind speed on the sampling rate was evaluated separately in a field test. The sampling rate was determined to be 40.0 mL/min with a CV of 22 %. There were no effects of NO₂ concentration or relative humidity on the sampling rate, but there was a small but significant negative effect of sampling time on the sampling rate.

In **paper II** the Willems badge sampler was evaluated according to the European standard for the validation of diffusive samplers for measurements in workplace atmospheres ⁸⁴. To test the sampler performance at the higher NO₂ concentrations and shorter sampling durations that are common in occupational environments, a similar set up was used as described above, and an eight-run multifactorial test was run. The samplers were exposed to NO₂ concentrations in the range of 0.2 mg/m³ to 17.8 mg/m³ at exposure durations from 15 minutes to 8 hours (**paper II**). The lower concentration was chosen because this concentration corresponds to 1/10 of the 8-hour Swedish occupational exposure limit, and the higher concentration (17.8 mg/m³) was used because this concentration corresponds to about twice the occupational 15-minute ceiling value (10 mg/m³). The relative humidity was 20% or 80%. The sampling rate was determined to be 46 mL/min with a CV of 12%. No effects of NO₂ concentration, relative humidity, or sampling time on the sampling rate were found (**paper II**).

The effects of the wind velocity across the face of the sampler and sampler orientation (horizontal or perpendicular orientation) on the sampling rate were tested in another exposure chamber with wind velocities from 0.1 m/s to 2 m/s (**paper II**). The perpendicular orientation resulted in higher sampling rates than the horizontal orientation for all wind velocities, and thus all subsequent measurements were taken with the sampler in a horizontal orientation. There was a 24% reduction in the sampling rate at a wind velocity of 0.1 m/s in the horizontal orientation compared to the experimentally determined sampling rate in the multifactorial study (Figure 13) (**paper II**).

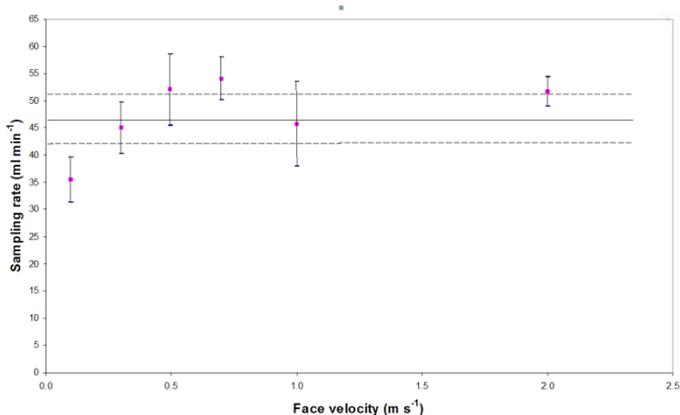


Figure 13. Effects of face velocity on the sampling rate (horizontal orientation) of the diffusive sampler ($n = 6$). The line shows the mean sampling rate \pm the 95% confidence interval for the mean at different wind velocities.

Storage stability tests showed that exposed samplers were stable for at least 14 days at room temperature ($+20\text{ }^{\circ}\text{C}$) or in a refrigerator ($+8\text{ }^{\circ}\text{C}$). The storage of samplers at room temperature for 14 days before exposure did not affect the sampling rate of the sampler. The desorption efficiency tests showed a recovery of 98%–103 % with a CV below 6% for three of the four nitrite concentrations. The lowest concentration, corresponding to an exposure of 10 minutes at the occupational exposure limit, resulted in a CV of 21% for the six samplers (**paper II**).

Field validation of the Willems badge and the Ogawa diffusive samplers for NO_2/NO_x measurements

Field evaluation studies in ambient air typically include co-located measurements with six diffusive samplers and the reference method at one or more sites. It is desirable to perform measurements in various environmental conditions. The samplers and the inlet of the chemiluminescence monitor should be placed as near as possible to each other, and environmental parameters such as temperature, relative humidity, and wind speed should be measured in close vicinity to the measurement site.

In **paper I**, the results from the laboratory validation of the Willems badge was confirmed by outdoor measurements with co-located diffusive samplers and a chemiluminescence instrument in eight runs with exposure durations of 2 days or 6 days. The mean temperature ranged from $-2\text{ }^{\circ}\text{C}$ to $-17.6\text{ }^{\circ}\text{C}$, the

mean relative humidity ranged from 48% to 82%, and the mean wind speed varied from 0.5 m/s to 1.8 m/s. The correlation between diffusive samplers and the chemiluminescence instrument was good (correlation coefficient (r) = 0.98) (Figure 14), and the mean ratio between concentrations obtained with the Willems badge and the reference instrument was 1.08 (Table 7).

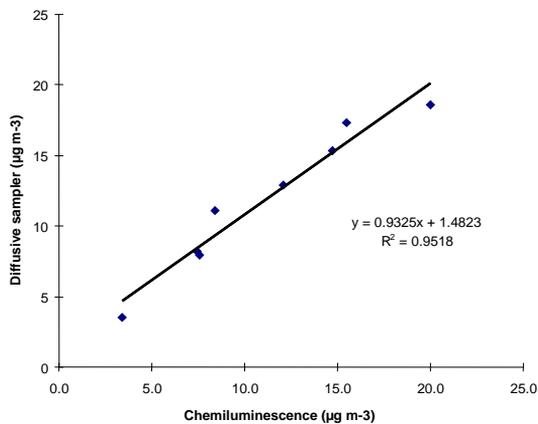


Figure 14. The relationship between the NO₂ concentrations in ambient air measured by the Willems badge and the concentrations measured by the reference instrument (**paper I**).

