

Markus Quante
Ralf Ebinghaus
Götz Flöser
Editors

Persistent Pollution – Past, Present and Future

School of Environmental Research –
organized by Helmholtz-Zentrum
Geesthacht

 Springer

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Foreword

Environmental problems and tasks are complex, and their solution requires interdisciplinary cooperation. Emissions may be local, but transport of pollutants – especially of persistent organic pollutants (POPs) – are transboundary. Thus, our activities to minimize these environmental impacts have to be international.

The identification and assessment of pollutants is an evident challenge for a more sustainable world. Great efforts in identifying, assessing and managing chemical pollutants have already been made within the last decades – often with legal consequences. On the other hand, we observe a long time from early evidences on environmental impacts of harmful chemicals to regulatory decisions, with e.g., more than 50 years from the first evidence of ecotoxicological effects of polychlorinated biphenyls (PCB) until their legal limitation. Since new classes of chemical compounds, e.g., nanomaterials or ionic liquids, are continuously developed and sooner or later “disseminate” in the environment, many problems for the environment will remain.

The idea of Green or Sustainable Chemistry can contribute to achieving sustainability in two key areas. First, the resources and reagents used by the chemical industry must increasingly be obtained from renewable sources. Second, polluting technologies and products must be replaced by benign, safe and inherent alternatives. According to its current guidelines, the German Federal Environmental Foundation (DBU) can support projects in these fields, comprising the topics of

- Sustainable Chemistry
- Renewable Materials
- White Biotechnology

Further on, our scholarship programme awards about 60 Ph.D.-scholarships per year in all fields of science, e.g., biology, chemistry, engineering, economics and law. Apart from this German programme meanwhile comparable programmes exist for students from Poland, Czech Republic, Baltic States, Hungary, Romania and Bulgaria. We are convinced that current and upcoming environmental tasks can only be solved by a generation of well educated scientists, engineers and politicians, who are able to act in a holistic and integrated way.

This book is mainly the result of the Fifth School of Environmental Research (organized by Helmholtz-Zentrum Geesthacht) “Persistent Pollution – Past, Present, Future”, sponsored by the DBU and held in summer 2007. The School of Environmental Research focused on persistent organic pollutants (POPs), heavy metals and aerosols. This workshop combined practical tools and lectures in the field of description, comparison and assessment of environmental data and their causes and consequences with respect to different time scales in a convenient and skillful way. The result is very impressive, with authors from international leading institutes and excellent reputation. I thank the organizers Ralf Ebinghaus, Markus Quante and Götz Flöser, for preparing the Fifth School of Environmental Research, and the editors and authors for this readable work.



Osnabrück, Germany

Dr. Maximilian Hempel

Preface

The contamination of the global environment by persistent pollutants is one key feature of the “Chemical Anthropocene”. This is the time period starting around the 1950s, where the distribution of chemical substances in our environment reached global dimensions, i.e., chemical analysis could demonstrate that these substances accumulate in ecosystems far away from the locations of their production and usage. For an assessment of possible future changes it is imperative to understand how the “system environment” has responded to past pressures and changes induced by human activity. These human drivers include the input of chemical substances, metals and aerosols, but also policy action aiming at the regulation of the releases of harmful substances in order to reduce their impact on environmental health.

From past research it is evident that numerous factors are involved and influence the time frame in which pollution of the environment with a particular chemical substance reaches global dimensions. On the other hand, the response time of contaminated environments to political measures taken to reduce pollution is also strongly dependent on various physico-chemical and environmental parameters.

This book evolved from the Fifth School of Environmental Research entitled “Persistent Pollution – Past, Present and Future”, which has set a focus on persistent organic pollutants (POPs), heavy metals and aerosols. The Summer School was held from May 9 to 18, 2007 in the Göhrde Hunting Castle, about 50 km south of Hamburg, Germany. Thirty-six Ph.D. students and post-docs from 25 countries attended the school in the middle of a large northern German forest area.

Research topics covered by the Fifth School included the

- Reconstruction of past changes based on the scientific analysis of natural archives such as ice cores and peat deposits
- Evaluation of the present environmental state by the integration of measurements and modelling and the establishment of cause-effect-patterns
- Assessment of possible environmental future scenarios including emission- and climate change perspectives

Leading scientists in the field of marine and atmospheric chemistry, meteorology and modelling, environmental chemistry and physics, as well as environmental policy and management were invited lecturers at the Fifth School of Environmental

Research and a large number of them have prepared manuscripts published in this book. In order to complement some of the covered topics additional authors have been invited to contribute to the book in their special field of expertise.

