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APPLICATION OF MAGNETIC BIOMONITORING IN AIR POLLUTION RESEARCH

Spatio-temporal properties of magnetic particle matter

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SUMMARY

Air quality has a significant impact on the comfort of the cities and the health of humans, other organisms, and the whole environment. The implementation of air quality legislation requires continuous measurements. The direct air pollution measurements using air quality monitoring stations and the air pollution dispersion models suffer from poor spatial representativeness. Consequently, local scale variation in pollution levels and pollution sources can easily remain undetected. In this thesis, the air pollution research is conducted using magnetic biomonitoring. The focus is on the omnipresent iron-bearing mineral particles and heavy metals bound to them. Magnetic biomonitoring combines the methods of traditional biomonitoring and enviromagnetic research. It is useful for the identification of pollution or emission sources and routes, for determining the magnetic particle matter (PM) sizes, and for constructing spatially representative pollution maps.

This thesis investigates the spatio-temporal properties of anthropogenic magnetic particle matter. The samples were collected from industrial and urban environments in southwest (SW) Finland using the active moss bag technique as the main sampling method. The thesis evaluates the applicability of magnetic (bio)monitoring for enhancing the representativeness of air quality assessments, and establishes the basis for its application, particularly in mid-latitudes with seasonal variation. The study indicates that active biomonitoring is a powerful tool for enhancing the spatial accuracy of air quality assessments and for evaluating the spatial representativeness of air quality monitoring stations. Both industrial and urban environments benefit from magnetic screening. The joint use of spatially representative sampling networks as well as magnetic, micro-morphological, and chemical research methods provide quantitative air pollution data, and also guide, for example, the identification of emission sources and pollution impact areas. Magnetic air pollution monitoring with the active moss bag technique is shown to be more applicable than the examined epiphytic lichen or snow samples. The four-seasoned year, which is typical for mid-latitudes, sets limitations on the application of biomonitoring for air quality assessments. Autumn and winter are suggested as the most representative seasons for obtaining a general assessment of the air quality using the moss bag technique.

Keywords: air quality assessment, air pollution, magnetic biomonitoring, active biomonitoring, the moss bag technique, magnetic method, industrial, urban, Finland

TIIVISTELMÄ

Ilmanlaadulla on merkittävä vaikutus kaupunkien viihtyisyyteen sekä ihmisten, muiden organismien ja koko ympäristön terveyteen. Ilmanlaatua koskevan lainsäädännön toimeenpano vaatii jatkuvia mittauksia. Ilmansaasteiden suorat mittaukset ilmanlaadun mittausasemilla ja ilmansaasteiden leviämismallit kärsivät heikosta alueellisesta edustavuudesta. Tämän seurauksena paikallinen vaihtelu ilmansaasteiden tasoissa ja lähteissä jää helposti huomaamatta. Tässä väitöskirjassa ilmansaasteiden tutkimus on toteutettu magneettisella biomonitoroinnilla. Työ keskittyy kaikkialla läsnä oleviin rautapitoisiin mineraalipartikkeleihin ja niihin sitoutuneisiin raskasmetalleihin. Magneettinen biomonitorointi yhdistää perinteisen biomonitoroinnin ja ympäristömagneettisen tutkimuksen menetelmät. Se on käyttökelpoinen saasteiden tai päästöjen lähteiden ja reittien tunnistamisessa, magneettisten partikkelien koon määrittämisessä sekä alueellisesti edustavien saastekarttojen rakentamisessa.

Tämä väitöskirja tutkii ihmisperäisten magneettisten partikkelien alueellis-ajallisia ominaisuuksia. Aineisto on kerätty teollisuus- ja kaupunkiympäristöistä Lounais-Suomesta käyttämällä näytteenkeruun päämenetelmänä aktiivista sammalpallotekniikkaa. Väitöskirja arvioi magneettisen (bio)monitoroinnin käyttökelpoisuutta ilmanlaadun arviointien edustavuuden lisäämisessä ja luo perustan menetelmän käyttämiselle erityisesti lauhkealla ilmastovyöhykkeellä, jossa on vuodenaikaista vaihtelua. Työ osoittaa, että aktiivinen biomonitorointi on tehokas työkalu ilmanlaadun arviointien alueellisen tehokkuuden lisäämisessä sekä ilmanlaadun mittausasemien alueellisen edustavuuden tarkastelussa. Teollisuus- ja kaupunkiympäristöt hyötyvät magneettisesta seulonnasta. Alueellisesti edustavien näyteverkostojen ja magneettisten, mikro-morfologisten sekä kemiallisten tutkimusmenetelmien yhteiskäyttö tuottaa kvantitatiivista dataa ilmansaasteista ja ohjaa, esimerkiksi, päästölähteiden ja päästöjen vaikutusalueiden tunnistamista. Ilmanlaadun magneettinen monitorointi aktiivisella sammalpallotekniikalla on osoittautunut käyttökelpoisemmaksi kuin työssä testatut jäkälä- ja luminäytteet. Keskileveyksille tyypilliset neljä vuodenaikaa asettavat rajoitteita biomonitoroinnin käyttämiselle ilmanlaadun arvioinneissa. Syksyä ja talvea suositellaan edustavimmiksi kausiksi sammalpallotekniikalle, koska niiden aikana ilmanlaadusta saa yleisemmän arvion.

Avainsanat: ilmanlaadun arviointi, ilmansaaste, magneettinen biomonitorointi, aktiivinen biomonitorointi, sammalpallotekniikka, magneettinen menetelmä, teollinen, kaupunki, Suomi

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When looking back over the past, I find that my interest in environmental research – and particularly in the environmental and biomonitoring research of Harjavalta – has followed me for over 10 years. My high school essay about the bioindication of the environment of Harjavalta expanded into a bachelor's thesis at university, after which I determinedly swore I would never touch this topic again. Never say never. I ended up doing my master's thesis about the magnetic biomonitoring of Harjavalta and, to a great extent, this PhD thesis. Hence, Harjavalta and its environment have always accompanied me, even if the very frequent visits to my hometown (which have amused some of my colleagues greatly) are disregarded.

This PhD process required a lot of persistence, patience, and determination. The scientific discipline and research of environmental magnetism is still rather rare in Finland, making such work a very solitary job. At the same time, it has been both fun and difficult to struggle with the application of new research methods and the development of magnetic biomonitoring of the environment. Being a kind of a 'pioneer' in the Finnish enviromagnetic research, I can hope that the road is easier now for others to follow. After many, many applications I was fortunate enough to be funded by the High Technology Foundation of Satakunta, Turku University Foundation, Valto Takala Fund, TOP Foundation, Geography Section, and BGG Doctoral Programme. This work would not have been completed without this valuable support.

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CONTENTS

LIST OF ORIGINAL PUBLICATIONS

This thesis consists of an abstract, summary, and the following four papers. The papers are referred to in the text with Roman numerals.

I Salo H, Bućko MS, Vaahtovuo E, Limo J, Mäkinen J, Pesonen LJ 2012. Biomonitoring of air pollution in SW Finland by magnetic and chemical measurements of moss bags and lichens. *Journal of Geochemical Exploration* 115, 69–81.

II Salo H, Mäkinen J 2014. Magnetic biomonitoring by moss bags for industry-derived air pollution in SW Finland. *Atmospheric Environment* 97, 19–27.

III Salo H, Berisha A-K, Mäkinen J 2016. Seasonal comparison of moss bag technique against vertical snow samples for monitoring atmospheric pollution. *Journal of Environmental Sciences* 41, 128–137.

IV Salo H, Paturi P, Mäkinen J 2016. Moss bag (*Sphagnum papillosum*) magnetic and elemental properties for characterising seasonal and spatial variation in urban pollution. *International Journal of Environmental Science and Technology* 13, 1515–1524.

1 INTRODUCTION

Ambient air quality is an outcome of natural and anthropogenic air pollutants (e.g., gaseous carbon monoxide (CO), sulphur dioxide (SO_2), and nitrogen oxides (NO_x), heavy metals, particle matter (PM)), climate and weather conditions as well as topography. The main anthropogenic emission sources are the same worldwide: energy production, industry, and traffic. Anthropogenic air pollution is originally an urban phenomenon but today it enacts on all geographical and temporal scales via long-range transboundary transport (Fenger 1999, 2009). Therefore, it is both a local, regional, continental, and global phenomenon and issue. In Finland, air quality is averagely good but local impacts and anomalies do exist. Urban pollutant levels may rise in difficult weather conditions to a level that corresponds with Central European cities of a similar size (Environmental Administration 2016).

Poor air quality impairs comfort in cities and threatens the health of humans and other organisms, and deteriorates the whole environment. Health effects are observed at all exposure levels, which indicates that some individuals are more prone and at risk even at low concentrations (Nel 2005; WHO 2006a). The most vulnerable groups are people with pre-existing pulmonary and cardiovascular diseases, children, and elderly (WHO 2006a). The exposure to PM is a great concern since particles are small enough to reach the upper and/or deeper parts of the lungs and even enter the human body (Pope & Dockery 2006; Schwarze et al. 2006; WHO 2006b; Kampa & Castanas 2008). PM also contains several toxic components, such as heavy metals.

The typical effects of short-term exposure to air pollution include eye, nose, and throat irritation, inflammation, and breathing difficulties (Nel 2005; WHO 2006b). Long-term exposure can contribute to lung cancer and cardiovascular problems, such as changes in blood pressure or heart rhythm, and even lead to untimely death. Environmental damages include: negative impacts on climate change and ozone depletion; the acidification of vegetation, soils, and water systems; the eutrophication of water systems; changes in the ecosystems and habitats of flora and fauna; and detriment to the built environment (Environmental Administration 2016). The economic consequences from direct and indirect impacts are vast. For example, the World Health Organization (WHO) estimates that the annual economic costs of air pollution in Europe are US$ 1.431 trillion for premature deaths and US$ 1.575 trillion for overall health impacts and mortality (WHO 2015).

Urban air quality is regulated by air quality standards. The development of ambient air quality standards and legislation for emission reductions started in the 1990s when the health effects of PM at concentrations believed to be safe were proved (Harrison & Yin 2000). The European Union (EU) controls the individual air pollutants by the EC Directive 2008/50/EC. The member states implement the Directive by ratifying it in their national legislations. The air quality in Finland is regulated by the Environmental Protection Act, the Government Degree on Air Quality, the Government Degree on Arsenic, Cadmium, Mercury, Nickel, and

Polycyclic Aromatic Hydrocarbons in Air, and the Government Degree on Ozone in Ambient Air (Ministry of the Environment 2015). The legislation requires continuous air quality measurements for the monitoring of pollution concentrations and making public announcements.

The most conventional methods for air quality protection are the direct measurements of pollutants in the air by fixed or movable monitoring stations, the construction of air pollution dispersion models, and the application of bioindicators and/or biomonitors. The spatial representativeness of the first two methods is poor since the information is normally based on a few stations with a limited spatial range (Fenger 1999; Beelen et al. 2009). The last method provides qualitative or quantitative information about the pollution levels and environmental changes based on the organisms or their parts (Markert et al. 2003). The spatial representativeness of this last method is high as long as suitable bioindicator/biomonitor species are available in the area under investigation. Bioindication/biomonitoring is extremely practical since the environment is so complex that it is impossible to measure and monitor all of its components simultaneously in all locations (Lindenmayer et al. 2015).

At present, mosses and lichens are the most used species in bioindication/ biomonitoring. The first air quality reports, which focused on the bioindication of lichens, were made in the 19th century in Europe (Nash 2008). The reports noted the decrease of lichen diversity in the city centres, for example, in Paris. Moss monitoring, however, first became common in Scandinavia and then in most other European countries during the 1970s–1990s (Markert et al. 2003; Poikolainen 2004). The many valuable features of mosses and lichens make them a practical choice for air quality investigations. To sum up briefly, lichen and most moss species absorb moisture and nutrients directly from wet and dry deposition because they lack a cuticle and true roots. The uptake from the atmosphere is enhanced while the influence from the substrate is minimal (Szczepaniak & Biziuk 2003). However, areas rich in anthropogenic air pollution, such as city centres, may experience a shortage or a poor condition of *in situ* species. In these total or partial moss/lichen deserts, the active approach is a practical substitute. The most known and used active biomonitoring method is the moss bag technique with several variations evolving over its 45 years' of use (extensively reviewed by Ares et al. 2012).

Traditional biomonitoring of air quality has increasingly been supplemented with magnetic research methods. Magnetic biomonitoring is a section of environmental magnetism, which evolved as a discipline in the 1980s. In environmental magnetism, the magnetic properties of the materials are applied as proxy parameters in order to acquire information on the concentration, composition, and grain sizes of widely present iron-bearing minerals and PM. PM, including magnetic minerals, are released from natural and/or anthropogenic sources and subjected to diverse environmental processes, and, more importantly, heavy metals can be bound to them. In air quality assessments, magnetic methods give data concerning the characteristics, levels, and distribution of magnetic PM-bound pollutants. These methods are utilised for

the identification of pollution or emission sources and routes, for determining the magnetic PM sizes, and for constructing spatially representative pollution maps.

In this thesis, the main aim is to investigate the spatio-temporal properties of anthropogenic airborne magnetic PM collected using active biomonitoring. This task is tackled by combining magnetic parameters – so far underutilised in Finland – to micro-morphological and conventional chemical analyses in order to quantify the characteristics of magnetic PM and to examine the usability of active biomonitoring in magnetic air pollution studies. The research is focused on both industrial and urban environments situated in southwest (SW) Finland. The emphasis is on the heavy metal pollution but other elements, such as sodium (Na) and aluminium (Al), are investigated as well because they are indicative of the pollution sources. The novelty of this study resides in the application, for the first time, of active biomonitoring in magnetic air quality assessments. The active moss bag technique is selected as the main sampling method while other methods and materials are implemented in addition to the moss bags. Before this research, magnetic studies applying mosses and/or lichens were few in number (Jordanova et al. 2010; Fabian et al. 2011). Now they are increasingly used especially in regard to the active approaches in urban environments (e.g., Chaparro et al. 2013; Vuković et al. 2015a, 2015b; Paoli et al. 2016). The following specific research questions are addressed:

i. How well does active biomonitoring enhance the spatial and temporal representativeness of air quality assessments?

ii. What insights do magnetic methods bring to extensively investigated industrial areas as well as to less investigated urban areas?

iii. How do epiphytic lichen and snow sampling perform when compared to moss bags in magnetic monitoring?

iv. How does seasonal variation of mid-latitudes affect the (bio)monitoring of air quality?

Paper I presents the effective application of magnetic measurements on moss bags and *in situ* lichens collected from industrial (Harjavalta) and urban (Turku) environments in SW Finland in three different projects. The moss bags were applied in magnetic biomonitoring worldwide for the first time. The temporal and spatial distribution of magnetic PM and heavy metals, and the sources of anthropogenic air pollutants, were identified with magnetic methods, conventional chemical analyses, and micro-morphological methods, i.e. scanning electron microscopy connected to energy-dispersive X-ray spectrometer (SEM-EDX).

Paper II expands the spatial resolution of magnetic biomonitoring in the industrial environment in order to identify and evaluate various emission sources and their role. A wider range of industrial reference samples were measured, and the temporal resolution of two periods of 6 months were tested with the moss bags.