Table 7. Results from field studies with co-located Willems badge samplers and chemiluminescence monitors (**paper I**)

Experiment number	Sampling time (days)	Mean reference concentration ($\mu\text{g}/\text{m}^3$)	CV (%)	Mean wind velocity (m/s)	Mean relative humidity (%)	Mean temperature ($^{\circ}\text{C}$)	Ratio between Willems badge and reference method
1	6	15	3	1.5	78	-11.2	1.05
2	2	8	6	1.8	73	-2	1.11
3	2	16	6	1.4	82	-14.0	1.03
4	2	20	11	1.2	80	-17.6	1.06
5	6	8	3	1.3	64	-5.6	1.04
6	2	7	10	1.5	48	-5.2	1.32
7	2	3	12	1.7	69	-5.3	1.11
8	2	12	6	0.5	75	-6.4	0.93
		Mean	7				1.08

The precision for six samplers in eight runs ranged from 3% to 12% (mean 7%) (Table 7). Multiple regression analysis showed no statistically significant effects of exposure time, NO_2 concentration, wind velocity, relative humidity, or temperature on the sampling rate of the diffusive sampler.

In **Paper II**, the results from the laboratory test were confirmed by stationary and personal sampling in an environmental exposure chamber in which the subjects were exposed to diesel exhaust. Simultaneous measurements with diffusive samplers and a chemiluminescence monitor were performed on 25 persons at $0.9 \text{ mg}/\text{m}^3$ and $2.4 \text{ mg}/\text{m}^3$ NO_2 . The lower concentration corresponded to levels occurring at various workplaces such as tunnel construction and mines (Table 4). The higher concentration was more unusual to find at workplaces, but it was still comparable to the highest levels seen for the most exposed tunnel construction workers and fire fighters who experienced a mean exposure of $5.5 \text{ mg}/\text{m}^3$ and $4.8 \text{ mg}/\text{m}^3$, respectively (Table 4). The reason for performing the study in an exposure chamber was the difficulty in making personal reference instrument measurements of NO_2 . There is no small, unobtrusive, and accurate reference instrument for NO_2 measurements that can be deployed on individuals in working environments, so the solution of the problem was to make the exposure assessment in an exposure chamber (**paper II**).

The diffusive samplers were attached close to the breathing zone—one on each shoulder—and the exposure time was 15 minutes, 120 minutes, or 160 minutes. The reference monitor concentrations for the 120-minute and 160-minute measurements were recorded on a data logger. In addition, two sets

of 160-minute stationary measurements, each with six diffusive samplers, were performed at a NO₂ concentration of about 2.4 mg/m³ (**paper II**). For the two stationary measurement sets, the ratios between the concentrations measured with the diffusive samplers and the concentrations measured with the reference method were 0.93 and 0.85, respectively.

For personal sampling, the sampling rate for 22 measurements of 2-hour exposures at a NO₂ concentration of 0.9 mg/m³ was 49 mL/min (CV = 11%) (Table 8) (**paper II**). This was similar to the sampling rate determined in the laboratory study of 46 mL/min. However, for the 15-minute and 60-minute measurements at higher NO₂ concentration, the sampling rates were higher; 57 mL/min and 55 mL/min, respectively. There were no significant differences in the concentrations of NO₂ between the left and right shoulders (**paper II**).

Table 8. Personal sampling with the Willems badge compared to chemiluminescence measurements in the diesel exhaust exposure chamber.

Sampling time (min)	n	Chemiluminescence		Willems badge		
		Mean reference concentration (mg/m ³)	Mean concentration (mg/m ³)	Sampling rate (mL/min)	CV (%)	Ratio of the Willems badge to the reference method
120	22	0.87	0.92	49	11	1.06
60	28	2.44	2.84	55	13	1.16
15	27	2.38	2.84	57	15	1.19

The Ogawa sampler was only evaluated in field tests because at the time of the study we lacked the special laboratory facilities needed for laboratory validation. **Paper III** describes the field validation of the Ogawa diffusive sampler for ambient air measurements of NO₂ and NO_x. The aim was to determine the sampling rates (in **paper III** these were referred to as the uptake rates) for NO₂ and NO_x in field conditions and to compare the concentrations obtained from the manufacturer's calculation protocol⁷⁵ to the concentrations obtained by using the field-determined sampling rate. In addition, the effects of different factors (temperature, absolute humidity, relative humidity, wind velocity and NO₂/NO_x concentration) on the sampling rate were assessed.

NO₂ and NO_x were measured in the ambient air with Ogawa samplers and co-located chemiluminescence monitors at five different locations. Three of the sites (one traffic site, one urban background site, and one low traffic intensity site) were located in Umeå in northern Sweden. Two sites (one traffic site and one urban background site) were located in Malmö in southern Sweden. In total, 55 one-week co-located measurements of NO₂ (33

measurements in Umeå and 22 measurements in Malmö) and 47 one-week measurements of NO_x (25 measurements in Umeå and 22 measurements in Malmö) were made. Measurements were performed in all seasons except for spring (April and May). The mean weekly temperature ranged from -13.8 °C to 17.3 °C for the NO₂ measurements and from -13.8 °C to 13.0 °C for the NO_x measurements. The concentrations of NO₂ ranged from 5.4 µg/m³ to 54.4 µg/m³ and the concentrations of NO_x ranged from 17 µg/m³ to 175 µg/m³. Hourly data from the reference monitors were averaged over the sampling periods to get valid comparisons of each method. Five different chemiluminescence monitors were used in the study to measure the reference concentrations of NO₂ and NO_x at the different sites. The monitors were verified weekly with certified gas of known NO concentration.