The present book consists of 20 contributions prepared by more than 40 authors. The structure of the book has been outlined according to the topics addressed by the school and includes synthesis chapters which look into the history and reconstruction of environmental pollution, address emission questions, provide a closer look on selected persistent pollutants, deal with transport and modelling aspects, shed light on some health issues related to persistent pollutants, and discuss emerging contaminants in the atmospheric and marine environment.

The editors thank all authors contributing to this volume and are grateful to the *German Federal Environmental Foundation* (DBU) and the Association “Gesellschaft zur Förderung des Helmholtz-Zentrums Geesthacht” (friends and supporters of Helmholtz Centre Geesthacht), who substantially supported the school. Many other persons have helped us to make the school and the book possible, in particular Mrs. Sabine Hartmann, Mrs. Ilona Liesner, Mrs. Beate Gardeike and Dr. Merja Schlüter. Thanks a lot to all of them.

Geesthacht, Germany
The editors, 31 July 2010

Dr. Ralf Ebinghaus
Dr. Markus Quante
Dr. Götz Flöser

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Part I
Introduction, History and Reconstruction

Chapter 1

A History of the Causes and Consequences of Air Pollution

Peter Brimblecombe

Persistent pollutants remain in the environment for a long time. This obvious statement makes historical analysis important. Such analysis can be useful at times for even very practical issues such as the record of the activity at old industrial sites, which are planned for redevelopment. Because the atmosphere has a relatively rapid turnover, persistent materials are frequently found as deposits on the earth's surface. This means there is a transition in the way we approach air pollution in comparison to earlier concerns over the pollutants smoke and sulphur dioxide from coal burning. These have relatively short lives in the atmosphere. There are long-lived pollutants such as nitrous oxide or carbonyl sulphide from aluminium production, that account for an increasing interest in such pollutants and their potential impact on the stratosphere. The best known example of persistence among the long-lived gases is the issue of CFCs and their relation to the widespread concern over the impacts they have on global climate and stratospheric ozone depletion.

The historical review here will not be limited to persistent pollutants, but rather look at how pollutants have been generated over time and how societies have viewed this process. There will be a special focus on the cities of London, Lüneburg and Los Angeles which show features that characterise certain aspects of human activity in relation to the atmosphere.

1.1 Antiquity of Understanding

Pollution was known from the earliest times and smoke frequently drew negative connotations. In the ancient Persian world:

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Don't cause the oven in a man's house to smoke . . . it will ruin the bread.

Proverbs from Nibru: c.6.2.1

my mood and heart. As if during the night watch
 . . . like excrement. . . my countenance like smoke.

A hymn to Inana for Išme-Dagan: c.2.5.4.

It wasn't simply an aesthetic concern because in the ancient world, air and health were strongly linked. Not surprisingly because the act of breathing is so readily associated with life. More thoughtfully classical medical writers linked air and health perhaps most notably in *The Hippocratic Corpus* which has a major section on air and health, although for the modern reader much of this would seem to be related to climate rather than air pollution. Nevertheless there is a continued miasmatic approach to disease origin (Brimblecombe 1987b). This view saw disease associated with the foul air and odours from swamps. It is clear that architects such as Vitruvius argued for the proper choice of location for dwellings. Nero's tutor Seneca blamed the culinary odours of Rome for his ill health. The survival of this classical learning in the Middle East gave a particular focus on air pollution among and health in Arabic medical writings tenth century (Gari 1987). Evidence is also found in the Hebrew *Bava Batra* and *Ktubot* which describe a law that: "You can't take a wife out of the village to a city . . ." which Rabbi Shlomo Yitzhaqi ("Rashi" 1040–1105) interpreted as arising "because the city is crowded and has no air . . . in the village the air is nice". The blackening of buildings was another effect of air pollution recognised in the ancient world e.g.,

Your fathers' guilt you still must pay,
 Till, Roman, you restore each shrine,
 Each temple, mouldering in decay,
 And smoke-grimed statue, scarce divine
 Odes and Carmen Saeculare
 Horace