Air pollution impact zones were established around the Industrial Park on the basis of the magnetic susceptibility results. The combination of spatial location, wind pattern, and magnetic and micro-morphological results guided the identification of the pollution sources, especially in the hot spot area.

Paper III focuses on the seasonal application and comparison of moss bags and vertical snow samples in winter, and is the first of its kind. The sampling was targeted on the most contaminated industrial area and its surroundings as recognised in papers I and II. Magnetic, chemical, SEM-EDX, K-means clustering, and Tomlinson pollution load index (PLI) were used for testing the comparability of the two methods and the applicability of moss bags in winter conditions.

Paper IV investigates the seasonal and spatial variation of traffic-related PM in an urban area of Turku. The seasonal samplings were done in spring during road dust episodes and in summer with full-grown vegetation. The magnetic and elemental results were used to evaluate the air pollution distribution and the representativeness of the single air quality monitoring station in the city centre.

2 BACKGROUND

2.1 Environmental magnetic research

2.1.1 Overview

In the scientific discipline of environmental magnetism, magnetic properties of various natural and anthropogenic materials are applied as proxy parameters for different environmental processes and changes, as well as human-environment interaction. Enviromagnetic research methods are based on the mineral-magnetic principles of rock- and palaeomagnetism (Dekkers 1997). They give detailed information on the concentration, composition and grain sizes of iron-bearing minerals and PM. Overall, the studies on environmental magnetism have applied a wide range of different materials (Table 1).

The discipline emerged from lake sediment and soil studies conducted in the UK and Ireland from the 1950s to the 1980s (e.g., Le Borgne 1955, 1965; Mackereth 1971; Thompson 1973; Thompson et al. 1975; Mullins 1977). These studies, in turn, were derived from Sweden where Gustav Ising made the first measurements of magnetic susceptibility and natural remanence on varved clay sediments in 1926 (Ising 1942, 1943; as cited in Sandgren & Snowball 2001). Environmental magnetism evolved into a separate discipline in the 1980s and experienced a boom along with the publication of the essential book *Environmental magnetism* by Thompson and Oldfield (1986). The application of magnetic studies to climatic and environmental issues was reviewed by Maher and Thompson (1999) in *Quaternary climates, environments and magnetism*. A comprehensive update to the discipline was provided by Evans and Heller (2003) in the book *Environmental magnetism. Principles and applications of enviromagnetics.*

Today, magnetic research methods are used in diverse fields, for example, in archaeology, ecology, geography, hydrology, meteorology, soil science, and pollution studies (Verosub & Roberts 1995; Dekkers 1997; Liu et al. 2012). Two of the major enviromagnetic research areas are climate change studies (i.e. the magnetic signals of past climates recorded by natural archives, such as loess-paleosol sequences or lake and marine sediments) and pollution studies, which has recently especially focused on air quality assessments using biomonitors (i.e. magnetic biomonitoring). The typical focus of magnetic air quality studies is detecting the characteristics, levels, and spatial as well as temporal distribution of PM-bound pollutants, in identifying pollution or emission sources, for assessing magnetic PM sizes, and for constructing spatially representative pollution maps both in urban and industrial environments. Enviromagnetic research is done worldwide, for instance, in Argentina, China, Czech Republic, Italy, Nepal, Poland, Slovenia, and UK. However, this research field and its methods are rather unknown in Finland and limited, until recently, to lake sediment or peat studies. A few years ago a thesis about traffic pollution accumulated on roadside soil and snow was completed (Bućko 2012).

Table 1. A short review (not extensive) of the manifold sample materials used in enviromagnetic research with references.

Material	References
Artificial materials	Salo (2014); Cao et al. (2015a)
Dust	Flanders (1994, 1999); Chaparro et al. (2006); Sagnotti et al. (2009); Magiera et al. (2011); Sagnotti & Winkler (2012); Gargiulo et al. (2016)
Fly ash	Hunt et al. (1984); Veneva et al. (2004); Blaha et al. (2008); Szuszkiewicz et al. (2015)
Lake, river, and sea sediment cores	Chan et al. (2001); Korhola et al. (2002); Booth et al. (2005); Haltia-Hovi et al. (2010); Ma et al. (2015)
Leaves	Georgeaud et al. (1997); Matzka & Maher (1999); Hanesch et al. (2003); Jordanova et al. (2003); Moreno et al. (2003); Gautam et al. (2005); Hu et al. (2008); Maher et al. (2008); Szönyi et al. (2008); Sagnotti et al. (2009); Jordanova et al. (2010); Hansard et al. (2011); Sagnotti & Winkler (2012); Cao et al. (2015b); Rai & Chutia (2016)
Lichen bags/ transplants	Salo (2014); Paoli et al. (2016)
Lichens (*in situ*)	Jordanova et al. (2010); paper I; Chaparro et al. (2013); Marié et al. (2016)
Moss bags	paper I, II; Salo (2014); Vuković et al. (2015a, 2015b); paper III, IV
Mosses (*in situ*)	Jordanova et al. (2010); Fabian (2011)
Needles	Jordanova et al. (2003, 2010); Urbat et al. (2004); Veneva et al. (2004); Lehndorff et al. (2006); Zhang et al. (2006)
Particle matter (PM) on filters	Georgeaud et al. (1997); Shu et al. (2001); Muxworthy et al. (2003); Sagnotti et al. (2006, 2009); Blaha et al. (2008); Petrovský et al. (2013); Castañeda Miranda et al. (2014); Revuelta et al. (2014)
Peat	Oldfield et al. (1979); Oldfield (1981); Strzyszcz & Magiera (2001)
Plants	Chaparro et al. (2015); Castañeda Miranda et al. (2016); Rai & Chutia (2016)
Road dust	Goddu et al. (2004); Kim et al. (2009); Jordanova et al. (2014)
Roots	Jordanova et al. (2003)
Snow	Bućko et al. (2011, 2013); Reynolds et al. (2014); paper III
Soil	Maher (1986); Hay et al. (1997); Hoffmann et al. (1999); Jordanova et al. (2003); Gautam et al. (2005); Chaparro et al. (2006); Magiera et al. (2008); Bućko et al. (2010); Cao et al. (2015b)
Tree ring cores	Zhang et al. (2008)
Wind-blown loess	Verosub et al. (1993); Sun & Liu (2000); Kim et al. (2008); Ma et al. (2013)

2.1.2 Basic magnetic properties of materials

Magnetism is a fundamental property, which essentially arises from an atomic level and the behaviour and number of electrons (Dekkers 1997; Evans & Heller 2003). All materials respond to a magnetic field but the type and strength of the response is dissimilar for materials (Table 2). Dunlop and Özdemir (1997), for

example, provide a comprehensive physical background for magnetic types and properties.

Table 2. Five different types are distinguished for magnetic behaviour.

Magnetic behaviour	Response to magnetic field	Examples of materials
Diamagnetism	Weak, negative	Water, organic matter, quartz, calcite, feldspar
Paramagnetism	Weak, positive	Iron-bearing minerals and salts, e.g., biotite, siderite, pyrite, olivine
Ferromagnetism	Very strong, positive	Metallic iron
Ferrimagnetism	Strong, positive	Some iron oxides and sulphides, e.g., magnetite, maghemite, titanomagnetite, titanomaghemite, greigite, pyrrhotite
(Canted) Antiferromagnetism	(Moderate, positive) No net magnetisation	Some iron oxides, e.g., hematite, goethite

Diamagnetism is the fundamental form of magnetism which causes a magnetic moment to be in the opposite direction to the applied magnetic field. A weak and negative diamagnetism is lost once the magnetic field is removed. Other magnetism types easily override it (Thompson & Oldfield 1986; Dearing 1999; Evans & Heller 2003). In **paramagnetism**, magnetic moments are aligned parallel in the magnetic field. Paramagnetism is weakly positive but thermal disturbances cause it to be lost after the magnetic field is removed.

Ferromagnetism is the strongest magnetism type. The exchange coupling of adjacent atoms gives rise to a strong, parallel alignment of magnetic moments, i.e. spontaneous magnetisation, even without the external magnetic field (Thompson & Oldfield 1986; Dekkers 1997; Evans & Heller 2003). Magnetic moments remain aligned after the magnetic field is removed and the magnetisation is permanent or remanent (Dekkers 2007). Moreover, the magnetic moment is strong enough to withstand thermal disturbances. Ferromagnetism is seldom found in nature whereas ferrimagnetism and (canted) antiferromagnetism are the most common types (Dekkers 1997). **Ferrimagnetism** leads to a net magnetisation even though the magnetic moments are antiparallel with different magnitudes (Thompson & Oldfield 1986). The magnetic moments are sufficiently unequal for strong magnetisation to form (Evans & Heller 2003). Ferrimagnetism is the most important category of the main natural minerals, for example, magnetite and maghemite. In **antiferromagnetism**, the magnetic moments of adjacent atoms are identical in magnitude but aligned antiparallel resulting in a zero net magnetisation. If adjacent magnetic moments are slightly tilted due to impurities, lattice defects or electron spin canting, a weak net magnetisation exists (Thompson & Oldfield 1986; Dekkers 1997, 2007). This type is referred to as **canted antiferromagnetism**. Hematite and goethite are typical antiferromagnetic minerals.

Ferro-, ferri- and antiferromagnetic mineral particles are divided internally into special regions called **magnetic domains**, which form in order to minimize the overall energy of the grain. The domain is a uniformly magnetised region but the direction of the magnetisation changes from one domain to another (Halgedahl 2007). A strong magnetisation arises when domains align parallel under an external magnetic field. Domain behaviour is the reason for the distinct magnetic properties of ferromagnetic materials, such as spontaneous magnetisation, hysteresis, magnetic remanence, and coercivity. Four domain types have been distinguished: **multi-domain (MD)** particles are the largest with several domains; **pseudo-single-domain (PSD)** particles have two or three domains; **single-domain (SD)** particles have one domain; and **superparamagnetic (SP)** particles are ultrafine SD particles with unique properties (Thompson & Oldfield 1986; Evans & Heller 2003; Liu et al. 2012). SP particles do not have remanent magnetisation or experience hysteresis (Thompson & Oldfield 1986).

The number of domains is generally indicative of the grain size. However, the actual grain sizes depend on the mineral in question (Evans & Heller 2003). For example, magnetite grains above diameters of about 110 μm are termed MD, between 0.2–110 μm as PSD, below 0.2 μm as SD while ultrafine forms below 0.03 μm are SP (Dekkers 1997; Dearing 1999). The formation and subsequent environmental processes of the magnetic grains define the domain types, which are dominant in the samples. Burning and pedogenic processes produce SP and SD particles while fossil fuel combustion and industrial fly-ash formation produce MD, PSD, and SD particles (Dearing 1999; Petrovský et al. 2000). To summarise, magnetic domains are used for assessing the grain sizes of magnetic particles and their origin.

2.1.3 Magnetic parameters

Magnetic parameters are used to investigate the magnetic properties of various environmental samples. The applicability of magnetism in environmental research is based on the fundamental nature of magnetism and the abundant presence of iron (Fe) in nature. Iron is often combined with other elements, especially oxygen (O) and silicon (Si), to build many rock-forming minerals (Thompson & Oldfield 1986; Evans & Heller 2003). Thus, iron oxides (e.g., magnetite, hematite, maghemite), iron oxyhydroxides (e.g., goethite), and iron sulphides (e.g., pyrrhotite, pyrite, greigite) are omnipresent in the environment. They are the most important minerals having relevant magnetic properties for environmental research.

Since the magnetic properties of natural and anthropogenic particles are distinctive (Oldfield et al. 1985), investigations related to, for example, the origin, distribution, and level of pollutants are possible. Magnetic measurements are typically fast, non-destructive, and sensitive whereas the obtained data are dependent on the grain size and concentration (Thompson et al. 1980; Dekkers 2007). Due to the non-destructive nature of magnetic measurements in and below room temperature, the same samples are available for further analyses using, for instance, chemistry

or scanning electron microscopy (SEM). Magnetite is the most important magnetic mineral on Earth (Dunlop & Özdemir 1997; Petrovský et al. 2000) and it dominates the magnetic signal in minute quantities when present in samples. For example, magnetic instruments easily detect 1 ppm of magnetite (Dekkers 1997). Samples are, however, easily contaminated by magnetic material.

Magnetic methods provide information on the concentration, composition (i.e. mineralogy), and grain sizes (i.e. domain states) of iron-bearing magnetic mineral particles and heavy metals, which can be bound to them. However, other analysis methods, such as chemical ones, are required when precise data of the element composition and concentrations are necessary. Magnetic parameters can be used as proxy methods to screen large study areas or sample volumes without difficulty, and to recognise the most interesting and essential sites or samples worth additional analyses; such further analysis is usually more expensive and time-consuming. Some of the most used magnetic parameters and magnetic properties are listed in Table 3 and discussed below.

Low-field or initial magnetic susceptibility (volume-specific, κ, or mass-specific, χ) is one of the most used magnetic parameters and determinable in all materials (Verosub & Roberts 1995). It measures the magnetisation (M) obtained by a material in an applied low magnetic field (H). Volume-specific susceptibility (κ, kappa) is defined as magnetisation acquired per unit field (Evans & Heller 2003):

$$\kappa = M / H \quad (1)$$

κ is dimensionless since M and H are measured in A m^{-1} in SI units. Mass-specific susceptibility (χ, chi) is in m^3 kg^{-1} because it is derived by dividing κ with density (ρ):

$$\chi = \kappa / \rho \quad (2)$$

All five magnetisation types, if present, contribute to the susceptibility signal, but ferro- and ferrimagnetism typically dominate the signal since they contribute the most. The paramagnetic contribution is often significant in sediments and soils (Dekkers 1997). Dia- and paramagnetic materials loose the induced magnetisation once the external magnetic field is removed. Magnetic susceptibility is indicative of the magnetic PM concentration and indirectly also the heavy metal levels in a sample (e.g., Petrovský et al. 2000). Other analysis techniques, such as conventional chemical analyses, need to be used when data about the elemental composition and concentration are required. In magnetic air quality studies, magnetic susceptibility is typically used as a preliminary tool to quickly screen large areas or sample volumes, in order to detect the pollution levels and distribution, help identify hot-spots, and also to build magnetic pollution maps. Furthermore, SP particles can be identified by measuring magnetic susceptibility at low- and high-frequencies; the parameter is then called frequency-dependent susceptibility (e.g., κ_{FD}, $\kappa_{FD\%}$) (Mullins 1973; Oldfield 1991; Dearing 1999). This parameter is typically used in soil studies.