For each sampling week, the sampling rate of the sampler was determined according to Equation 11 by regarding the mean chemiluminescence monitor concentration during the sampling period as the true concentration. The mean temperature was calculated for each sampling week and modelled with sampling rates in a simple linear regression analysis. Thus for every temperature in the observed temperature range, the model estimated a unique sampling rate (Figure 15). The equations for the estimated regression line for NO₂ and NO_x were

$$\text{For NO}_2: UR_{\text{NO}_2} = 7.501 + (0.109 \times T) \quad \text{Eq. 14}$$

$$\text{For NO}_x: UR_{\text{NO}_x} = 8.405 + (0.175 \times T) \quad \text{Eq. 15}$$

where T is temperature in °C, UR_{NO₂} is the sampling rate for NO₂, and UR_{NO_x} is the sampling rate for NO_x.

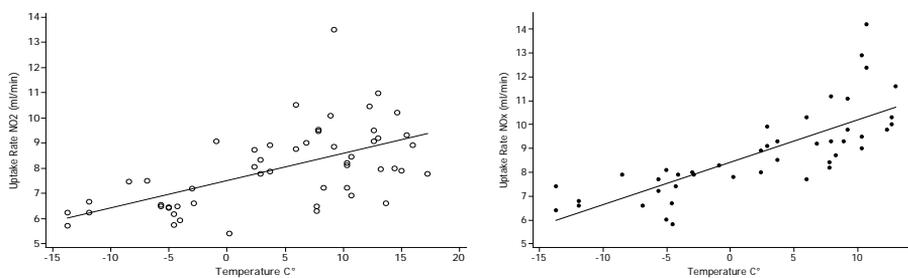


Figure 15. The NO₂ (left figure) and NO_x (right figure) sampling rates of the Ogawa sampler *versus* temperature.

The linear regression analysis showed that the sampling rates for NO₂ and NO_x were dependent on the temperature with lower sampling rate at lower temperatures. The sampling rate for NO₂ was assessed to be in the range of 6.0 mL/min to 9.4 mL/min for mean temperatures from -13.8 °C to 17.3 °C (Figure 15), which is lower than the theoretical sampling rate of 12.1 mL/min for all temperatures in the measured interval. For NO_x, the sampling rate was in the range of 6.0 mL/min to -10.7 mL/min for mean temperatures from -13.8 °C to 13.0 °C. In cases where the mean temperature of the sampling period is not known, we propose the use of one sampling rate for temperatures above 0 °C and one sampling rate for temperatures below 0 °C. The reason for choosing 0 °C for dividing the groups is solely for practical reasons and is not referring to the appearance of the linear regression curve. The sampling rate for NO₂ at temperatures above 0 °C was determined as the mean sampling rate for 36 weekly measurements above 0 °C (Table 9). The corresponding sampling rate at temperatures below 0 °C was determined as the mean sampling rate for 17 weekly measurements below 0 °C. For NO_x, the sampling rates above and below 0 °C were based on the mean sampling rates for 28 and 17 weekly measurements, respectively (Table 9).

Table 9. The sampling rates at temperatures above and below 0 °C for NO₂ and NO_x

	NO ₂	NO _x
Sampling rate above 0°C (RSD %)	8.60 (17.6)	9.88 (15.8)
Sampling rate below 0°C (RSD %)	6.64 (12.2)	7.17 (10.9)

The NO₂ and NO_x concentrations (Ogawa_{UR}) in each sample were determined using Eq. 11 with sampling rates based on the regression lines

(Eq. 14 and Eq. 15, respectively). The concentrations ($Ogawa_{OP}$) in the samples were also calculated according to the manufacturer's protocol (the Ogawa protocol)⁷⁵. The concentrations obtained from the two calculation methods were compared with the reference method concentration for each sample. The bias, defined as the difference between the concentration obtained with the diffusive sampler (p) and the concentration measured by the reference monitor (r), was calculated for each sample and for both of the $Ogawa_{UR}$ and $Ogawa_{OP}$ calculation methods as:

$$Bias (\%) = \frac{p - r}{r} \times 100 \quad \text{Eq. 16}$$

Table 10 shows that the NO_2 concentration was consistently underestimated if the concentration was calculated as described by the Ogawa protocol. The bias was -9.1% as a mean for all measurements, and the underestimation was higher for measurements below $0\text{ }^\circ\text{C}$ (-17%). If the field-determined sampling rates were used to calculate the Ogawa concentrations, the agreement between the Ogawa sampler and the reference method was improved. The ratio between $Ogawa_{UR}$ and the concentrations measured by the reference monitors was 1.02 (Table 10). As a mean for all 53 measurements, the absolute difference between the $Ogawa_{UR}$ concentrations and the reference method concentrations was $1.1\text{ }\mu\text{g}/\text{m}^3$.

Table 10. The mean bias of NO_2 concentrations. $Ogawa_{UR}$ is the concentration calculated with the experimentally determined sampling rate, and $Ogawa_{OP}$ is the concentration calculated according to the Ogawa protocol.