Along side this recognition of the effects of air pollution a variety of laws developed (Brimblecombe 1987a). In Aristotle's *Athenian Politics* the duties of the *astymomoi* (controllers of the town) are described, among other things, as ensuring that for rubbish to be deposited beyond city walls. The Roman Governor of Britain from AD75–78, Sextus Julius Frontinus, was later appointed as Curator Aquarum in Rome. He improved Rome's water supply and argued, presumably through a miasmatic connection that he also reduced the effects of the city's "infamis aer . . . [or] gravioris caeli . . .". It also marked the rise of the professional administrator, as he saw his position as a very important one and left a book about the administration of Rome's water supply: *De aquis urbis Romae*. Roman nuisance law which treated issues of neighbourly responsibility in cities were known as the urban servitudes and these treated smoke as though it was water arguing: you could no more let water drain across a house than smoke. Relatively few solutions were available to solve air pollution problems in the ancient world, but the idea of zoning was apparent and in Rome glass making was moved to the suburbs where it caused less offence.

In addition to documentary materials there is archaeological evidence of past pollution. Tissue from Egyptian mummies shows evidence of air pollutants through the presence of anthracotic pigmentation in the lungs. This hints at anthracosis and silicosis in the ancient population, as mild forms of the occupational lung diseases that arise from inhalation of dusts. Capasso (2000) has argued that lesions found of the ribs of victims of the eruption of Vesuvius suggest that pleurisy was common in Roman times and this may be evidence of indoor pollution from burning vegetable matter lamp oils. There is skeletal evidence that Anglo-Saxon Britain had a high incidence of sinusitis and Wells (1977) believed this was related to the lack of chimneys in huts at the time which meant that the interiors became filled with smoke and thus aggravating the disease.

1.2 Air Pollution in Medieval Europe

Industries in the ancient world were often small, but some were large. Strabo notes the pollution from Spanish mining activities that occasionally spread over large areas. Mieck (1990) has termed the emissions from smaller localised industries as *pollution artisanale* and distinguished this from *pollution industrielle*. This distinction can be relevant when considering the development of legislation, as smaller scale enterprises can be controlled at a local level through by-laws, but large-scale pollution requires national legislation that did not arise until the nineteenth century.

A substantial shift in air quality medieval London came about through the use of coal after the depletion of convenient nearby wood supplies. This can be seen clearly in orders for building operations at Westminster in 1253 Henry III specify oak brushwood, while just 11 years later an order of 23 July 1264 reads “purvey for the King in London . . . a boat load of sea-coal”. Large quantities of fuel were required for the production of lime that was used as a mortar. While there were economic pressures to change fuel, coal gave rise to a smoke with an unfamiliar smell and the triggered miasmatic concerns over its effects on health (Brimblecombe 1987b).

One response was to promulgate legislation forbidding the use of coal and requiring a return to wood. Punishments were likely fine or confiscation of tools and destruction of the kiln, more than the death sentences imagined in more colourful accounts of medieval pollution (Brimblecombe 1987b). There is some evidence that chimney heights were of relevance in fourteenth century London as a case before the *Assize of Nuisance* reads “. . . the chimney is lower by 12 feet than it should be And the stench of smoke from the sea-coal used in the forge penetrates their hall and chambers so that (earnings drop to a third)”. Clearly there were also economic reasons for this case being brought. It may also be that some groups recognised that greater stability at night increased the potential for air pollution as the *Calendar of Early Mayor's Court Rolls for London* (1301–1431) reveals that a group of black smiths in fourteenth century thought that sea-coal should not be burnt at night. However this might have been a noise issue as there are

many complaints of the noise blacksmiths made late into the night (Brimblecombe 1987b).

Even where coal was not used large wood-burning industrial activities could create pollution problem, as it did in Imperial Rome. It is interesting to explore the situation during the medieval and early modern period of salt making in Lüneburg. This city is far enough north in Germany to make solar evaporation an inefficient method of salt production, so brines were heated to extract the salt. Lüneburg's salt was first mentioned in the year 956, when Emperor Otto the Great gave the customs for to the monastery of St. Michael's. Salt became a key product and important from 1276.