Ferro-, ferri- and antiferromagnetic materials retain a memory of an applied magnetic field and are left with a permanent magnetisation after the magnetic field is removed. This behaviour is referred to as **magnetic hysteresis** (Evans & Heller 2003). The hysteresis loop of a sample is obtained by gradually cycling the magnetic field in a positive, then a negative, and then back to a positive direction (e.g., +1 tesla (T), –1 T and +1 T), and measuring the magnetisation after each change in the field strength. A hysteresis loop is indicative of magnetic mineralogy and dominant grain size (Dekkers 1997). Mineral and grain size specific **hysteresis parameters** are distinguished from the loop: **saturation magnetisation (M_S)**, the maximum saturation, is obtained by the sample when the magnetic field is sufficiently strong; **saturation remanence (M_{RS})**, the maximum remanence, is left after the field is removed; and **coercive force (H_C)** is the reversed field needed for the overall magnetisation (M) to be zero. The fourth hysteresis parameter, **coercivity of remanence (H_{CR})**, is a stronger negative field required to leave the sample with zero remanence after the field is removed (Thompson & Oldfield 1986; Verosub & Roberts 1995; Evans & Heller 2003). The coercivity parameters H_C and H_{CR} are independent of magnetic mineral concentration and controlled by composition and grain size. Therefore, they are indicative of magnetic minerals. For example, magnetite yields lower coercivity values than hematite or goethite (Evans & Heller 2003; Peters & Dekkers 2003; Krása & Fabian 2007; Sagnotti 2007). When the dominant magnetic mineral is magnetite, hysteresis parameters can be plotted as the ratios of magnetisation (M_{RS}/M_S) and coercivity (H_{CR}/H_C) in the Day plot (Day et al. 1977; Dunlop 2002) to evaluate the grain sizes of magnetic minerals via the investigations of the domain states of the magnetic particles.

The hysteresis parameters represent the composite response of all particles in a sample and provide a bulk measure for their magnetic properties (Roberts et al. 2000). In the Day plot, samples with variable mixtures of magnetic particles (e.g., minerals, grain sizes) can be similar and do not necessarily show information of the individual magnetic components (Roberts et al. 2000; Muxworthy & Dunlop 2002). **First-order reversal curve (FORC)** diagrams are used for detailed characterisation of the hysteretic response of a sample to an applied magnetic field (Pike 2003). They are used to identify, for example, the contributions of different domains (i.e. SP, SD, PSD, MD) to the magnetisation of a sample (Roberts et al. 2000). A FORC diagram is generated from partial hysteresis loops, which are known as First-order reversal curves (Roberts et al. 2000; Pike 2003). For a FORC measurement, a sample is first saturated, then the magnetic field is decreased to a some field H_a and then the sample is saturated again (Roberts et al. 2000; Muxworthy & Dunlop 2002; Evans & Heller 2003). A FORC is the resulting magnetisation curve (Pike 2003). The measurement process is repeated for different values of H_a in order to obtain many FORCs (Roberts et al. 2000; Muxworthy & Dunlop 2002).

Table 3. Review of the most used magnetic parameters and their indication.

Magnetic parameter/ratio (abbreviation [unit])	**Indicative of**
Magnetic susceptibility, volume-specific (κ) or mass-specific (χ [m^3 kg^{-1}])	Concentration
Frequency-dependent susceptibility (κ_{FD}, $\kappa_{FD\%}$ [%], χ_{FD} [m^3 kg^{-1}], $\chi_{FD\%}$ [%])	Grain size, SP particles
Isothermal remanent magnetisation (IRM [A m^{-1} or Am^2 kg^{-1}])	Concentration, composition, grain size
Saturation isothermal remanent magnetisation (SIRM [Am^{-1} or Am^2 kg^{-1}])	Concentration, composition, grain size
Anhysteretic remanent magnetisation (ARM [A m^{-1} or Am^2 kg^{-1}])	Grain size, SD particles
ARM susceptibility (χ_{ARM} [m^3 kg^{-1}])	Grain size, SD particles
Saturation magnetisation (M_S [A m^{-1} or Am^2 kg^{-1}])	Concentration
Saturation remanence (M_{RS} [A m^{-1} or Am^2 kg^{-1}])	Concentration
Coercive force (H_C or B_C [mT])	Composition, grain size
Coercivity of remanence (H_{CR} or B_{CR} [mT])	Composition, grain size
Curie temperature (T_C [°C])	Composition
Neel temperature (T_N [°C])	Composition
Verwey transition temperature (T_V [°C])	Composition, magnetite
Morin transition temperature (T_M [°C])	Composition, haematite
ARM/SIRM	Grain size
SIRM/κ [A m^{-1}]	Composition, grain size
χ_{ARM}/χ	Grain size, SD particles
ARM/χ [A m^{-1}]	Grain size, SD particles
Magnetisation ratio (M_S/M_{RS})	Grain size
Coercivity ratio (H_C/H_{CR})	Grain size
S-ratio (S=–IRM_{-300mT}/SIRM)	Composition, ferrimagnetic vs. antiferromagnetic minerals

Remanent magnetisation or remanence is experienced by ferromagnetic materials (*sensu lato*) after the external magnetic field is removed. Magnetic remanence can be obtained in several ways, such as through the exposure of the sample to magnetic fields either in nature or the laboratory. For example, thermoremanent magnetisation (TRM) is acquired through cooling from a high temperature and detrital remanent magnetisation (DRM) through the parallel alignment of magnetic minerals with the Earth's magnetic field (Thompson & Oldfield 1986; Evans & Heller 2003). **Isothermal remanent magnetisation (IRM)** is one of the most used remanences in enviromagnetic air pollution studies. IRM is acquired by the application and subsequent removal of an applied magnetic field, usually in the laboratory at room temperature, but it can also originate naturally, for example, by a lightning strike (Evans & Heller 2003; Jackson 2007). The IRM increases along with the magnetic field until it reaches the saturation IRM (SIRM),

which is the maximum remanence (Verosub & Roberts 1995). The remanence acquisition and the saturation reach are mineral specific: for example, ferrimagnetic minerals acquire saturation in a magnetic field up to +1 T, whereas the saturation of antiferromagnetic materials requires a stronger field (Verosub & Roberts 1995). The SIRM also reflects the concentration of magnetic minerals, especially magnetite, when the grain sizes and mineralogy remain rather constant (Liu et al. 2012). **Anhysteretic remanent magnetisation (ARM)** is acquired by subjecting a sample to a slowly decreasing alternating magnetic field in the presence of a small direct current (DC) field (Verosub & Roberts 1995; Maher et al. 2010). The ARM is a concentration-dependent parameter (Dunlop & Özdemir 1997). It is also diagnostic of SD magnetic particles, particularly magnetite and maghemite, because they acquire more magnetic remanence than MD particles (Dekkers 1997; Liu et al. 2012). The ARM is proportional to the DC constant field and gives a parameter called the susceptibility of ARM (χ_{ARM}) (Verosub & Roberts 1995; Dekkers 1997; Liu et al. 2012). It is sensitive to SD and PSD grains (Verosub & Roberts 1995).

Magnetic susceptibility and magnetisation can be measured either above or below room temperature. The thermomagnetic behaviour of these parameters is essentially mineral specific (Verosub & Roberts 1995). Therefore, an assemblage of different magnetic minerals can be separated through **temperature-dependent properties** and the acquisition curve of thermomagnetic analyses. In **high-temperature measurements**, ferromagnetic materials loose spontaneous magnetisation, and minerals become paramagnetic at mineral-specific temperatures (Liu et al. 2012). This is shown as a sudden decrease in susceptibility or magnetisation. Temperature is referred to as the Curie temperature (T_C) for ferrimagnets and the Néel temperature (T_N) for canted antiferromagnets (Verosub & Roberts 1995; Liu et al. 2012). For example, T_C for magnetite is about +580 °C and T_N for pure hematite is +675 °C (Dunlop & Özdemir 1997). Hematite is often impure in natural environments, which reduces the T_N. Moreover, many minerals have T_C values in the +300–400 °C temperature range, which complicates their identification. Therefore, magnetic mineralogy should also be confirmed using other analyses. Some disadvantages of high-temperature measurements are the destruction of the sample and the possibility of mineralogical transformations due to chemical alterations (Henry 2007; Liu et al. 2012). If the heating and cooling curves are similar, alteration has not occurred. In **low-temperature measurements**, sudden changes in magnetic properties at specific transition temperatures result from crystallographic redistribution. The transition temperature for magnetite is the Verwey transition (T_V) at –150 °C and for hematite it is the Morin transition (T_M) at about –15 °C (Dekkers 1997; Liu et al. 2012). Partial or full oxidation of the sample in the presence of oxygen changes the magnetic mineral phases and thus alters the ordering temperatures.

Combinations of different magnetic parameters are used in **bivariate ratios** to investigate further mineral composition and especially grain sizes. Initial

susceptibility and/or remanent magnetisations are the most used parameters since they are quickly measured (Dekkers 2007). For example, the IRM remaining after acquiring the SIRM and exposure to a –300 mT field is divided by SIRM to form S-ratio ($-IRM_{-300mT}$/SIRM). The S-ratio indicates the main magnetic carrier in a sample by discriminating between ferrimagnetic and canted antiferromagnetic minerals (Thompson & Oldfield 1986; Verosub & Roberts 1995; Evans & Heller 2003). Ferrimagnetic minerals, like magnetite, have an S-ratio close to 1.0 while the increasing concentration of canted antiferromagnetic minerals, such as hematite or goethite, leads to lower values (Verosub & Roberts 1995; Dekkers 1997). As for the grain size ratios, a plot of χ_{ARM}/χ can be used for assessing the amount of fine versus coarse magnetic grains when the dominant mineral is magnetite (Verosub & Roberts 1995; Peters & Dekkers 2003). The ratios ARM/SIRM and SIRM/κ are also indicative of magnetite grain sizes: small SP-SD particles yield higher ratios (Evans & Heller 2003).

2.2 Air pollution

2.2.1 Defining air pollution

Air pollution is defined by the European Commission as "any substance present in ambient air and likely to have harmful effects on human health and/or the environment as a whole" (EC 2008). Ambient air refers here to the outdoor air in the troposphere, i.e. the lowest layer of the atmosphere. Primary air pollutants are emitted into the atmosphere from natural and anthropogenic sources whereas secondary air pollutants are formed within the atmosphere from chemical and physical reactions of primary pollutants (Vallius 2005; WHO 2006b). As for the physical state, air pollutants are either in a gaseous form or a particle form. The latter is further divided into a solid or liquid phase (WHO 2006b).

The main primary air pollutants include CO, NO_x, SO_2, volatile organic compounds (VOCs) and hydrocarbons (HC), and PM. Secondary air pollutants cover, for example, ozone (O_3), NO_x, sulphuric acid (H_2SO_4), and secondary PM. Secondary particles form from precursor gases via gas-to-particle conversion (Vallius 2005). Air pollutants are grouped into the following categories: gaseous pollutants (e.g., CO, SO_2, NO_x, VOCs), persistent organic compounds (e.g., dioxins), heavy metals, and PM (Kampa & Castanas 2008).

2.2.2 Sources of air pollution

Air pollutants, which have manifold natural and anthropogenic sources, move between the spheres (Fig. 1). Typical natural sources include volcanic activity, lithospheric erosion, dust storms, wildfires, and sea spray, while industrial operations, traffic, heating, and burning of fossil fuel are examples of anthropogenic sources. On the global scale, natural sources contribute about 98% of PM emissions with on average almost 12,000 teragram (Tg) $year^{-1}$ while anthropogenic sources contribute about 2% of aerosols (Viana et al. 2014). The situation is reversed on the

local scale where anthropogenic sources contribute 80% and natural sources 20% of PM emissions. Air pollution impacts all geographical and temporal scales (Fenger 1999). Because pollutants can be transported both for short and long distances, their impact ranges from local problems, such as health issues or material damage, to regional (e.g., acidification) and global phenomena (e.g., climate change).

Air pollution sources can be categorised into area, line, and point types (Kibble & Harrison 2005; WHO 2006b). Area sources consist of emissions from many smaller stationary sources, for example, heating systems in homes producing PM (Kibble & Harrison 2005). These smaller sources are aggregated over an area and treated as one source within that area (WHO 2006b).

Line sources are the transportation routes of both road (i.e. cars) and off-road vehicles (e.g., trains, ships, aircrafts). Traffic-related air pollution typically has an impact on local and urban scales (Vallero 2008). The emissions of all transportation modes can be grouped into exhaust and non-exhaust. Exhaust emissions (e.g., CO, NO_x, VOC, and PM) originate from the combustion of petrol or diesel fuel (WHO 2006b). Non-exhaust emissions include PM derived from mechanical or chemical processes, such as the abrasion of the motor and the brakes of a vehicle, road pavement and tire wear, as well as the corrosion of vehicles. Leakages are also possible. Busy intersections and roads/highways, traffic lights with a stop and go -movement, and street canyons are typical places for high pollution concentrations. PM deposited in the vicinity or on the road can be resuspended into the air through wind, vehicle-induced turbulence or shear forces acting between the tires and the road surface. In spring, road dust is a significant source of PM in the sub-arctic regions of the world, such as Nordic countries, North America, and Japan (Kupiainen 2007). Snowy and icy winter conditions incur the use of traction sand, ice melting salt, and special winter tires (studded or friction tires, snow chains). These amplify the wear on the pavement and of the traction sand itself making the road dust a significant source of mineral PM and dominant in urban coarse PM (PM <10 μm) in spring. After the snow has melted and surfaces have dried out, road dust is released and resuspended into the environment and air by the wind, traffic-induced turbulence, and street cleaning activities. An intensive road dust episode typically lasts about 4–8 weeks.

Point sources, such as power stations, coke-burning, metal and chemical factories, paper mills, and foundries, represent stationary locations. They occur typically on a local scale (Vallero 2008). Pollutants are released through smokestacks at a height which is usually sufficient to dilute the concentrations before pollution reaches the ground-level. Ground-level sources, like waste treatment ponds, have the highest pollution concentrations near the source. In both cases, the dispersion of the pollutant plume by wind leads to decreasing pollution concentrations with an increasing distance from the source (Matthias et al. 2006; Vallero 2008). This is known as a concentrations gradient (Vallero 2008). Topographical and meteorological conditions, for example, valleys, weak wind-generated turbulence

or high air pressure, can prevent the dispersion and trap pollutants near the source and cause poor air quality at ground-level (Kibble & Harrison 2005; Matthias et al. 2006). Fugitive emissions, which are released, for instance, from resuspended dust from stockpiles or waste piles, can be significant at a local level (Kibble & Harrison 2005). Typical emissions from point sources are NO_x, SO_2, VOC, dusts, heavy metals, and PM.

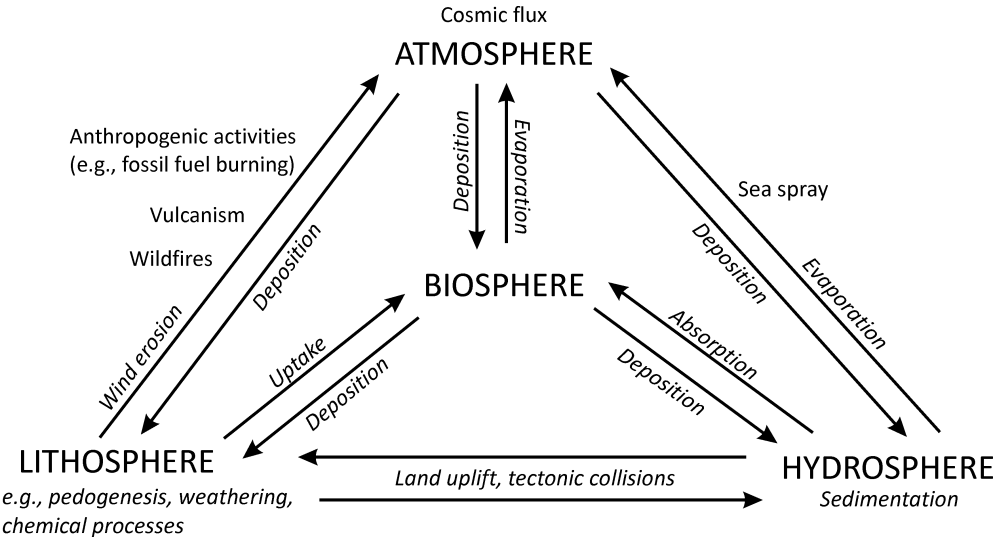

Fig. 1. Simplified presentation of the sources, movements (arrows), and processes (*italics*) of air pollutants between the Earth's spheres (figure adapted by author from Thompson et al. 1980).