	N	Mean bias between NO_2 $Ogawa_{UR}$ and $Ogawa_{OP}$ (%)	Mean bias between NO_2 $Ogawa_{UR}$ and the reference monitor (%)	Mean bias between NO_2 $Ogawa_{OP}$ and the reference monitor (%)	Ratio $Ogawa_{UR}$ /reference monitor
All measurements	53	13	1.9	-9.1	1.02
Umeå, measurements above $0\text{ }^\circ\text{C}$	14	5.7	-3.3	-9.0	0.94
Umeå, measurements below $0\text{ }^\circ\text{C}$	17	28	4.6	-17	1.05
All measurements above $0\text{ }^\circ\text{C}$	36	5.5	1.6	-5.6	1.02
Umeå all	31	18	-0.2	-13	1.00
Malmö all	22	5.1	4.7	-3.4	1.05

For NO_x , however, the concentrations for the Ogawa sampler were overestimated if calculated according to the manufacturer's protocol. The mean bias between concentrations obtained with the Ogawa sampler and the reference method was 15% over all 45 measurements. The overestimation was less at temperatures below 0 °C (3%) and higher at temperatures above 0 °C (21%). If the field-determined sampling rate was used for the NO_x concentration calculations, the agreement between Ogawa_{UR} and the reference method was enhanced. The mean ratio between Ogawa_{UR} and the reference monitor for all measurements was 1.00, and the absolute difference between Ogawa_{UR} concentrations and the reference method concentrations, as a mean for all 47 measurements, was $-0.4 \mu\text{g}/\text{m}^3$ (**paper III**).

The effects of different factors on the sampling rate were examined by regression analysis of one factor at a time (it was not appropriate to use a multiple regression model because the explanatory variables were found to be highly correlated). Correlations between sampling rate and temperature, relative humidity, absolute humidity, wind velocity, and concentrations of NO_2 and NO_x were determined. Temperature was found to significantly affect the sampling rate of the sampler by 0.109 mL/min and 0.175 mL/min per °C for NO_2 and NO_x , respectively (Figure 15). Temperature significantly explained 34% and 60% of the variability in sampling rate for NO_2 and NO_x , respectively. Absolute humidity also significantly affected the sampling rate and explained 35% and 63% of the variability for NO_2 and NO_x , respectively. The sampling rate increased with increasing absolute humidity by 0.417 mL/min and 0.751 mL/min per g $\text{H}_2\text{O}/\text{kg}$ for NO_2 and NO_x , respectively (Figure 16). Relative humidity, however, was significantly negatively correlated with the sampling rate for both NO_2 and NO_x and explained 6% and 25% of the variability in the sampling rate for NO_2 and NO_x , respectively.

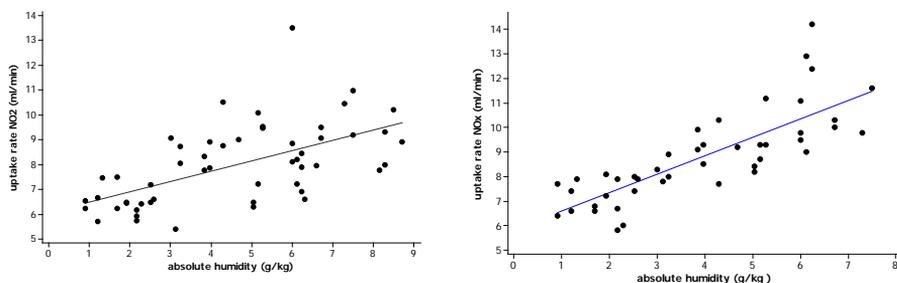


Figure 16. The NO₂ (left figure) and NO_x (right figure) sampling rates of the Ogawa sampler *versus* absolute humidity. The dotted lines represent the 95% confidence interval for the regression line.

The precision of the sampler was evaluated by six and five sets of 6-replicate measurements for NO₂ and NO_x, respectively, taken at the traffic site in Umeå. The precision expressed as the mean CV for all sets was 6.4% (range 3.6%–12%) and 3.7% (range 1.3%–5.6%) for NO₂ and NO_x, respectively

Personal measurements with the Willems badge and the Ogawa sampler

In **paper IV**, diffusive samplers were used for personal measurements of some carcinogenic substances and of NO₂. The aim of the study was to assess the environmental exposure of the general Swedish population aged 20 years to 50 years to benzene, 1,3-butadiene, formaldehyde, and NO₂. The study also aimed to evaluate the contributions of some environmental factors (smoking, environmental tobacco smoke (ETS), time spent in traffic, and other potential factors) on exposure.

The measurement campaign was conducted in one of five Swedish cities each year, and after measurements were taken in all five cities the campaign started all over again. The cities included in the study were Göteborg, Umeå, Stockholm, Malmö, and Lindesberg. The study described in **paper IV** included eight measurement campaigns from 2000 to 2008. In each campaign, personal one-week measurements of benzene, 1,3-butadiene, formaldehyde, and NO₂ were made on 40 individuals. Repeated measurements were performed on 20 of the 40 participants. The participants were randomly recruited to the study in each city.

To determine the contribution of the determinants of indoor and outdoor levels of the measured substances, the participants filled in a questionnaire and a time-activity diary. The questionnaire included questions about home characteristics, smoking habits, occupation, work address, means of transportation to work, and exposure to exhaust fumes or gasoline or to solvents during work or leisure time. In the time-activity diary, the participants recorded the number of hours spent in different microenvironments every day (e.g. outdoors in traffic, outdoors at their workplace, outdoors elsewhere, indoors at home, indoors at their workplace, and indoors elsewhere). Time spent near smokers as well as time spent in homes during the burning of wood or pellets was also recorded. Special activities, such as refuelling of vehicles, handling of gasoline, painting, and welding were also documented.