The mean production between 1554 and 1614 (the most productive time) was about 21,300 t per year. This required a wood consumption in the fifteenth and sixteenth centuries that is estimated between 48,000 and 72,000 m³ per year (Lamschus 1993; Witthöft 1989). At the peak of its production Lüneburg salt-brine was boiled in 54 boiling huts each with four lead pans (see Fig. 1.1) at salt-works close to the now-demolished St. Lambert's Church. The boiling huts were buried in the ground, so loss of brine and heat was minimised. The huts were more or less completely made of wood. The clay kilns and the lead pans had to be replaced after about 4 weeks of use. As the boiling huts had no smoke stack, smoke and steam was lost from the entrance and windows as described in Georg Agricola's *De Re Metallica* (1556):



Fig. 1.1 The salt works in Lüneburg from the Braun/Hogenberg plan of the year 1574. The works with the huts are shown within a circular enclave near St. Lambert's church



Fig. 1.2 A view of Lüneburg from Braun and Hogenberg *Civitates Orbis Terrarum* (1572) in a woodcut of Sebastian Munster (1550). This shows the smoke cloud near St Lambert's church, which was close to the salt works

At the top of the end wall are two small windows, and a third is in the roof, through which the smoke escapes. This smoke, emitted from both the back and the front of the furnace, finds outlet through a hood through which it makes its way up to the windows; (translated by Hoover and Hoover)

The works used a large amount of fuel, so pollution would have been inevitable. We can gauge the magnitude of this from early drawings of the town which show the smoke cloud above the city near St Lambert's church as especially noticeable (Fig. 1.2).

As in ancient Rome the technical control of air pollution from these early industries was difficult. Rather along the lines of the classical Mediterranean, activities such as tile, glass and brick making were moved to the outskirts and downwind of towns and cities such as York in England (Bowler and Brimblecombe 1990). Another possibility is to control the fuel type or permitted procedures, but there is no widespread evidence that this was tried, because as late as the 1660s the English environmentalist John Evelyn, was unable to raise much enthusiasm for these approaches.

1.3 Air Pollution in Early Modern Europe

The growth of interest in science characterised the seventeenth century and this was also apparent in the understanding of air pollution. In England this was seen in the work of many scientists within the early Royal Society (e.g., Brimblecombe 1978). John Evelyn in particular was noted for his pamphlet *Fumifugium* of 1661 which explored the causes and effects of air pollution in a coal burning city. However he

was not alone and Sir Kenelme Digby's atomic view on the corrosive effect of coal smoke deriving from his *Discourse on Sympathetic Powder* (1658) can be traced (Brimblecombe 1987b) even earlier to Margaret Cavendish's *Poems and Fancies* (1653) who wrote:

Is, Atomes sharpe are in that coale entire
Being strong armed with Points, do quite pierce through;
Those flat dull Atoms, and their forms undo.

Evelyn's work is notable because he can be seen as modern and taking a more environmental perspective being concerned with the broader social issue of pollution and their regulation. He was aware of the health effects as were other scientists such as Nathaniel Henshaw the author of a treatise entitled *Aero-chalinos, or, A Register for the Air* (1664). John Graunt an early demographer who looked at death rates and thought the high rates in London compared to the country might be the result of the pervasive coal smoke.

The botanist Nehemiah Grew wrote to the Secretary of the Royal Society in 1682, on the effect of pollution from lead smelters on health (Brimblecombe 1978). This was much in line with a long concern over the general health problems for miners. The issue is much discussed by Georg Agricola in the mid sixteenth century in *De Re Metallica*, although illustrations of the salt-workers from Lüneburg do not show them wearing a face-cover that Agricola had recommended. Nevertheless the salt-workers of Lüneburg were well cared for and they had access to the Hospital of the Holy Ghost. This dates from the thirteenth century and was located near to old St. Lambert's Church, adjacent to the salt workings. The ready access salt-workers had to the hospital may well have suggested they needed its services, but this could well have been because of workplace accidents rather than problems of industrial hygiene.

The descriptions of the smoke in salt huts described by Agricola would indicate that workers were exposed to high concentrations of combustion-derived particulate materials. Our knowledge of the importance of fine particles suggests this would have exacerbated a range of health impacts, either respiratory health directly or cardio-vascular health via the oxidative stress imposed after fine particles that make their way into the alveoli of the lung.