2.2.3 Particle matter

In ambient air, PM is a mixture of suspended solid and liquid particles, which form the atmospheric aerosol (Nel 2005; Vallius 2005; Heinrich & Slama 2007). The aerosol contains particles with various chemical and physical properties, number, sizes, sources, etc. (Heinrich & Slama 2007). Coarse PM is typically primary in nature, forming at a point or area source (Grantz et al. 2003). Fine PM, in contrast, is secondary in nature. Fine PM can form from anthropogenic and natural gases through coagulation (smaller particles combine to form a larger particle), condensation (gas or vapor molecules condensate on the surface of a particle), nucleation, and chemical reactions (Grantz et al. 2003; Heinrich & Slama 2007). Both primary and secondary particles can grow and undergo transformations after they are emitted into the atmosphere.

Size: Size is the most important property of PM (Fig. 2). It is typically defined by the aerodynamic diameter, which is the size of a unit density sphere of the same settling velocity as the particle in question (Vallius 2005; WHO 2006a). Particles of the same aerodynamic diameter can vary substantially as for size, shape, and density. PM is not necessarily spherical or solid; for example, industrial

fly ashes can contain hollow spheres and aggregates of smaller particles (Sehmel 1980). The total suspended particles (TSP) include particles of all sizes (WHO 2006b). TSPs are trimodal and, thus, can be subdivided into coarse (PM <10 µm, PM_{10}), fine (PM <2.5 µm, $PM_{2.5}$), and ultrafine (PM <0.1 µm, $PM_{0.1}$) particles (e.g., Harrison & Yin 2000; Vallius 2005; Pope & Dockery 2006; WHO 2006a). In Europe, PM_{10} is measured to a greater extent than $PM_{2.5}$ and $PM_{0.1}$ (WHO 2006a). PM_{10} has also attracted renewed attention because non-exhaust emissions of traffic are becoming increasingly important because the exhaust emissions have been reduced (Hoek et al. 2013). Ultrafine PM, which is unregulated, is potentially the most dangerous since it has the largest surface area and the highest content of potentially toxic hydrocarbons (Nel 2005). The aerodynamic properties of PM control their transport and removal from the air and their deposition within the respiratory system (WHO 2006a).

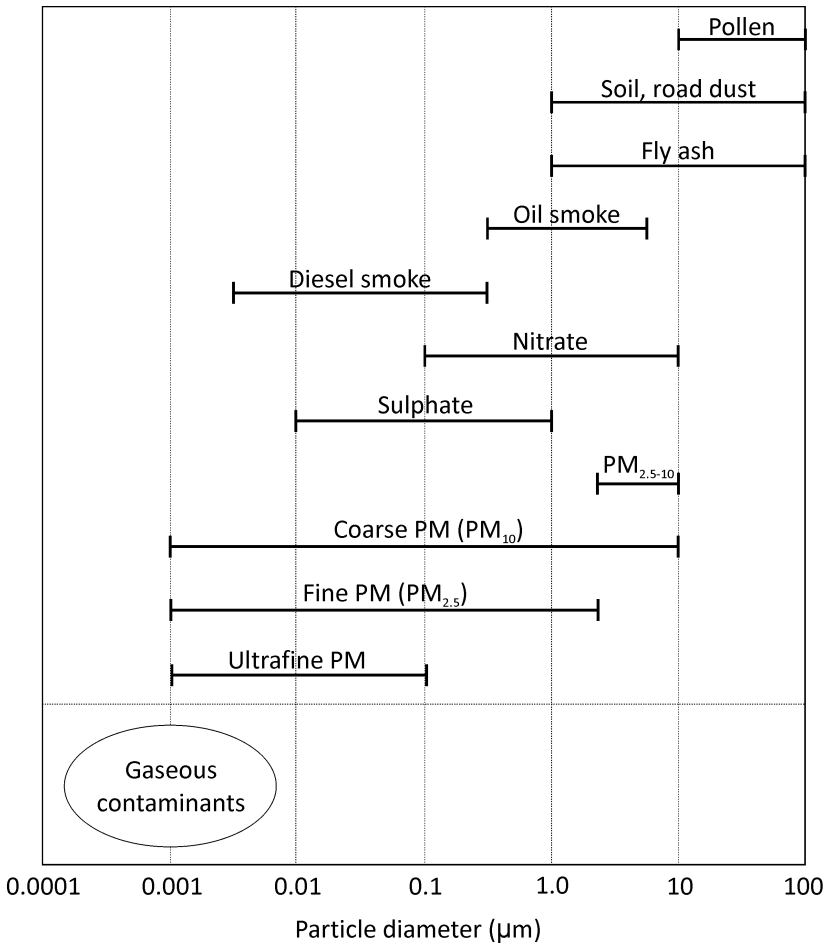

Fig. 2. Size range of atmospheric particles (PM) and some major components (figure adapted by author from WHO 2006b).

Composition: PM is composed of several organic and inorganic components. The typical major components are sulphate, nitrate, ammonium, chloride (especially from sea spray and de-icing salt in winter), elemental carbon and organic carbon, crustal materials, including soil dusts and wind-blown crustal materials, and biological materials, such as bacteria, pollens, spores, and plant pieces (Harrison & Yin 2000). PM also contains magnetic minerals, such as iron oxides. Coarse PM is mostly derived from soil, dust, and other crustal materials, sea salts, and biological materials (Nel 2005; Pope & Dockery 2006). Fine PM, instead, originates from combustion of fossil fuel. The proportion of components varies considerably based on the sampling location; for example, crustal materials are more common in dryer climates (Harrison & Yin 2000). Pollutants, such as metals, organic compounds, and reactive gases, can be absorbed to and transferred by PM (Kampa & Castanas 2008). Metals, such as cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), Fe, mercury (Hg), nickel (Ni), vanadium (V), and zinc (Zn) are important for particle toxicity and can be toxic at very low concentrations (Schwarze et al. 2006).

Transport and removal: Wind and turbulence transport pollutants after they are emitted into the atmosphere. Pollutants are removed from the atmosphere through deposition on surfaces (Fig. 3). Dry deposition of PM occurs through gravitational settling and it is almost continuous. Dry deposition is most effective for coarse PM (Grantz et al. 2003). Particles with a diameter greater than 10 µm are quickly removed while smaller particles can remain airborne for days or months (Grantz et al. 2003; Matthias et al. 2006). Therefore, fine PM may be transported long distances, 1000–10,000 km or more from the source whereas coarse PM usually travel less than 10 km (WHO 2006a). Ultrafine PM has a very short life ranging from minutes to hours and they grow rapidly to larger aggregates through coagulation and condensation (Pope & Dockery 2006). Wet deposition is most effective for small particles and gases: falling raindrops increase in size and capture more pollutants on the way to the ground. Deposited particles below 100 µm can be resuspended into the air due to, for example, wind, vehicle-induced turbulence or tire stress (Sehmel 1973; Nicholson 1988). Large particles with a diameter between 500–1000 µm either roll along the ground (i.e. surface creep) or move by small jumps (i.e. saltate) (Kupiainen 2007). Descending particle can also push another particle into movement (i.e. reptation). Urban air quality is significantly impacted by atmospheric PM.

Health effects: Humans are exposed to PM mainly via inhalation and ingestion (Kampa & Castanas 2008). Health effects are observed at all exposure levels, which indicates that some individuals are more prone and at risk even at low concentrations (Nel 2005; WHO 2006a). People with pre-existing chronic lung and heart diseases, children, elderly, socially disadvantaged and poorly educated people form the more vulnerable groups (WHO 2006a). Children's lungs and immune systems are not fully developed and they spend more time outdoors than adults (Schwartz 2004; Gasana et al. 2012).

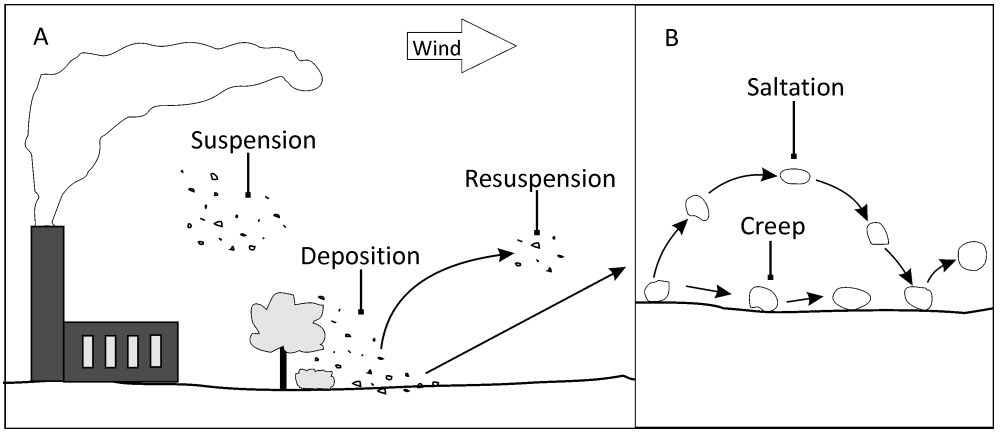

Fig. 3. Suspended particles are eventually deposited on surfaces from where they can be resuspended into the air (A). On the ground, large particles move via surface creep, saltation, and reptation (not shown) (B).

PM_{10} includes $PM_{2.5}$ and small inhalable particles, which can penetrate into the thoracic region, whereas $PM_{2.5}$ is capable of deposition in the smaller conducting airways and alveoli (WHO 2006b). Thus, smaller particles are more harmful since they enter the deeper parts of lungs and enter the body while coarser particles typically reach the upper airways (Pope & Dockery 2006; Schwarze et al. 2006; Kampa & Castanas 2008). Furthermore, smaller particles enter more readily into indoor environments from where the most exposure is received (Pope & Dockery 2006; WHO 2006b). Respiratory/pulmonary reactions are the first ones to appear upon PM exposure. The typical effects of short-term exposure include eye, nose, and throat irritation, inflammation, asthma, airway obstruction, and decreased gas exchange (Nel 2005; WHO 2006b). Long-term exposure (i.e. a year or more) can contribute to lung cancer and cardiovascular risk factors, which are associated, for example, with changes in blood coagulation or blood pressure, heart rhythm variabilities, and heart attacks (Nel 2005; WHO 2006a; Kampa & Castanas 2008; Hoek et al. 2013). Heavy metals may affect the nervous system (e.g., memory or sleep disturbances) or cause kidney damage. Moreover, heavy metal exposure during pregnancy can increase the risk of miscarriage or birth defects and reduce foetal growth (Kampa & Castanas 2008). Respiratory and cardiovascular diseases can lead to chronic morbidity and untimely mortality. The long-term exposure of local residents to metal-rich PM is associated with increased mortality from circulatory diseases near the copper-nickel (Cu-Ni) smelter in Harjavalta, Finland (Pasanen et al. 2012). The WHO estimates that 3.7 million premature deaths occurred globally due to ambient air pollution in 2012 (WHO 2015) and that, on average, it reduces life expectancy by 8.6 months in EU countries (WHO 2006a). Furthermore, the annual economic costs of air pollution in Europe are US$ 1.431 trillion for premature deaths and US$ 1.575 trillion for overall health impacts and mortality (WHO 2015).

2.2.4 Magnetic PM

Primary magnetic minerals are present in the parent material, i.e. igneous, sedimentary, and metamorphic rocks, from which secondary magnetic minerals are formed. Magnetic PM is deposited, weathered, and transported as well as subjected to (bio)chemical and thermal transformations (Thompson & Oldfield 1986; Oldfield 1991; Verosub & Roberts 1995; Evans & Heller 2003). Thus, they are present in the environment with different assemblages based on the source and subjective history following their formation (Maher 2007). Magnetic minerals move between the different spheres of Earth, in a similar manner to air pollutants (Fig. 1).

Magnetic minerals and the majority of air pollutants, besides the gaseous phases, are transported particle-bound in the atmosphere (Petrovský & Ellwood 1999; Urbat et al. 2004). Natural and anthropogenic sources produce PM with distinctive magnetic properties. The dissimilarities are beneficial when distinguishing the origin of the particles. Anthropogenic PM, especially those present in the fly-ashes of industrial smelters and coal-burning power plants, are the richest in heavy metals (Petrovský & Ellwood 1999). Heavy metals can be incorporated into crystal lattices or be absorbed onto the surfaces of magnetic minerals, especially iron oxides (Georgeaud et al. 1997; Petrovský et al. 2000; Kukier et al. 2003; Sharma & Tripathi 2008). For this reason, magnetic techniques are highly applicable for pollution studies.

2.2.5 Air pollution regulations and monitoring techniques

Ambient air pollution is historically an urban phenomenon. Cities, which are the clusters of humans, materials, and activities, experience the largest number of possible targets and the highest pollution levels (Fenger 1999). Before the Second World War, attitudes towards pollution were mixed and it could be seen as a depiction of wealth and growth. Since 1950, the world population has more than doubled, the global energy consumption has increased by nearly a factor of five, and both the industrial production and the global number of vehicles by a factor of ten (Fenger 1999, 2009). The start of modern air pollution control can be traced to the London smog in 1952 after which the legislation, such as the Clean Air Act in England in 1956, was developed and the number of monitoring stations was increased. Governments and international organisations started to set ambient air quality standards and legislation for emission reductions in the 1990s, when the health effects of PM at concentrations believed safe were proved (Harrison & Yin 2000).

Today, urban air quality is regulated by air quality standards. The WHO published the first air quality guidelines in 1987. The guidelines are based on the scientific evidence on air pollution and its health consequences (WHO 2006b). Furthermore, the guidelines provide the basis for air quality limit values. The second and the most recent update of the guidelines, which was published in 2005, applies worldwide (WHO 2006b). For PM_{10} and $PM_{2.5}$, the annual average guideline values are 20 $\mu g/m^3$

and 10 µg/m³ while the one day average guideline values are 50 µg/m³ and 25 µg/m³, respectively (WHO 2006a). Guidelines for ultrafine PM are not yet provided since the epidemiological evidence is insufficient. Meeting the one day average guideline values should protect against pollution peaks that may lead to excess morbidity or mortality. Update reveals that over 80% of people living in urban areas, which monitor air pollutants, are exposed to air quality levels exceeding the limits (WHO 2016). Overall, the WHO sets tighter guidelines for air pollutants than the EC Directive.

The EU has specified the limit values of individual air pollutants by means of the EC Directive 2008/50/EC, which the member states ratify through their national legislations. In Finland, the air quality is regulated by the Environmental Protection Act (86/2000), the Government Degree on Air Quality (38/2011, in Finnish, Finlex), the Government Degree on Arsenic, Cadmium, Mercury, Nickel, and Polycyclic Aromatic Hydrocarbons in Air (164/2007, in Finnish, Finlex), and the Government Degree on Ozone in Ambient Air (783/2003, in Finnish, Finlex) (Ministry of the Environment 2015). Air quality limit values (Table 4) are the highest levels, which are not to be exceeded once attained. The public and appropriate organisations have to be informed of the ambient air quality. This requires continuous air quality measurements.