In this thesis the NO₂ results from the study were in focus. Personal measurements of NO₂ were performed with the Willems badge diffusive sampler from 2001 to 2005. From 2007 onwards, the Ogawa sampler was used instead. No NO₂ measurements were performed in Göteborg in 2000 or 2006.

The diffusive samplers were attached on a string around the neck near the breathing zone. The participants wore the samplers all day except when showering or bathing. The samplers were placed outside the clothes, but during rain or snowfall they were worn underneath the outer layer of clothing. At night the participants hung the sampler on a chair near the bed. The results of the measurements in each year are shown in Table 11.

Table 11. Personal exposure ($\mu\text{g}/\text{m}^3$) to NO₂ in Göteborg (Gtb), Umeå (Um), Stockholm (Sthlm), Malmö (Ma), and Lindesberg (Lbg) in 2000–2008.

Pollutant	Study area	Year	Subjects	Median ($\mu\text{g}/\text{m}^3$)	Mean ($\mu\text{g}/\text{m}^3$)	Range
NO ₂	Gtb	2000	-	-	-	-
	Um	2001	40	8.0	9.6	3–21
	Sthlm	2002	40	17	18	7–32
	Ma	2003	39	13.4	15.5	0.1–49
	Lbg	2005	33	5	8	1–45
	Gtb	2006/2007	-	-	-	-
	Um	2007	40	11	10	6–33
	Ma	2008	41	15	15	3–28

The statistical analysis used was mixed effects modelling, and this makes it possible to identify determinants of exposure and variability between and within individuals as well as to estimate the general population's exposure.

The results for NO₂ showed that the estimated arithmetic mean concentration for the general Swedish population from 2000 to 2008 was 14.1 µg/m³. The estimated exposure level for NO₂ was 11% higher for smokers compared to non-smokers. For NO₂, the between-city variance dominated and this indicates that the exposure between individuals is more evenly distributed within the cities, and that the biggest differences in exposure are between the cities.

Significant determinants and their effect on NO₂ exposure are shown along with time trends in Table 12. For all subjects (307 observations, 209 subjects), the NO₂ exposure was significantly higher in Stockholm compared with Umeå and significantly lower in Lindsberg compared with Umeå. Umeå and Malmö were the only cities with measurements in different years, and a significant increase (48%) between the two years was found in Umeå. The exposure was 16% higher for those who had occupational exposures and 42% higher for those who had a gas stove in their home. No significant effect of smoking was found. The exposure was lower for the subjects who had oil heating in their single-family houses. The exposure decreased with higher proportions of time spent indoors at home. For all subjects, 45% of the total variance was explained by the determinants in the model.

Table 12. NO₂ exposure, estimates of fixed effects for all subjects and for non-smokers. (No observations were excluded). Personal measurements of NO₂ were not performed in Göteborg.

Variable	All (307 observations, 209 subjects)		Non-smokers (257 observations, 175 subjects)		
	Estimate (SE)	p	Estimate (SE)	p	
Intercept	2.769 (0.177)	<0.001	2.954 (0.196)	<0.001	
City	Lindesberg	-0.803 (0.132)	<0.001	-0.704 (0.144)	<0.001
	Malmö	0.131 (0.091)	0.152	0.072 (0.101)	0.476
	Stockholm	0.222 (0.0977)	0.0250	0.160 (0.105)	0.131
	Umeå	0		0	
City*Year (Time Trend)	Umeå 2001	-0.394 (0.095)	<0.0001	-0.372 (0.101)	<0.001
	Stockholm 2002	0		0	
	Malmö 2003	0.031 (0.089)	0.730	0.0955 (0.109)	0.384
	Lindesberg 2005	0		0	
	Umeå 2007	0		0	
	Malmö 2008	0		0	
Occupational Exposure	no	0		n.s.	
	yes	0.152 (0.075)	0.0491		
Home ¹	(proportion)	-0.434 (0.216)	0.0473	-0.707 (0.245)	0.005
Oil heating	no	0		0	
	yes	-0.275 (0.131)	0.0379	-0.308 (0.131)	0.021
Gas stove	no	0		0	
	yes	0.353 (0.105)	0.0011	0.317 (0.112)	0.006
Smoke*ETS	no no		n.s.	Not included	
	no yes		n.s.		
	yes (no and yes)		n.s.		
ETS	no	Not included		0	
	yes			0.195 (0.074)	0.011

¹ Values of this variable are the proportion of time spent in a specific environment. The range of proportions was 0.14-0.98 (home).

Variables in the starting model were City, City*Year, Sex, Smoke*ETS, Type of house, Occupational exposure, Open fire, Outdoor, Traffic, Home, Garage, Gasoline, Oil heating, and Gas stove.

The results for non-smokers (257 observations, 175 subjects) were similar to those for all subjects, but no statistically significant difference was found between Stockholm and Umeå, and no significant effect of occupational exposure was found. The exposure was 22% higher among non-smokers exposed to ETS. Those non-smokers who had a gas stove had a 37% higher exposure.