There may also have been contaminants on the particles that could have enhanced their health impact. The high chloride concentrations of the process of salt-making could lead to the production of chlorinated compounds such as the polychlorinated dibenzodioxins and polychlorinated dibenzofurans. These have the potential to cause chloracne and induce cancers.

The medieval and early modern period saw the first of industrial epidemiology with the work of Agricola and the seventeenth century Italian physician, Bernardino Ramazzini (*De Morbis Artificum Diatriba*). However, occupational cancer was not recognised till the late eighteenth century when Percival Pott made studies of scrotal and nasal cancers among chimney sweeps who were exposed to coal tars in the soot. Chloracne, an industrial disease, which reveals itself as blackheads, cysts, and pustules, often noticed around the cheeks, was not discovered until 1897 when Von Bettman noticed its occurrence among German industrial workers.

Initially it was thought to be the result of chlorine and only later associated with chlorinated aromatic hydrocarbons.

There was also an early awareness of air pollutant damage to crops from writers such as the Roman Pliny or the medieval Hildegard von Bingen (1140) who regarded salt and dust as unhealthy for plants. John Evelyn wrote of damage to plants in *Fumifugium* (1661) and Fabri (1670) that volcanic acid rain damages fruit (Brimblecombe 1987b; Camuffo 1992).

We cannot ascertain the importance of any impact of the air pollutants from Lüneburg's salt-making. Nevertheless it would be worth looking for descriptions of chloracne among its salt-workers and although agricultural practice was hardly likely to be affected by the deposition of pollutants the soils around the site might well still show evidence of deposits of carbon, and the polychlorinated dibenzodioxins and dibenzofurans. The history of these chlorinated aromatic compounds in agricultural soils is now well known, but also leads to the surprising conclusion that there are widespread natural sources of polychlorinated dibenzodioxins and dibenzofurans (Green et al. 2004).

1.4 Sanitary Reform and National Regulation

The growing industrialisation of late eighteenth century Europe, most particularly the wide adoption of the steam engine meant that regulators had to consider a more formal approach to controlling air pollutants. Early regulations can be found in France and England from the beginning of the 1800s. These regulations were driven by a growing enthusiasm for sanitary legislation to improve urban health. Although much of this legislation was concerned with housing and sewage, in England it was frequently accompanied by smoke abatement clauses from the late 1840s. These were not effective, but signalled a political awareness that grew through the century (Brimblecombe 2003c), so by the early twentieth century it was clear that the key to controlling smoke was controlling furnaces, especially with automatic stoking (Brimblecombe 2003b), although Germany had earlier emphasised training of stokers.

There was also a need to incorporate science into policy and ensure that legislation was national rather than local in extent. In England this was characteristic of the Alkali Act (1863) which regulated the emissions of hydrogen chloride from a growing industry that produced sodium hydroxide for soap making etc. The hydrochloric acid emissions had destroyed vast tracts of vegetation and a national approach to its control came to be overseen by a government scientist the Alkali Inspector, Robert Angus Smith. The sources of air pollution from large chemical plant and smelters were of increasing concern in the latter half of the nineteenth century, with important scientific developments in Germany, especially science of pollution damage to crops (Schramm 1990) along with work by the US Bureau of Mines (Holmes et al. 1915).

The changes we see reflect a growing professionalisation that characterised the late nineteenth century. The men, and by the 1890s women (Brimblecombe 2003a), who regulated environmental health in cities needed a considerable amount of training. The specialist role for smoke inspectors emerged by the first years of the twentieth century to add to the improved academic understanding of air pollution (Brimblecombe 2003b).

The First World War, economic crises and another war slowed the arrival of legislation, although these years were not without developments such as studies of the problem of burning coal waste piles (Sheail 2003). After the Second World War and particularly the London smog of 1952, legislation appeared in terms of the Clean Air Act 1956. This legislation was one of the first purely modern pieces of air pollution regulation and although it may not have been as successful as some imagine as a key factor in improved air quality, it was an important step. It seems to have gone beyond mere legislation and affects our concept of environment – it has made us aware that personal freedom may have to be limited if we desire environmental improvement (Brimblecombe 2006).