Air quality can be investigated by several techniques. The most conventional methods are the direct measurements of pollutants in the air (fixed or movable monitoring stations; mobile car laboratories), the construction of air pollution dispersion models, and the use of bioindicators or biomonitors. Direct and continuous measurements using fixed air quality monitoring stations have a high temporal resolution but poor spatial representativeness with hidden local variations and pollution sources (Hansard et al. 2011). The monitoring locations are point-like and limited in number, and use expensive equipment which relies on external power supplies and are prone to malfunctions and vandalism (Mitchell & Maher 2009). Element levels are rarely monitored automatically or even sampled routinely. Monitoring stations only partially outline the air pollution situation in any area; thus, there is a need to understand more thoroughly the geographic variation of pollutants and to obtain information about pollution levels at unmonitored sites (Beelen et al. 2009). Information from the monitoring stations is extrapolated to wider areas in order to model the spatial distribution of pollutants (Violante et al. 2006). The construction of dispersion models requires powerful computing facilities and detailed input data, such as source distribution, emission rates, meteorological conditions, and surface terrain (Beelen et al. 2009). Pollution mapping can also be done by other methods, for example, kriging, regression, or stochastic techniques. Nevertheless, modelling requires both resources (facilities, information, time, funds) and knowledge. The spatial resolution is still weak and does not capture local scale variation (Beelen et al. 2009). Bioindication/biomonitoring applies organisms or their parts for qualitative/quantitative information about the pollution levels, especially heavy metals, and environmental changes. Because the bioindication/ biomonitoring of air quality is easy and cheap, large sample numbers and spatially

extensive areas are easily covered without the need for external power supplies. The spatial representativeness is high as long as suitable species are available in the investigated area. Some species react to specific pollutants and some, especially cryptogams, collect many pollutants at the same time. However, bioindicators/ biomonitors can be incapable of indicating the timing, duration, magnitude, and frequency of the pollution exposure. Furthermore, environmental conditions or species' specific properties may cause local and natural variability in accumulated pollutant levels (Wolterbeek & Bode 1995). This, in turn, causes problems in the selection of sampling sites and species, particularly in large scale surveys.

Table 4. Air quality limit values for PM and specific elements in Finland set by the EC Directive 2008/50/EC and the Government Degrees 38/2011 and 164/2007. The date by which the limit value was to be met is given in the brackets.

	Calculation time of the average value	**Limit value**	**Allowed exceedances per calendar year**
2008/50/EC (1.1.2005)			
PM_{10}	One day	50 µm/m³	35
	Calendar year	40 µm/m³	-
Pb	Calendar year	0.5 µm/m³	-
38/2011 (1.1.2015)			
$PM_{2.5}$	Calendar year	25 µm/m³	-
164/2007 (1.1.2013)			
As	Calendar year	6 ng/m³	-
Cd	Calendar year	5 ng/m³	-
Ni	Calendar year	20 ng/m³	-

2.3 Magnetic biomonitoring of air quality using mosses and lichens

2.3.1 Review on moss biomonitoring

The terms biomonitoring and bioindication are often used interchangeably while in reality they have different meanings. **Biomonitoring** is the quantitative measurement of elements and compounds accumulated on organisms or their parts. **Bioindication**, in contrast, refers to the use of organisms or their parts to reflect the qualitative changes in species richness, distribution or condition caused by environmental pollutants or changes (Markert et al. 2003). Various animal and plant species, such as *Tillandsia* sp., are used in biomonitoring/bioindication but mosses and lichens are most often employed. Since this thesis focuses on active moss biomonitoring, lichens are covered to a lesser extent in this chapter.

Biomonitoring, and bioindication as well, can be passive or active. Native *in situ* species occurring naturally in the environment are utilised in **passive** biomonitoring while species from remote, clean areas are transplanted to target areas in **active** biomonitoring. The active approach is advantageous when the temporal and/ or spatial resolution of the pollution data needs enhancement or when the investigated area lacks *in situ* species. Moreover, *in situ* species are able to adapt to

ambient environmental conditions and pollution levels by developing detoxification mechanisms or decreasing retention capacity (e.g., Fernández & Carballeira 2000). This can distort the deposition and pollution level data (Fernández & Carballeira 2000; Boquete et al. 2013). Overall, lichens are the species most used in passive studies while mosses are more usual in active biomonitoring.

Moss biomonitoring was introduced in the investigation of traffic-originated lead (Pb) in Sweden in the 1960s (Rühling & Tyler 1968). It first became common in Scandinavia in the 1970s, and then in most other European countries in the 1980s and 1990s (Markert et al. 2003; Poikolainen 2004). In contrast, the first reports of the decrease of lichen diversity from the city centres in Europe were made in the 19th century (Nash 2008). Moss biomonitoring studies typically focus on detecting heavy metals, nitrogen (N), sulphur (S), radionuclides, persistent organic pollutants (POPs), and recently magnetic mineral particles (e.g., Berg et al. 1995; Äyräs et al. 1997; Gerdol et al. 2002; Aničić et al. 2009; Poikolainen et al. 2009; Jordanova et al. 2010; Shotyk 2015).

According to Vuković et al. (2016), moss is the most efficient biomonitor for air pollution entrapment. Mosses have many superior features, which make them an excellent choice for air quality investigations (Table 5). Most bryophytes lack a developed cuticle, specialised vascular tissues, and true roots. Moisture and nutrients are absorbed over their entire external surface from wet and dry depositions. The uptake from the atmosphere is enhanced while the influence from the substrate is minimal (Szczepaniak & Biziuk 2003). However, it seems that the element uptake efficiency is affected by the intensity of the rain: slowly passing precipitation enhances the uptake while the strong flow of fast occurring precipitation (e.g., rain shower) minimizes the uptake and causes leaching (Szczepaniak & Biziuk 2003). Nevertheless, a large number of air pollutants are accumulated simultaneously in mosses without selection (Ares et al. 2012). Pollutants are deposited in aqueous solutions, in gaseous forms or attached to particles (Poikolainen 2004).

Table 5. Review of the valuable features of mosses (and lichens as well) for air quality investigations.

Feature
Nonexclusive pollutant accumulation
Long (and determinable) lifespan
Stabile morphology
Geographically widespread
Lack of cuticle, roots, and vascular tissues (in ectohydric mosses)
Direct uptake of moisture, nutrients, and pollutants from wet and dry deposition
Minimal influence from the substrate
Sensitive to air pollution and environmental changes with varying tolerance of species

The morphology of moss shoots with numerous branches and tiny leaf-like structures provide a large surface area to weight ratio for ion-exchange processes (Martin & Coughtrey 1982; Poikolainen 2004). This is especially the case in *Sphagnum* spp. The cation exchange capacity of *Sphagnum* is estimated to be 0.9–1.5 milliequivalent (meq) g^{-1} dry weight (Puustjärvi 1955). Berg et al. (1995) reported variation in the uptake efficiency of species for individual elements while Zechmeister et al. (2003) found natural variation in the chemical composition between individual species, between populations and individuals of the same species, and between the separate parts of the individuals. Garty et al. (1993) point out that a biomonitor may also reach a saturation point for the element uptake. Secondary sources, such as windblown soil dust, leaching/drip from dead/living vegetation or canopy, and natural cycling processes (e.g., sea salt transportation), can also contribute to the element concentrations of mosses (Berg et al. 1995; Berg & Steinnes 1997; Čeburnis et al. 1999).

Moss morphology does not change with the seasons (Szczepaniak & Biziuk 2003), and sampling is effortless and cheap. Thus, spatially extensive areas are covered with ease given that suitable species are present. The slow growth rate and long lifespan (usually of 2–5 years, but up to 10 years) mean that *in situ* mosses reflect the long-term accumulation of air pollution and changes in the environment. Some species, such as *Sphagnum* spp. and *Hylocomium splendens*, grow annually a new segment, which can be used to determine the plant age and exposure time and to enhance the temporal resolution. Bryophytes are sensitive to air pollution but their tolerance varies between species. Heavily polluted environments may have a partial or total shortage of *in situ* species. The species that remain in the first case are either the most resistant ones or are in a poor condition, whereas the second case is known as a moss desert.

2.3.2 The active moss bag technique

In active biomonitoring, moss is most often transplanted as moss bags than as moss mats. The moss bag technique was introduced by Goodman and Roberts (1971), and modified a few years later by Little and Martin (1974). After 45 years of use, the technique still lacks internationally standardised protocols and, consequently, has met with several modifications regarding, for example, the moss species used, pre-treatments, the bag preparation, and the exposure (extensively reviewed by Ares et al. 2012). Thus, the results of different studies are not directly comparable. The application of the technique is mainly limited to Europe (Ares et al. 2014).

Recommendations for protocol establishment have recently emerged (e.g., Ares et al. 2012, 2014). In Finland, the moss bag technique is nationally standardised (SFS 5794, Finnish Standards Association 1994). The greatest deviation is in the devitalisation process of the moss material: acid washing is defined in the Finnish standard, while treatment with cellular extractants (EDTA and dimercapol) and oven drying (>100 °C for 24 h) is outlined in the recommended protocol. However,

otherwise the Finnish standard fulfils the recommendations: the spherical bags are made either from *Sphagnum papillosum* or *S. girgensohnii* and the exposure period is defined as 8 weeks (see, e.g., Ares et al. 2012, 2014).

Overall, the devitalised moss material has less variable results with no influence from moss metabolism (Ares et al. 2012; Giordano et al. 2009). Acid washing increases the bioconcentration capacity of moss by releasing metals bound to cation exchange sites on the cell walls (Ares et al. 2012). Oven drying is not capable of this without the help of chelating agents. Adamo et al. (2007) compared four pre-treatments of *Hypnum cupressiforme* -moss bags: water washing, acid washing, oven drying, and NH_4-oxalate extraction (for oven-dried and acid-washed materials). Live and dead moss showed a similar performance and, moreover, the devitalisation by acid or oven did not affect the accumulation efficiency. The latter is related to the unchanged surface texture since surface interception of PM has a major role in accumulation in moss bags (Ares et al. 2012). However, oven drying over acid washing is recommended since it is eco-friendly and does not fragile the moss material (Adamo et al. 2007; Giordano et al. 2009).

The moss bag technique provides several advantages for air pollution monitoring. Spatially representative monitoring networks are easy to establish in different environments (i.e. industrial or urban areas; point, line or area sources), the exposure period is pre-determinable, the collection time is precisely known, the pre-exposure concentrations of elements are determinable, and, thus, element accumulation is accurately quantified (e.g., Szczepaniak & Biziuk 2003; Aničić et al. 2009; Ares et al. 2012). The collection efficiency is greater for most elements (Adamo et al. 2003) and lithogenic impact can be disregarded. The moss bags do not require external power supplies or expensive sampling equipment and they are rarely subjected to vandalism (Mitchell & Maher 2009). The major limitation of the technique is that the collection efficiency for different contaminants is unknown (Adamo et al. 2003). The exposure time is also crucial (Bargagli 1998): moss bags tend to dry out and hence their efficiency in retaining metals varies depending on the environmental conditions (Al-Radady et al. 1993; Szczepaniak & Biziuk 2003; Aničić et al. 2009a). Furthermore, exchange sites on the moss membrane may become saturated, and a displacement or exchange of elements may also occur (Aničić et al. 2009). The final concentrations represent the balance between inputs and loss of elements due to various factors, such as differences in the atmospheric levels of contaminants, weather conditions affecting the pollutant availability, and the impact and interception of airborne PM (Aničić et al. 2009; Ares et al. 2014).

Moss bags are more common than lichen bags. Comparisons between moss bags and lichens bags have, in general, showed moss bags (*S. capillifolium* or *H. cupressiforme*) to be more efficient element accumulators than lichen bags (*Pseudevernia furfuracea*) (e.g., Adamo et al. 2003, 2007, 2008; Giordano et al. 2013). Adamo et al. (2007) tracked the higher element loads of moss bags to be the result of their higher specific surface areas. Wet conditions improved the accumulation

capacity of lichen, but did not cause a washing effect of elements by rainfall in either moss bags or lichen bags (Adamo et al. 2003).

2.3.3 Biomagnetic research with a focus on mosses and lichens

While mosses and lichens are the most used species in traditional bioindication/ biomonitoring, tree leaves are the most typical samples used in magnetic biomonitoring (Table 1). However, an increase in the application of mosses and lichens in magnetic air quality assessments can be observed in recent years. Magnetic research applications have particularly involved the use of moss bags.

The first magnetic study with *in situ* mosses (two species: *H. cupressiforme* and *Pseudoscleropodium purum*) and lichens (two species: *Hypogymnia tubulosa* and *P. furfuracea*) was made in Bulgaria by Jordanova et al. (2010). Broad-leaf trees and conifer trees were sampled at the same time. The study indicated that *in situ* mosses and lichens are effective in magnetic biomonitoring of air pollution due to their high accumulation capacities. These species also gave the strongest contrast in magnetic signals between polluted and clean areas when compared to the other species.

Only a minority of the magnetic air quality assessments published so far have employed *in situ* species mainly in urban environments. One study has sampled the moss *H. splendens* along a route crossing the city of Oslo, Norway (Fabian et al. 2011) while the remaining have sampled different epiphytic lichen species in urban areas (paper I; Chaparro et al. 2013; Marié et al. 2016; Paoli et al. 2016). For example, in Tandil city, Argentina, the samples of lichen *Parmotrema pilosum* showed the greatest magnetic enhancement near the metallurgical areas and roads with high traffic flows (Marié et al. 2016). Furthermore, the coarsest magnetic particles were found at the industrial sites while areas with decreasing traffic intensity, such as urban parks, had finer grain sizes. The magnetic mapping, which was based on both the mass-specific susceptibility χ and χ_{ARM}/χ -ratio, was indicative of areas with high pollution loads.

The active moss bag technique (species *S. papillosum*) was applied for the first time in magnetic biomonitoring of industrial and urban environments in Finland (paper I). The technique proved efficient for magnetic studies of temporal and spatial distribution of anthropogenic air-borne PM. In Belgrade, Serbia, Vuković et al. (2015a) monitored urban air quality in different microenvironments (i.e. street canyons, parking garages, and a city tunnel) by *S. girgensohnii* -moss bags. The exposure periods of 5 and 10 weeks were also investigated in the city tunnel. The order of the microenvironments, from the highest to the lowest SIRM values, was: the city tunnel, street canyons, and parking garages. Traffic intensity and the ventilation by air were identified as the main reasons for the site-specific spatial differences in the magnetic PM loads. The SIRM enrichment was statistically higher in the 10 week exposure period. However, the 5 week exposure period was also sufficient for the assessment of the pollution distribution. The study strengthened

the effectiveness of moss bags for monitoring the small-scale spatio-temporal distribution of air pollutants in urban areas.