Summary and Discussion

This thesis summarizes the validation of two diffusive samplers for measurements of NO₂ and NO_x. The main aim of the validation was to determine the sampling rate of the samplers as well as to assess the effects of various factors on their sampling rates. A laboratory validation has the advantage of allowing various factors to be assessed simultaneously under controlled conditions. On the other hand, this controlled evaluation minimizes interference by other substances, and the concentrations of the substances are kept constant during the experiment. The temperature and wind speed do not fluctuate, and the relative humidity is stable during the experiment. In ambient air, the opposite situation prevails. A mixture of hundreds of substances in the air can interfere with the measurement of the molecule of interest, and temperature, wind velocity, and concentrations can fluctuate to extremes during the measurement period. Another notable difference that distinguishes laboratory validation from field validation is that weather shelters, which are compulsory in field tests, are generally not used for the samplers in the laboratory tests. Laboratory validation studies are important, but it is essential to also validate the samplers in the environment where they are intended to be used and together with weather shelters as specified by the manufacturer.

Factors affecting the sampling rate of a diffusive sampler

Wind speed

For the Willems badge the wind velocity laboratory tests in **paper II** showed a lower sampling rate at 0.1 m/s whereas at higher wind speeds the sampling rates were similar to those determined in the laboratory tests. The results from the field tests in ambient air in **paper I** showed no statistically significant effects of wind velocity on the sampling rate of the diffusive sampler. One possible explanation for this might be that in the field tests the samplers are protected under weather shelters that are not used in the laboratory tests. Within the shelter the wind speed is probably almost constant. However, the ratio between the concentrations determined by the Willems badge and the concentrations determined by the chemiluminescence instrument was highest in the runs with the highest mean wind velocity and was lowest (<1) in the runs with low mean wind velocity. Even though we did not find any statistically significant effects of

the wind speed on the sampling rate in the field study, this might be explained by an effect of wind speed and depletion of NO₂ from the air at the face of the sampler.

As for the field tests in ambient air, the ratio between concentrations with diffusive samplers and concentrations with the reference method was < 1 for the stationary measurement sets in the exposure chamber (**paper II**). This lower concentration with diffusive samplers could be explained by the low wind velocity in the chamber (0.03 m/s), that generates stagnant conditions in which the pollutant of interest is depleted from the air around the sampler.

The Ogawa sampler was not tested at lower wind velocities than those experienced in the ambient air. In the ambient air, the sampling rate increased slightly with higher wind velocities. The design of the sampler, with a diffuser end cap comprised of holes makes it probably less sensitive to effects from wind speed than the “open-ended” Willems badge with a greater cross-sectional area. We have, however, no explanation for the differences in sensitivity to wind effects between NO₂ and NO_x measurements.

Our results are in accordance with other studies showing that the sampling rate of a diffusion sampler is dependent on wind speed^{69, 91-93}. Gair and Penkett (1995) showed that air turbulence has a great influence on the sampling efficiency of a tube sampler⁹¹. Plaisance et al. (2004) showed that the sampling rate for the Palmes tube increased with increasing wind velocity⁹². The short diffusion path length of the badge type samplers makes them even more sensitive to the effects of wind speed than tube samplers⁶⁹. Therefore a membrane or grid at the face of the sampler is often mounted to reduce the effect from wind, and is vital for the functioning of the badge sampler⁶⁹. Thus the sampling rates of badge-type samplers might differ from the theoretical sampling rate to a greater extent than tube-type samplers⁶⁵. Whenever the conditions of a sampler are changed by mounting a membrane or grid at the face of the sampler, the sampler must be re-validated because changes in the design of the sampler can lead to altered sampling rates. The high sampling rate of badge-type samplers results in rapid depletion of NO₂ at the face of the sampler if not replenished by external air movement⁹³. The depletion leads to an increased diffusive path in the sampler and a decreased sampling rate²².

Temperature

For the Willems badge, we did not discern any statistically significant effects of temperature on the sampling rate even though the mean temperature in

the field tests went down as low as $-18\text{ }^{\circ}\text{C}$ (**paper I**). The sampler performed well at such low temperatures.

One of the aims of **paper III** was to determine the sampling rate of the Ogawa sampler under the predominating conditions in a Swedish climate with cold winters. The sampling rate was found to be dependent on temperature, and the sampling rate decreased with decreasing temperature. This corresponds with other studies⁹³⁻⁹⁶. Hansen et al. (2001) noticed a large decrease in sampling rate below $-8\text{ }^{\circ}\text{C}$ for the Palmes tube⁹⁴. Kirby et al. (2000) examined the freezing point of aqueous TEA solutions and found that although the freezing point of TEA is $21.2\text{ }^{\circ}\text{C}$, the TEA solutions remained viscous liquids down to $-10\text{ }^{\circ}\text{C}$ ⁹⁵. This indicated that TEA forms a gel at low temperatures rather than freezing, and the authors concluded that the collection efficiency of NO_2 is unlikely to be impaired by low temperature⁹⁵. Warm air can contain more water than cold air, consequently the absolute humidity (which is defined as the quantity of water in a particular volume of air), is lower at low temperatures. Hence, the decrease in sampling rate at low temperature was suggested to be caused by a lack of water vapour (low absolute humidity) rather than the low temperature *per se*²².

Due to the dependence on temperature, we use a linear regression model to adjust the sampling rates to the mean temperature during the measurement period for the Ogawa sampler.

Humidity

Absolute humidity

The increase in the sampling rate due to increased absolute humidity for the Ogawa sampler is in accordance with other studies^{22, 97}. The effects of humidity on the sampling rate seem to be connected to the use of TEA as an absorbent for NO_2 . In a review on passive NO_2 sampling, Cape (2009) concluded that the efficiency of TEA as an absorbent for NO_2 appears to be dependent on water and that TEA does not perform quantitatively at low humidity²². Gold (1977) showed that when reacting NO_2 with TEA in an aqueous solution, equimolar amounts of NO_2^- and TEA-nitrate were formed⁹⁷. The same reaction in the absence of water at $-5\text{ }^{\circ}\text{C}$ yielded nitroso ammonium salt but no NO_2^- . Other laboratory validation studies have shown the sampling rate of diffusive samplers to be dependent of relative humidity, but only a few studies have studied the effects of absolute humidity on sampling rate, which would be more important, according to Cape (2009)²². The author concludes that the most important environmental factor affecting the sampling rate of sampler using TEA as absorbent is most likely humidity²².