Magnetic comparisons of the active bag technique with different species are low in number. The study by Vuković et al. (2015b) showed statistically significantly higher pollutant enrichment in the moss bags of *S. girgensohnii* than of *H. cupressiforme*. Furthermore, the former species was found to be more sensitive indicator of small-scale spatial monitoring while the latter one expressed effectively large-scale pollution levels. The comparison of *S. papillosum* moss bags and *H. physodes* -lichen bags around an industrial point source indicated that the lichen bags were more efficient accumulators at greater distances (6 and 8 km sites) than the moss bags. The situation was the reverse near the source (1 km sites) (Salo 2014). The accumulation capacity of lichen may have been deteriorated by pollution levels exceeding its tolerance next to the source. Therefore, moss bags were considered more reliable in sampling, especially at highly polluted areas.

Twigs containing the lichen *Evernia prunastri* were transplanted in the surroundings of a cement plant in Bratislava, Slovakia, in the study by Paoli et al. (2016). The exposure periods were 30, 90, and 180 days. The deposition of dust-associated elements (e.g., Ca, Fe, Ti, and V) was significant after 30 days, whereas the deposition of combustion-related elements (e.g., S) increased from 30 to 180 days. The *in situ* lichen *Xanthoria parietina* was compared with the transplants exposed for 180 days. The magnetic data for native lichens were similar to the transplanted lichens. However, the native samples had higher concentrations of magnetic minerals most likely due to the longer exposure period. As a result, both *in situ* and transplanted lichens were recognised as suitable for magnetic air pollution studies. Moreover, the magnetic measurements of the lichens contributed to the source identification of element depositions.

3 MATERIALS AND METHODS

3.1 Study areas

This thesis focused on two study areas, both located in SW Finland (Fig. 4). The town of Harjavalta (paper I–III) represents an industrial environment and the city of Turku (paper I, IV) represents an urban environment, where traffic is the main pollution source.

Harjavalta has about 7500 citizens and an area of 128 km^2. The largest physical features are the Kokemäenjoki River and an esker (glaciofluvial ridge) both running in the direction of southeast-northwest (SE-NW). The main wind direction is SW. The Industrial Park, the largest cluster of heavy metal and chemical industries in Finland, is the most important anthropogenic feature having an impact on the environment and air quality of the region. Industrial activities include a Cu-Ni smelter (Boliden Harjavalta Ltd), a Ni-refinery with adjacent industrial operations (Norilsk Nickel Harjavalta Ltd), and a fertilizer plant (Yara Finland Ltd). The Industrial Park covers an area of 300 ha close to the town centre. The main products are Cu, H_2SO_4, Ni and special Ni-chemicals, and fertilizers. Common air pollutants are SO_2, dust and heavy metals, such as arsenic (As), Cd, Hg, and Ni. Fugitive gases and dust emissions originate from many sources: for example, the smokestacks; the moving and storing of raw materials, products and wastes; the resuspension from slag heaps; and the heavy industrial traffic (Nieminen et al. 2002). In Harjavalta, a considerable number of environmental studies have been conducted regarding, for example, the spatial distribution of pollutants and their impacts on the flora and fauna (e.g., Nieminen et al. 2002; Salemaa et al. 2004; Eeva & Lehikoinen 2015). The air quality of the region is constantly monitored using fixed monitoring stations, which measure PM_{10} and SO_2 levels. Furthermore, the heavy metal spread from the Industrial Park is regularly surveyed by bioindicator studies and the moss bag technique SFS 5794. The sampling design followed (paper I) and added to (paper II) the transects of previous studies by Jussila (2003, 2009), and focused on the most contaminated area (paper III) identified in previous magnetic and heavy metal studies (e.g., paper II; Jussila 2009). The rural background levels were determined from the southern shore of Lake Sääksjärvi, Kokemäki, located 17.5 km to the NE of Harjavalta (paper I–III).

Turku has a population of 183,000 and a total area of 306 km^2 of which the land covers 246 km^2. The main physical features are the Aurajoki River and the location on the coast of Baltic Sea. The dominant wind direction is SW. Air quality in the Turku region is significantly impacted by traffic-derived NO_x and PM, while industrial or energy production emissions have low influence (Air Quality Expert Services 2010). Traffic intensity ranges from 0–30,000 vehicles per day in the centre, and up to 20,000 vehicles per day in the nearby Helsinki and Tampere motorways. Two air quality monitoring stations operate in Turku: NO_2 and PM_{10} are measured in the city centre and O_3 at 10 km to the west (W) of the centre. The sampling was focused on the city centre at parks and intensively trafficked areas (paper I, moss bags), randomly around

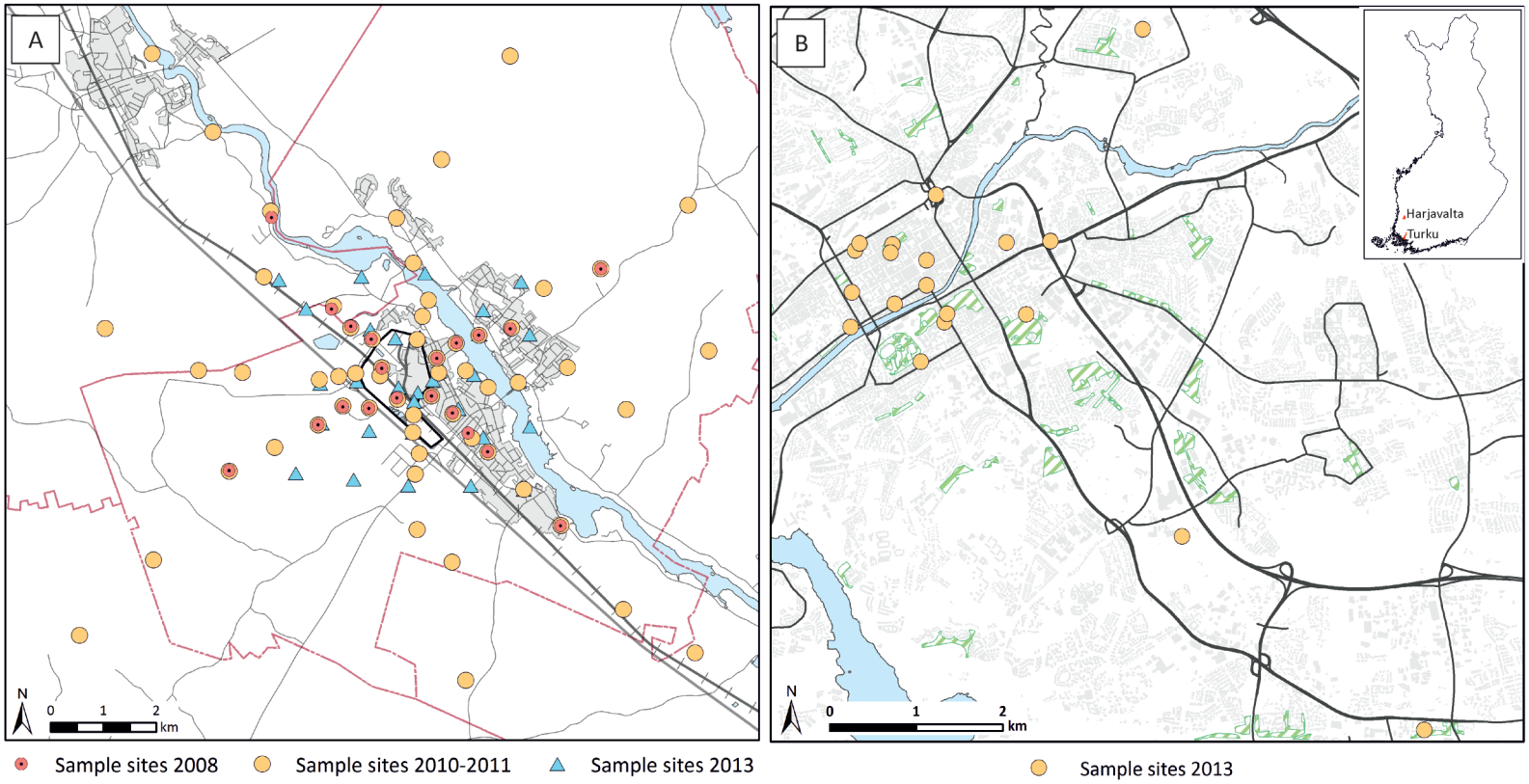

Fig. 4. The sampling networks in the study areas of Harjavalta (61° 18.8'N, 22° 08.5'E; A, papers I–III) and Turku (60° 27.1'N, 22° 16.0'E; B, paper IV), both located in SW Finland (index map). In Harjavalta, the fenced area of the Industrial Park is shown with a dashed line and the location of the Cu-Ni smelter's chimney is indicated with a cross in a white circle. National Land Survey of Finland 2013.

the Turku area (paper I, lichens), and near major roads, kindergartens, schools, and park areas (paper IV). The rural background levels were determined from the island of Kemiö, which is located about 50 km SE of Turku (paper I), and from Piikkiö, about 15 km SE of Turku, and the island of Parainen, about 35 km south (S) (paper IV).

3.2 Sampling

Active biomonitoring by standardised moss bag technique was the main sampling method in each paper. Other materials were used for sampling or reference purposes (Table 6, Fig. 5).

Table 6. Summary of sample (s) and reference (r) materials and methods used in papers I–IV. The numbers of sample sites, excluding the background sites, are indicated in square brackets.

	Paper I	**Paper II**	**Paper III**	**Paper IV**
Materials				
Moss bag (s)	x [20+22]	x [64 ×2]	x [18]	x [19 ×2]
Epiphytic lichen (s)	x [116]			
Snow (s)			x [29]	
Industrial references (r)	x	x	x	
Urban reference (r)	x			
Methods				
Magnetic susceptibility	x	x	x	x
IRM acquisition/backfield	x	x		
Thermomagnetic studies	x			x
Hysteresis loops and parameters	x	x		x
FORC	x			
Chemical analyses	x	x	x	x
SEM-EDX	x	x	x	
Tomlinson PLI	x	x	x	

Moss bags were prepared using the Finnish standard SFS 5794 (Finnish standards association 1994). The green parts of *S. papillosum* collected from a rural bog in Honkajoki, western Finland, were cleaned by hand from litter and other vegetation matter in the laboratory. Then the moss was acid-washed in 0.5 M hydrochloric acid (HCl) for 24 h and rinsed three times for 20 min with deionized water (H_2O) to equalise the element levels and to neutralise the material. Approximately 30 g (paper I–III) and 15 g (paper IV) of wet moss was closed to a nylon net (mesh size 0.64 cm^2) with cotton thread. At each sampling and background site, five (paper I, II), four (paper III) and three (paper IV) spherical moss bags were tied on the outer branches of trees at a height of 2.5–3 m. The samples were carried to the sites and back to the laboratory in closed plastic bags. The moss bags from each sampling site were combined into a composite sample. The moss material was dried at a temperature under +40 °C to a constant weight and homogenised. Approximately 2/3 of each composite sample was ground up: a Herzog swing mill equipped with an agate-grinding vessel was operated at 1500 rpm for 15 s (paper I), and a Retch

PM100 planetary ball mill equipped with a zirconium oxide (ZrO_2) grinding vessel and balls was operated at 500 rpm and 20 or 30 s (paper II–IV). One part of each acid-washed moss batch (approximately equivalent to 10 moss bags) was stored in the laboratory as a control moss, which was not exposed to air pollution. The control moss was used for determining the initial magnetic and elemental concentrations, which (the average values) were subtracted from the exposed moss bags. Therefore, the final moss bag data reflected the accumulation of air pollutants during the study periods in each paper. The rural background samples were used for comparison.

Epiphytic lichen *H. physodes* was collected *in situ* by hand and plastic tools from *Pinus sylvestris* tree trunks as three subsamples. The samples were transported and stored in closed plastic bags. In the laboratory, the samples were dried to a constant weight at a temperature under +40 °C, then crushed using a plastic knife and an agate mortar, and then homogenised. A clean reference sample of epiphytic lichen was collected from the island of Kemiö.

Snow was collected by pushing two parallel plastic tubes (A and B, Ø 10 cm) vertically through a snow column. In total, four subsamples were obtained within a 5 m distance. Samples were transported and stored in closed plastic bags, which were kept in cool boxes and freezers. For the magnetic analyses, the snow was melted and the water fully evaporated in the laboratory at a temperature under +40 °C. The remaining material was collected with 1.2 g of clean cotton wool, the premeasured magnetic susceptibility of which was subtracted from the data. For chemical analyses, snow was melted at room temperature in the laboratory before processing.

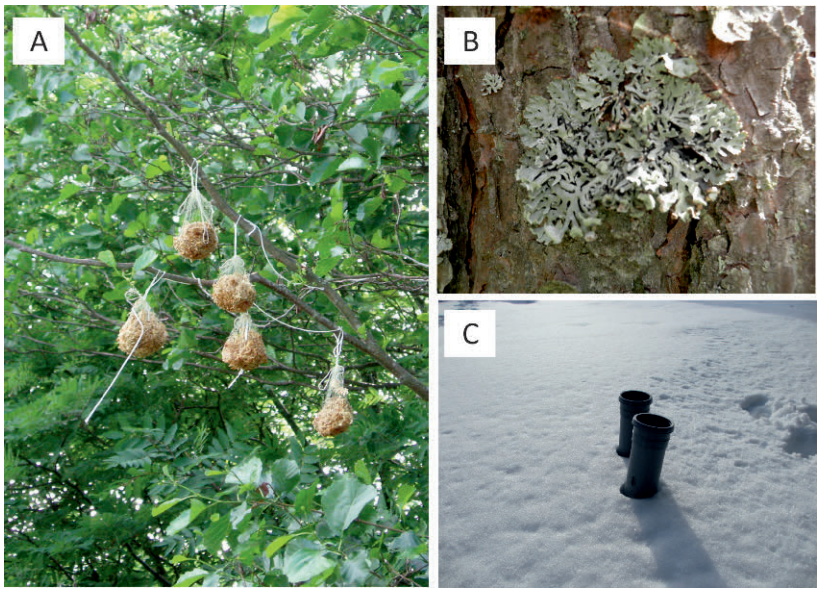

Fig. 5. The moss bag technique (A) was the main sampling method in papers I–IV whereas epiphytic lichen (B) was used in paper I and vertical snow samples (C) in paper III. Photos by H. Salo (A, B) and A-K. Berisha (C).

The industrial samples included two smokestack filters (paper I–III), final copper slag (Cu-slag), granulated nickel slag (Ni-slag), five different Cu-concentrates and three different Ni-concentrates (paper II, III) from Harjavalta Industrial Park. The filters were obtained from the smokestacks of the Cu-Ni smelter, where raw materials are smelted in the combustion process, and the Ni-dryer, where Ni-concentrates are pre-dried before the smelting process. Both fiberglass filters were exposed to the fumes for one month. Other industrial references were obtained during the different stages of the industrial processes. The **urban reference sample** of the resuspended road dust was collected on adhesive carbon tabs during a high resuspension period (paper I).

3.3 Methods

3.3.1 Concentration of magnetic minerals and elements

In this thesis, the main magnetic parameter used for measuring the magnetic mineral concentration in the samples was the mass-specific susceptibility ($\chi \times 10^{-8}$ m^3 kg^{-1}) (Table 6). The measurements were made using a Bartington MS2B sensor, which operates at two frequencies (0.47 and 4.7 kHz) in the Department of Geography and Geology, at University of Turku. A standard 10 cm^3 sample container was tightly filled with ground sample material. The number of subsamples evolved during the PhD process: paper I had one subsample from Harjavalta and two subsamples from Turku, paper II had two subsamples from randomly selected sites, while papers III and IV had two subsamples from each site. Mass-specific susceptibility values are the average of three (paper I) and five (papers II–IV) low-frequency measurements made for each subsample.

The concentrations of selected elements were determined with chemical analyses in the accredited laboratories (Table 7). Chemical methods were different (for details, see papers I–IV).

In paper I and III, the element concentrations were examined in relation to the natural environment (i.e. the background level) using the Tomlinson Pollution Load Index (PLI) (Tomlinson et al. 1980). The PLI was calculated as follows (Angulo 1996):

$$CF_{METAL} = C_{METAL} / C_{BACKGROUND\ VALUE} \quad (3)$$

$$PLI = \sqrt[n]{CF_1 \times CF_2 \times \ldots \times CF_n} \quad (4)$$

where each metal concentration (C_{METAL}) was divided by its background concentration ($C_{BACKGROUND\ VALUE}$) to obtain the concentration factor (CF_{METAL}). The PLI was calculated as the *n*th root of the multiplied CFs. Element loads close to background level have a PLI below 1 while values above 1 indicate the extent of the pollution. The PLI can be used for evaluating and comparing the overall pollution level of sample sites as well as the differences in sample materials. This index is sensitive to unusually high or low element concentrations (Tomlinson et al. 1980). Therefore, major elements impacting the PLI should be identified.

Table 7. Summary for the analysed elements, main analysis methods, and laboratories (A=Ambiotica, University of Jyväskylä, Finland; B=Boliden Harjavalta Ltd, Finland, AL=Acme Labs, Canada) for papers I–IV.

Paper	Elements (samples)	Main analysis method	Laboratory
Paper I	Al, Ba, Ca, Cr, Cu, Fe, Mn, Na, Pb, Ti, V, Zn (moss bags Turku)	ICP-MS (moss bags, lichens Turku)	A
	Al, As, Cd, Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, V, Zn (lichens Turku)		
	Cd, Cu, Fe, Ni, Pb, Zn (moss bags Harjavalta)	AAS (moss bags Harjavalta)	B
Paper II	Al, As, Cr, Cu, Fe, Hg, Ni, Pb, Ti, Zn (moss bags)	ICP-OES, ICP-MS	A
Paper III	As, Cd, Cu, Fe, Hg, Ni, Pb, Ti, Zn (moss bags, snow)	ICP-MS (moss bags), ICP-OES (both)	A (moss bags), B (snow)
Paper IV	Al, As, Ca, Cd, Cr, Cu, Fe, Hg, Na, Ni, Pb, Ti, V, Zn (moss bags)	ICP-MS	AL

3.3.2 Composition of magnetic minerals

Magnetic mineral compositions were identified from selected ground samples by the IRM acquisition curves, hysteresis loops, and temperature-dependent magnetic properties (Table 6).

In paper I and II, the IRM acquisition curves and hysteresis loops were determined using a Princeton Vibrating Sample Magnetometer (VSM) Model 3900 in the Department of Physics, at University of Helsinki. The determinations were made at room temperature in a magnetic field up to +1 T. M_S, M_{RS}, and H_C (see section 2.1.3 for the explanation of abbreviations) were obtained after paramagnetic slope correction. H_{CR} was determined from the direct current (D.C.) demagnetisation of M_{RS}.

In paper I, the temperature dependent susceptibility was determined with Agico KLY-3S kappabridge in the Department of Physics, at University of Helsinki. The device was operated at 875 Hz frequency and 300 Am^{-1} field intensity. The samples were warmed from –195 °C to room temperature.

In paper IV, the hysteresis loops and temperature dependent magnetisations were determined at temperatures of 10 K and 300 K using a Quantum Design SQUID-magnetometer in the Department of Physics and Astronomy, at University of Turku. The hysteresis loops were determined in a magnetic field up to 1 T and temperature dependencies in 10 mT. M_{RS}, M_S, H_C, and H_{CR} were obtained, after subtraction of the linear paramagnetic signal from the sample holder and clean sample, by fitting function:

$$M(B) = M_{RS} \times \mathrm{ArcTan}((B \pm H_c) / B_s) \quad (5)$$

to upward hysteresis loop (with – sign). M(B) is the magnetisation as a function of the magnetic field B and B_S is a scaling constant. The saturation remanence was

determined as the magnetisation value at zero field M(0). H_{CR} was determined by solving numerically the field where the difference of the upward and downward branches was equal to 0.5.

3.3.3 Grain sizes and shapes of magnetic minerals

In paper I, the First Order Reversal Curves (FORCs) were determined for selected samples. The FORCs were generated from a set of 52 partial hysteresis loops, which were determined in steps of 10 mT with an averaging time of 1 s and using a 0.5 T saturating field. FORC diagrams were produced with a MatLab code (FORCAM) with a smoothing factor 3 used for data processing. FORCs are a series of partial hysteresis loops made after the sample magnetisation is saturated (Pike et al. 1999; Roberts et al. 2000). In paper I–IV, the hysteresis ratios of M_{RS}/M_S and H_{CR}/H_C were plotted to the Day diagram (Day et al. 1977; Dunlop 2002) to investigate the domain states of magnetic PM.

In paper I–III, the scanning electron microscopy connected to the energy-dispersive X-ray spectrometer (SEM-EDX) was used to investigate the characteristics (i.e. the shape, size, and composition) of the magnetic PM. Before analysis, the organic part of the moss was burnt off with hydrogen peroxide (H2O2). Magnetic PM was extracted from samples with a strong hand magnet. The analyses were done with an SEM model JEOL JSM-5900 LV (paper I, II) in the Geological Survey of Finland, and an SEM model JSM-6490LV (paper III) in the Outotech Research Center (ORC), Pori.

4 RESULTS AND DISCUSSION

4.1 Active biomonitoring strengthens the spatio-temporal resolution of air quality measurements and assessments

The sampling design of active biomonitoring is the most important factor affecting the variations found in the results: local variations or pollution sources remain easily hidden and undetected if sampling is restricted to small areas. For this reason, one or even a few air quality monitoring stations cannot represent accurately enough the spatial variations in air quality and pollution loads within a city. For example, in Turku, one station in the centre monitors the air quality but the results of paper IV indicate that considerable spatial variation is left undetected. The same is true in Harjavalta, where the monitoring station is located in a residential area about 2–3 km north (N) of the Industrial Park. Thus, active biomonitoring is a powerful tool for enhancing the spatial accuracy of air quality measurements and assessments, and for evaluating the spatial representativeness of air quality monitoring stations. More research is, however, needed in order to establish the relationship between the monitoring stations and biomonitoring data sets in various environments.

Spatially flexible sampling networks are easy to launch in various environments using active biomonitoring. Furthermore, the temporal resolution is easily (pre) determined since the length of the collection period for the active biomonitors and/or their seasonal placing is controllable. The active approach is the most efficient and practical for small scale investigations focusing on local air pollution issues. Industrial point sources are typical targets for active biomonitoring (e.g., paper I–III; Culicov et al. 2005; Ares et al. 2011; Paoli et al. 2016). In Finland, for example, some of the largest industrial companies, such as those operating in the Industrial Park of Harjavalta, may be obliged by environmental permits to regularly monitor the air quality and the spread of metal emission with the moss bag technique. However, diffuse pollution originating in cities from traffic networks, residential areas, etc., can also be sampled with active biomonitors (e.g., paper IV; Vuković et al. 2016). The applicability of active methods is especially demonstrated in areas experiencing high pollution loads and thus lacking suitable (amounts of) *in situ* species. This is also the case in both study areas of this thesis.

In the environment of Harjavalta Industrial Park, the sampling design and its spatial extent was adjusted between papers I–III based on the results. In the first two papers the sampling was implemented in transects, with the numbers increasing from four to eight, while a sampling grid was set up in paper III. The grid was restricted to the most contaminated area identified in the previous papers. All the results indicate that the air pollution gradient (especially for coarse PM) decreased along with an increasing distance from the source, i.e. the Industrial Park. Similar trends have been reported in other studies from the same area

(e.g., Hynninen 1986; Uhlig et al. 2001; Jussila 2003, 2009) as well as from other industrial point sources (e.g., Hanesch et al. 2003; Hu et al. 2008; Hansard et al. 2011). The heaviest anthropogenic air pollution loads settled at sites located within or adjacent to, i.e. 0.5–1.5 km, the Park. The spatial emphasis of hot spots is slightly distinctive: SE transect in paper I, S–SW–W–NW transects in paper II, and sites within or immediately next to the fence of the Industrial Park in paper III. The effective distance of the industrial fly ash pollution is about 4 km. However, it reaches distances beyond 4 km in SE and NW transects, which follow the Kokemäenjoki river valley and prevailing wind directions. Monthly mass-specific susceptibilities of studies in 2008, 2010 (spring), and 2012 in Harjavalta are combined and interpolated to illustrate the spatial extent of seven air pollution impact zones around the Industrial Park (Fig. 6). The air pollution impact zones are originally presented in paper II.

In the city of Turku, the results of paper I were used to target the sampling in paper IV to intensively trafficked sites and places where children typically spend time. The active biomonitoring completes the spatial lack of *in situ* species in the city centre. Both papers show the highest pollution loads near busy traffic areas and the lowest accumulation in parks. Interestingly, courtyard/school sites in the paired samples with trafficked sites show higher pollution loads, which indicate that courtyards can be local places for potentially greater exposure to air pollutants (paper IV). Moreover, the location of a single air quality monitoring station in the centre seems to overestimate the element accumulation in the road dust episode and to underestimate the accumulation in the summer season (paper IV). The current location of the air monitoring station is not ideal and should be further assessed in order to improve the spatial representativeness of its air quality data.

The temporal resolution changes from about 50 days in paper III, to about 60 days in papers I and IV, and up to about 180 days in paper II. The longest collection period, 6 months, exceeds the time of 8 weeks defined in the moss bag standard SFS 5794 (Finnish Standards Association 1994) and in the recommendations (e.g., Ares et al. 2012, 2014). During the exposure period, the moss bags are open to changes in the weather, e.g., rain/snow, wind, and sun. The metal retaining ability of moss bags depends on environmental conditions, and the biomonitor might achieve saturation or start to release absorbed metals if the exposure time is too long (Garty et al. 1993; Szczepaniak & Biziuk 2003; Giordano et al. 2009). This may have occurred in paper II. Aničić et al. (2009), on the other hand, have found a linear accumulation trend up to 5 months in the elemental comparison between wet and dry moss bags. The collection period of biomonitors, despite the length, does not reflect hourly or diurnal variations but, instead, represents a larger picture of the accumulation and the current situation of pollution levels overall. Furthermore, the spatial representativeness and view of the air pollution distribution and its local variation remains distinguishable.

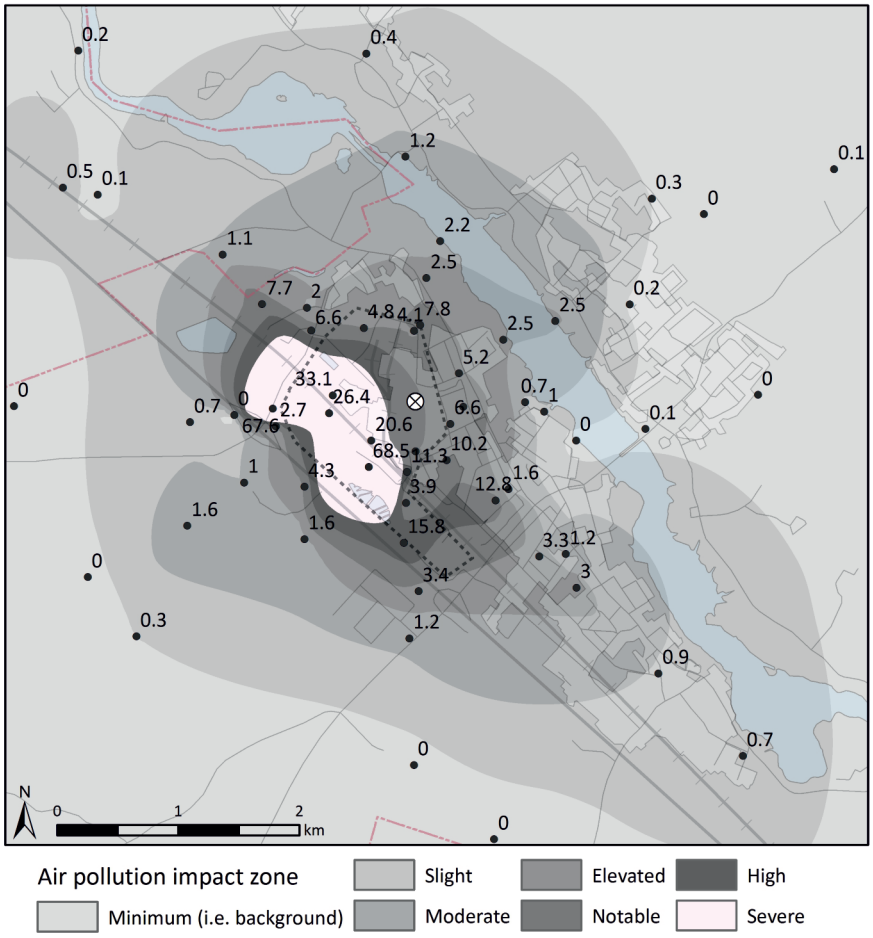

Fig. 6. Seven air pollution impact zones (based on paper II) around the Harjavalta Industrial Park derived from monthly mass-specific susceptibilities ($\chi \times 10^{-8}$ m^3 kg^{-1} $month^{-1}$) of studies in 2008, 2010 (spring), and 2012. The fenced area of the Industrial Park is shown with a dashed line and the location of the Cu-Ni smelter's chimney is indicated with a cross in a white circle. National Land Survey of Finland 2013.

4.2 The properties and sources of magnetic PM can be characterised using different combinations of magnetic, chemical, and micro-morphological methods

The concentration, composition, and grain sizes of magnetic PM-bound minerals are investigated in detail using magnetic methods. These analyses alone help to identify levels, distributions, and sources of magnetic PM, which act as the magnetic carriers of elements. A joint use of chemical and/or micro-morphological methods is required when precise quantitative data is needed for element concentrations, and for size, shape, and concentrations of magnetic PM. Papers I–IV all indicate good correlations between magnetic parameters, mainly mass-specific susceptibility, and

the investigated elements, which further enhances the applicability of magnetic methods to monitor the element levels and distribution in the environment. This linkage has been noted in many studies (e.g., Vuković et al. 2015a, 2015b; Paoli et al. 2016).