In our study, absolute humidity was an important factor affecting the sampling rate. A possible explanation for the differences in sensitivity to absolute humidity between NO₂ and NO_x measurements is that there is a difference in the behaviour of TEA on the NO_x filters compared to the NO₂ filters. The NO_x filters are coated with TEA together with the oxidizing substance PTIO to oxidize NO to NO₂.

As temperature and absolute humidity are closely related (low temperature implicates low absolute humidity), the results of this thesis suggest that temperature measurements should be used for adjusting the sampling rate for the Ogawa sampler.

Relative humidity

In **paper I**, the laboratory studies and the field tests in ambient air showed no statistically significant effects of relative humidity on the sampling rate for the Willems badge.

For the Ogawa sampler (**paper III**), relative humidity was significantly negatively correlated with the sampling rate for NO₂ and NO_x, and we found lower sampling rates at higher relative humidity. This is similar to a study of the Radiello sampler by Swaans et al. (2007) who found a decrease in sampling rate at a relative humidity of 70%-80%⁹⁸. The relative humidity only explained 6% of the variability in the sampling rate for NO₂, but it explained 25% of the variability in the sampling rate for NO_x. In a similar manner to absolute humidity, the differences in sampling rate due to relative humidity might be caused by differences in the behaviour of TEA together with PTIO on the NO_x filters⁹⁸.

Sampling time

In the laboratory experiments with low concentrations of NO₂ with the Willems badge, there was a small but statistically significant negative effect of sampling time on sampling rate that was not observed in the field tests. We have not tested the Willems badge samplers for longer sampling times than seven days, and the Ogawa samplers were tested only for sampling durations of seven days. However, a study referred to in a review by Hafkenscheid (2009) showed that the concentrations tend to be lower measured with the Ogawa samplers over prolonged sampling times (3–4 weeks) compared to the concentrations obtained by the reference monitors. At shorter sampling times (2 weeks) the mean results obtained by the Ogawa sampler and the reference monitor were comparable⁶⁶.

Concentration

We found no statistically significant effects of NO₂ concentration on the sampling rate for Willems badge in the laboratory study or in the field study in ambient air (**paper I**).

The sampling rate for 2-hour exposures of personal sampling in the diesel exposure chamber was similar to the rate determined in the laboratory study (**paper II**). However, when higher NO₂ concentrations were combined with shorter sampling times, the sampling rates were higher. This effect of higher NO₂ concentration and short sampling time was not seen in the laboratory validation test. One reason for this could be that the results from the reference instrument for the 15-minute measurements are more uncertain because the concentrations were paper-recorded and not with a data logger. Another reason could be that movements of the subjects within the exposure chamber caused higher turbulence and thus higher sampling rates. One difference between the laboratory study and the field study was the presence of additional gaseous compounds as well as relatively high concentrations of particles, PM₁₀ (300 µg/m³) in the field study, especially at high NO₂ concentrations. One explanation of the higher sampling rate at high NO₂ concentrations could be that the particles interact with NO₂ or that other gaseous compounds present in the diesel exhaust interact with NO₂.

For the Ogawa sampler, we found a small but not statistically significant decrease in the sampling rate at higher concentrations for both NO₂ and NO_x.

Evaluation of the manufacturer's calculated sampling rate for the Ogawa sampler

The Ogawa sampler has been widely used for measurements in warmer climates, but as far as we know it has not been used in countries with lower temperatures other than for measurements in Europe as part of the ESCAPE (European Study of Cohorts for Air Pollution Effects) study ⁹⁹.

In the ESCAPE study, which was performed in 15 European countries, the NO₂ concentration was calculated according to the Ogawa protocol. Cyrus et al. (2012) reported on the variations of NO₂ and NO_x observed in the different areas and concluded that the NO₂ concentrations measured by the Ogawa sampler were lower in most study areas compared to the reference monitors ⁹⁹. The mean ratio of NO₂ concentrations between the Ogawa sampler and the chemiluminescence monitor was smallest (0.71) in Umeå, the site with the coldest temperatures. This is consistent with the findings in **paper III** that the underestimation was more pronounced at temperatures

below 0 °C. For NO_x, the concentrations in the ESCAPE study were slightly overestimated with the Ogawa sampler. The NO_x concentrations in Stockholm were overestimated by 42% in comparison with the reference monitor, and this was in accordance with the findings in **paper III**. The results for NO_x in Umeå in the ESCAPE study were, however, an exception and there was an underestimation even of these concentrations⁹⁹. We did not find this underestimation in our study (**paper III**). This could be an effect of different measurement seasons in the ESCAPE project, with measurements in spring, summer, and autumn, compared to our study in which measurements were also performed during the winter.

In conclusion, these results show that the manufacturer's calculation protocol should not always be relied upon and that the sampler should be validated in the environment and at the temperatures where it is intended to be used. This same conclusion was drawn in the review by Hafkenscheid et al. (2009). A comprehensive evaluation of the Ogawa sampler was performed in conditions atypical for the EU, and this is why a correction of the sampling rate for EU conditions should be performed for it to satisfy the criteria for performing fixed measurements⁶⁶.