In Harjavalta, previous studies by, for example, Jussila (2003, 2009) and paper I show that the chimney of the Cu-Ni smelter is the main pollution source in the Industrial Park. Conversely, papers II and III pinpoint the concentrate and slag handling activities as the major dust emitters, which have a greater impact on the local air quality than the fly-ash load from the chimney of the smelter. The role of these dust-providing sources are derived from the combination of magnetic, elemental, and micro-morphological signals of the moss bags and industrial reference samples, the spatial emphasis of the hot spots (mapped via denser sampling networks), and wind patterns. The moss bags' magnetic susceptibilities, the IRM acquisition curves, and the hysteresis loops and parameters indicate a significant accumulation of low-coercivity ferrimagnetic mineral, such as magnetite, in and near the Industrial Park (paper I–III). Moreover, the element levels are clearly elevated at the same sites. Cu-Ni smelter's filter and Cu-slag show the presence of similar minerals as in the moss bags, whereas Ni-dryer's filter, Ni-slag and majority of the concentrates are characterised by high-coercivity minerals (paper I, II). The magnetic grains in the moss bags and the smelter's filter are located within the PSD region closer to the SD-MD mixing line than the SP-SD mixing line (paper II). The micro-morphological analysis shows that spherical PMs dominate in the smelter's filter, which is typical for the combustion processes, while angular PMs are dominant in the dryer's filter, Cu-slag, and the moss bags (paper II). Usually, angular particles are associated with the wear processes (e.g., Matzka & Maher 1999; Bućko et al. 2011) but they can originate from industrial processes as well (Sánchez de Rojas et al. 2008).

Traffic is the main source of urban PM in Turku. The highest magnetic and elemental concentrations were found at sites next to the roads with high traffic intensities (i.e. >30,000 vehicles per day) while the park sites had the lowest pollution accumulation (paper I, IV). Based on magnetic susceptibilities, the IRM acquisition curves, the hysteresis loops and parameters, and the low-temperature magnetisation, the main magnetic mineral found in the urban dust of Turku was low-coercivity magnetite (paper I, IV). Mass-specific susceptibilities of about $>8 \times 10^{-8}$ in road dust episode and $>3 \times 10^{-8}$ m^3 kg^{-1} in the summer season were regarded as typical values indicating traffic impact (paper IV). According to Sagnotti et al. (2006), the magnetic fraction of PM_{10} is a mixture of PSD (natural dust) and SP and MD (anthropogenic pollution) grains. The epiphytic lichen samples showed that the magnetic PM are PSD grains with a predominant MD fraction (paper I). In the FORC diagram, the main peak close to the origin may also indicate SP particles (Roberts et al. 2000). The moss bags were located in the PSD region close to the SP-SD mixing line in the Day plot (paper IV). Moreover, a smeared transition and a gradual rise of magnetisation after T_V in temperature-dependent magnetisation in most of the moss

bag samples indicated that magnetite was partly SP or partially oxidised, i.e. non-stoichiometric (Smirnov 2006; Mitchell & Maher 2009). The difference of magnetic grain sizes between epiphytic lichens and moss bags might be a result of the separate locations of the samples or from the species' prevalence for the distinctive grain sizes. The moss bags entrap finer PM (<2.5 µm) predominantly (79%) over coarser PM (2.5–10 µm) (Tretiach et al. 2011). However, magnetic studies by Chaparro et al. (2013) and Marié et al. (2016) indicate that lichens entrap both coarse and fine grains. The SEM analysis of the carbon tabs revealed the predominance of angular particles and aggregates. Greater amounts of PM were collected at the edges of the urban parks whereas lower element concentrations and smaller grains were detected in the centre of the urban parks. In paper IV, the courtyard sites showed higher element concentrations and smaller PM than the corresponding traffic sites. This may result from the sheltered nature of the courtyard, which prevents the air from mixing and pollutant levels from diluting.

4.3 Suitable sampling materials are manifold but active moss bags are hard to replace

Various organic and inorganic sampling materials have been exploited in the magnetic air quality assessments (Table 1). In this thesis, the data were mainly collected using active moss bags while other materials have been also tested and compared to them (Table 6). The moss bags, thus far, have indicated the best accumulation capacity of all the tested materials. It can be argued that, in the near future, active moss bags will be difficult to be replaced in air quality assessments with a material that has correspondingly excellent properties and accumulation efficiency.

Moss bags are a suitable choice for local small-scale studies while *in situ* lichen and moss species are more practical for extensive large-scale monitorings. Native species can suffer from high pollution loads, in which case samples are either hard to obtain or obtain in sufficient amounts. This weakens the spatial representativeness and accuracy. In paper I, both epiphytic lichen and the moss bags were used for monitoring the air quality in Turku. The lichen samples were collected from the surroundings of the city centre, whereas the moss bags focused on the centre where the given epiphytic lichen species was lacking. Active biomonitoring can be used to complement the spatial gaps of *in situ* species. However, active and passive biomonitorings are not directly comparable because they represent different temporal resolutions. The exposure and accumulation time for the active biomonitors typically ranges from a few weeks to months while the time for the passive biomonitors is generally as long as their lifetime. Thus, *in situ* lichens and mosses usually mirror the long-term pollution and do no indicate temporary changes in the pollution levels or distributions. The same holds true for soil samples since soil is a natural archive for air pollutants (e.g., Hanesch et al. 2003; Fialová et al. 2006). Moreover, the interpretation of soil data can be difficult due to their complex nature and the effect of the underlying geology (Petrovský & Ellwood 1999;

Bućko 2012). Deciduous tree leaves, in contrast, are easily available and they have a shorter lifespan. Their major setback is the washing effect of the surface caused by rainfall which causes a net decrease in the pollution concentrations and in the magnetic signal (Matzka & Maher 1999; Urbat et al. 2004). The project in Harjavalta (paper I) also tested *Betula* spp. leaves. The (unpublished) results indicate that the moss bags are more efficient pollution collectors than the tree leaves; for example, correlations between mass-specific susceptibility and investigated elements were better in the moss bags than in the tree leaves (Table 8).

Table 8. Pearson's correlation coefficient (*r*) between mass-specific susceptibility ($\chi \times 10^{-8}$ m^3 kg^{-1}) and the investigated element concentrations and Tomlinson's Pollution Load Index (PLI) for moss bags and *Betula* spp. leaves (N=21, including the background samples).

	χ	**Cd**	**Cu**	**Fe**	**Ni**	**Zn**	**PLI**
Moss bags	1.000*	0.541	0.893*	0.997*	0.712*	0.964*	0.895*
Leaves	1.000*	–0.084	0.721*	0.980*	0.263	0.130	0.708*

* Correlation is significant at the 0.01-level.

In certain environments the use of moss bags is hindered by the lack of suitable moss species. Mosses thrive in humid conditions. Southern Europe, for example, is mainly too dry for mosses to grow in substantial amounts in accessible places for the purposes of the bag technique. Lichens are the more common alternatives. One magnetic study applied moss and lichen species simultaneously as active biomonitors in the surroundings of the Industrial Park in Harjavalta (Salo 2014). Based on the mass-specific susceptibilities, the *H. physodes* -lichen bags in this study accumulated pollutants more efficiently at farther distances (3 and 6 km, and background sites) than the *S. papillosum* -moss bags, whereas the situation was the opposite close (1 km sites) to the source. The greatest differences between the moss and lichen bags were observed at 1 km sites in the SE and particularly in the NW (127.3×10^{-8} and 77.2×10^{-8} m^3 kg^{-1}, respectively), which may have been the result of the deterioration of accumulation capacity and/or the vitality of the lichen due to the high pollution levels (e.g., SO_2, NO_x, and heavy metals) near the source. In this case, the moss bags appeared to be more reliable biomonitors of airborne magnetic PM than the lichen bags. In the same study (Salo 2014), artificial bags made of filter fabric were pre-tested with promising results. In the urban area of Turku in 2015, a further seasonal comparison (i.e. road dust episode in the spring and autumn season) between filter bags and moss bags preliminary indicated that the filter bags accumulate statistically significantly more magnetic PM in spring than the moss bags while the situation is *vice versa* in autumn.

The seasonal comparison between the moss bag and snow samples in paper III show that both materials are efficient collectors of air pollutants. Interestingly, the mass-specific susceptibilities were consistently statistically higher in the snow samples than in the moss bags, whereas the element concentrations behaved *vice*

versa. This may result from the differences in the sample sizes and in the analysis methods or the materials' distinctive nature as pollutant collectors. Snow (pack) is a passive accumulator (Viskari et al. 1997) while moss is an active one. Nevertheless, the similar spatial dispersion of air pollutants in and statistically significant variable correlations between the two sample materials indicate the applicability of moss bags in winter conditions. According to Viskari et al. (1997), snow sampling should be combined with other monitoring methods, such as moss bags. Snow is free and easy to sample, whereas the difficulties in finding unimpacted snow depositions hinder its use in urban and industrial areas. Furthermore, climate change and warmer winters will hamper the availability of snow. The deposition time of precipitated snow is determinable from meteorological data (Hautala et al. 1995). However, the accumulation and enrichment of snow and pollutants is a dynamic process and an outcome of several factors, such as topography, vegetation, wind, and anthropogenic relocation. Changes in meteorological conditions affect the snow pack, for example, temperature above 0 °C cause the pollutants to stream down with the melt water and deposit on the ground (Viklander 1999). Some pollutants in the snow pack can be lost during the winter. The moss bags, in contrast, provide more homogeneous and better controlled sampling with less impact by the re-deposition of pollutants. Therefore, the air pollution assessment is more straightforward with the moss bags than with the snow samples.

4.4 Seasonal variation sets boundaries to air quality assessments using biomonitors in mid-latitudes

A season is a period of the year distinguished by special climate conditions. Polar regions experience seasonal variation but they are generally cold places whereas little seasonal variation is experienced near the Equator. The four-season year (spring, summer, autumn, winter) is typical only in the mid-latitudes. This thesis notes that seasonality sets boundaries to the biomonitoring of air quality, which must be recognised in the sampling design. Autumn and winter are suggested as the most representative seasons for air quality assessments using the moss bag technique.

Vegetation starts to germinate in spring along with the increasing temperatures and day light, and is fully grown by the summer. Vegetation is considered effective in mitigating air pollution dispersal and trapping PM. Gaseous pollutants are absorbed by the stomata of leaves, and particles also deposit on the leaves and branches (Vos et al. 2013). Vegetation can also have a negative impact on air quality on a local scale. Trees and shrubs obstruct wind flow, hold pollutants within the canopy and prevent fresh air ventilation (Roy et al. 2012; Salmond et al. 2013). Pollutants may be caught in whirlwinds and remain airborne for a longer time. The standard SFS 5794 defines the leafless time in spring and autumn as the most suitable exposure time for moss bags since the disturbing effect of vegetation is minimal (Finnish Standards Association 1994). Moreover, the moss bags are placed on the outer branches in

order to inhibit the elemental contribution from the tree/shrub itself. Anthropogenic structures can be utilised in urban areas, for example, Vuković et al. (2016) attached the moss bags to lampposts using plasticised aluminium holders. This further minimises any direct contribution from vegetation, but does not eliminate the overall impact of vegetation as regards local variation on pollution levels.

Intensive, yet short, road dust episodes are experienced in sub-arctic regions of the world during the spring season. Traction control methods, such as the use of traction sand and studded tires, greatly enhance the amount of mineral PM and related elements in the environment and air after the snow has melted. In paper II, period I (spring) shows statistically significantly higher Al and Ti concentrations than period II (autumn) in the industrial environment of Harjavalta. This is considered to result from the road dust input. Similarly, higher element loads were detected in the spring rather than in summer in the urban area of Turku (paper IV). Thus, the spring season should not be chosen for sampling when the aim is to achieve a representative view of the general air quality.

Autumn is typically rainy and vegetation is naturally diminished due to approaching winter season. Wet conditions prevent the moss bags from drying out and help them to retain their element capturing capacity (e.g., Al-Radady et al. 1993; Szczepaniak & Biziuk 2003; Aničić et al. 2009a). Vegetation is minimal in winter since many species remain dormant during the coldest time of the year. Deciduous species are leafless which restricts their use for biomonitoring. The leafless time also removes the obstructing effect of vegetation. The morphology of mosses and lichens is unaltered throughout the year (Szczepaniak & Biziuk 2003). However, snow cover hinders accessibility and prevents the pollution accumulation of *in situ* species. This is not the case with the active biomonitors. Paper III indicates that the moss bags are operable also in winter conditions. The spatial dispersion of air pollutants was similar in the seasonal comparison of the snow samples and moss bags. Furthermore, the variable correlations between these samples were good and statistically significant.

5 CONCLUSIONS

This thesis has set the basis for the applications of active magnetic biomonitoring in air quality measurements and assessments. The moss bag technique has proved to be a very efficient and convenient sampling method for magnetic investigations of airborne PM and elements. The research has provided insights as regards the magnetic monitoring of air pollution in the mid-latitudes. Here, the seasonal variation is an essential element that has to be considered when planning the research design, in order to achieve successful implementation.

First, active biomonitoring was indicated as a powerful tool for enhancing the spatial accuracy of air quality assessments and for evaluating the spatial representativeness of air quality monitoring stations. In this thesis, the study areas experienced a lack of *in situ* species. Sampling networks with high spatial resolution and (pre)determined temporal resolution were easy to establish using the moss bags. The active approach was shown applicable in the investigations of both point and diffuse emissions.

Second, urban and industrial environments, i.e. the areas most impacted by anthropogenic activities, benefitted from magnetic screening even though the main type of pollution source was different. The joint use of spatially representative sampling networks and magnetic, micro-morphological, and chemical research methods guided, for example, the identification of emission sources and pollution impact areas. In the industrial environment of Harjavalta, the concentrate and slag handling activities were indicated as the major dust emitters. Furthermore, they were shown to have a greater impact on local air quality than the fly-ash load from the Cu-Ni smelter, which has been traditionally labelled as the worst source of pollution. In the urban area of Turku, the magnetic biomonitoring has enhanced the understanding of the spatial variations in pollution levels throughout the city centre. As a result, reflections were made concerning the limitations in the spatial representativeness of the single air quality monitoring station.

Third, the moss bag technique was more applicable for air pollution monitoring than the epiphytic lichen or snow samples tested in this thesis. One of the greatest advantages of moss bags was the flexibility in placing the sample sites, thus ensuring spatio-temporal accuracy and the presence of samples. The winter-time use of moss bags was shown to be possible. Besides being beneficial in anthropogenically polluted environments lacking *in situ* species, the moss bags reflect the present-day pollution situation. The same holds true for snow samples as well, however, the availability of snow is no longer guaranteed due to global warming. Moreover, snow deposition is easily disturbed by human activities. The excellent structural properties and high accumulation efficiency of moss as a material ensure that it is difficult to find a replacement material with similar features for the moss bags.

Fourth, the four-season year, which is typical for mid-latitudes, presents challenges to the application of biomonitoring for air quality assessment. Deciduous

species are leafless for a considerable time during the autumn, winter and spring, which prevents their use for biomonitoring. When fully grown, vegetation is effective in mitigating air pollution dispersal and trapping PM. While the morphology of mosses and lichens does not change with season, snow can cover them hindering both the pollution accumulation and sampling for passive biomonitoring in winter. Active biomonitors, in contrast, were successfully applied throughout different seasons. However, road dust episodes, which are typical in the spring season of the sub-arctic regions, are intensive and significant sources of airborne PM. In this thesis, biomonitoring during these episodes resulted in a distorted view of the air quality. Therefore, autumn and winter were suggested as the most representative seasons for obtaining a general assessment of the air quality using the moss bag technique.

In the future, fast and economical methods, such as magnetic parameters, will become increasingly important research tools. While authorities and the general public demand more accurate information and data about the environmental pollution, funding and research resources are simultaneously diminishing. Magnetic biomonitoring provides a way to produce elaborate data for environmental planning aimed at protective action against the air pollutants.

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