Applications in different environments

Many studies have measured environmental levels of air pollutants at fixed monitoring sites, but these levels probably do not correspond to people's personal exposure levels¹⁰⁰⁻¹⁰³. It is a challenge to estimate personal exposure levels because the exposure levels will likely vary depending on where people live, their habits, and their daily activities. One direct way to measure the individual's exposure, including contributions from the various microenvironments in which the individual has spent time, is by personal sampling. In **paper IV**, the personal exposure was measured by diffusive samplers over the course of seven days. The participants also filled in time-activity diaries and questionnaires.

Because the measurements were performed over the course of a week, measurements were taken in all sorts of environments where the participants had spent their time, both indoors as well as outdoors. NO₂ measurements were performed with the Willems badge diffusive sampler from 2001 to 2005, and then the Ogawa sampler was used from 2007 onwards. Both samplers have been validated as shown in this thesis and in (Hagenbjörk-Gustafsson et al., 2012)¹⁰⁴ so most likely there are no differences in concentration measurements with a possible exception for

measurements taken during the night. When diffusive samplers are worn by a person, turbulence is created around the sampler. This is due to a rising airflow around the human body, because of the temperature difference between the ambient environment and the body ¹⁰⁵. The samplers need a small amount of turbulence around them, and thus they probably work better if worn by a person than if they are used for static area sampling. In **paper IV**, the samplers were hung close to the bed at night. A depletion of molecules from the air around the samplers might then occur, and this might lead to a decreased sampling rate. Due to the design of the Willems badge sampler with its higher sampling rate, the risk of depletion around this sampler is higher than for the Ogawa sampler. This might lead to different concentration measurements between the two samplers during the night.

An evaluation of the samplers in parallel with a reference instrument under stagnant conditions would have shown to what extent the concentrations differ. We evaluated the Willems badge and the Ogawa sampler in parallel with a reference monitor in an environmental exposure chamber ¹⁰⁴ that was equipped with a fan, that caused turbulent conditions. Stationary and personal measurements were performed at different NO₂ concentrations. The results showed that the sampling rates for personal sampling are similar to those determined in the laboratory and field studies for both samplers. A minimum exposure of 8 hours is recommended for personal measurements for both samplers even though the Willems badge works for 4-hour measurements. For 8-hour personal measurements, the accuracy was higher for the Ogawa sampler (within 16%) although the precision was higher for the Willems badge ¹⁰⁴.

As the study in **paper IV** incorporates measurements of personal exposure on randomly chosen individuals, it offers an opportunity to identify determinants of exposure and variability as well as exposure estimations for a general population. In addition, because the study is on-going and measurements are made in each city every fifth year, time trends can be studied. The NO₂ exposure was significantly higher in Umeå in 2007 than in 2001. The reason for this might be an effect of more traffic and a higher proportion of diesel cars in the vehicle fleet in 2007 compared to 2001. In Malmö, we found no differences in exposure between the two years.

For NO₂, the between-city variance dominated. This indicates that the exposure between individuals is more evenly distributed within the cities and that the biggest differences in exposure are between the cities.

An evaluation of which determinants are most important for the exposure is essential in order to take steps to minimize the exposure. In this study, using

a gas stove was a significant determinant for NO₂ exposure. Other studies also support these results of higher NO₂ exposure with the use of gas stoves^{103, 106-108}. We did not find any significant effect of smoking, which was probably due to too few smokers among the participants. On the other hand, we found significantly higher NO₂ exposures among non-smokers who were exposed to environmental tobacco smoke. This has also been shown in other studies^{103, 109-111}.

Occupational exposure was also a significant determinant for NO₂ exposure, but there might be a source of error in this result because the question was formulated so as the individuals themselves decided if they were exposed at their workplace. In addition, exposure to both solvents and vehicle exhaust/petrol fumes were included in the same question. The exposure decreased with higher proportions of time spent indoors at home. In Sweden, major indoor sources such as gas stoves are rare, and in an earlier study we found the mean indoor/outdoor ratio for NO₂ to be 0.4 in 23 homes in Umeå⁷⁰. This supports the results of lower exposure with a higher proportion of time spent indoors in the present study. We found significantly lower exposures for those persons who had oil heating in their homes. One possible explanation could be that houses with oil heating might be situated in less trafficked areas in the outskirts of the city where there is no district heating.

Conclusions

The Willems badge is suitable for measurements of NO₂ in ambient air with sampling times from 1 day to 7 days. It can be used for measurements of NO₂ both indoors and in occupational settings at wind speeds above 0.3 m/s. It is also suitable for personal measurements.

The Ogawa sampler can be used to measure NO₂ and NO_x in ambient air within a particular geographic area with a cold climate. The sampling rate was found to be dependent on temperature and should be corrected for this. The Ogawa sampler should be validated within the environment it is intended to be used instead of using the manufacturer's theoretically determined sampling rate.

Identifying the determinants for exposure is essential for policy-makers to design action plan programs to minimize exposure. Important determinants for NO₂ exposure in this study were occupational exposure, using a gas stove, and ETS for non-smokers. Having an oil boiler and a higher proportion of time spent indoors decreased the exposure. The estimated NO₂ exposure in the general population was 14.1 µg/m³.

In epidemiological studies, it is crucial to make reliable exposure assessments in order to draw the right conclusions about health effects. A misclassification of the exposure might bias the results. Validation of diffusive samplers in relevant environments is, therefore, essential and can ensure that the measurements are accurate and precise.

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