1.5 Increasing Complexity

The twentieth century witnessed new forms of air pollution and health impacts that were quite unique. Air pollution increasingly derived from liquid fuels, mostly used in automobiles, became mediated by atmospheric photochemistry. Photochemical pollution was first recognised in Los Angeles of the 1950s by Haagen-Smit and was later to be found almost everywhere. The ozone in smog has no ground level sources, but is a product of atmospheric chemistry. Thus pollution became separated from the precursor pollutants via complex chemistry. The sophistication and high level of technical input required to manage modern air pollution has raised concern among politicians and decision makers (Brimblecombe and Schuepbach 2006), especially when results of the modelling seem counter-intuitive as it might when increasing roadside nitric oxide concentrations can react with ozone thus lowering its concentration.

We can also trace parallels in the health impacts of air pollutants. In the past they often seemed to have respiratory impact, but the modern understanding of the effects of fine particles indicates that they impose a broad cardio-vascular insult (Brimblecombe 2009). The carcinogens also create uncertainty over the problems whether they have thresholds for injury. Lead has been identified as a neurotoxin. Persistent organic pollutants have been seen as endocrine disruptors have been associated with a range of reproductive problems, behavioural problems and impaired immune functions. More recently exposures to a widening range of chemicals have promoted the controversial issue of multiple chemical sensitivity. Such complications draw attention to the increasing need to sound science to be able to integrate with well informed policy.

References

- Bowler, C. and P. Brimblecombe, 1990: The difficulties of abating smoke in late Victorian York. *Atmospheric Environment* 24B, 49–55.
- Brimblecombe, P., 1978: Interest in air pollution among early members of the Royal Society. *Notes and Records of the Royal Society* 32, 123–129.
- Brimblecombe, P., 1987a: The antiquity of smokeless zones. *Atmospheric Environment* 21(11), 2485–2485.
- Brimblecombe, P., 1987b: *The Big Smoke*. Methuen, London.
- Brimblecombe, P., 2003a: Historical perspectives on health: The emergence of the Sanitary Inspector in Victorian Britain. *The Journal of the Royal Society for the Promotion of Health* 123, 124–131.
- Brimblecombe, P., 2003b: Origins of smoke inspection in Britain (circa 1900). *Applied Environmental Science & Public Health* 1, 55–62.
- Brimblecombe, P., 2003c: Perceptions of late Victorian air pollution. In: M. De Puis (Editor), *Smoke and Mirrors*. University of New York Press, NY, pp. 15–26.
- Brimblecombe, P., 2006: The clean air act After fifty years. *Weather* 61, 311–314.
- Brimblecombe, P., 2009: Transformations in understanding the health impacts of air pollutants in the 20th century. *The European Physical Journal Conferences* 1, 47–53.
- Brimblecombe, P. and E. Schuepbach, 2006: Communicating air pollution science to politicians and the public. *Journal de Physique* 139, 413–423.
- Camuffo, D., 1992: Acid rain and deterioration of monuments: How old is the phenomenon? *Atmospheric Environment* 26, 241–247.
- Capasso, L., 2000: Indoor pollution and respiratory diseases in Ancient Rome. *Lancet* 356 (9243): 1774.
- Gari, L., 1987: Notes on air pollution in Islamic heritage. *Hamdard* 30(3): 40–48.
- Green, N.J.L., A. Hassanin, A.E. Johnston, and K.C. Jones, 2004: Observations on historical, contemporary, and natural PCDD/Fs. *Environmental Science and Technology* 38, 715–723.
- Holmes, J.A., E.C. Franklin, and R.A. Gould, 1915: Report of the Selby Smelter Commission. Department of Interior, Bureau of Mines, Washington, DC.
- Lamschus, C., 1993: Die Holzversorgung der Lüneburger Saline in Mittelalter und früher Neuzeit. In: S. Urbanski, C. Lamschus, and J. Ellermeyer (Editors), *Recht und Alltag im Hanseraum. Förderkreis Industriedenkmal Saline, Lüneburg*, pp. 321–333.
- Mieck, I., 1990: Reflections on a typology of historical pollution: Complementary conceptions. In: P. Brimblecombe and C. Pfister (Editors), *The Silent Countdown*. Springer-Verlag, Berlin, pp. 73–80.
- Schramm, E., 1990: Experts in the smelter smoke debate. In: P. Brimblecombe and C. Pfister (Editors), *The Silent Countdown*. Springer-Verlag, Heidelberg, pp. 196–209.
- Sheail, J., 2003: Burning bings: A study pollution management in mid twentieth century Britain. *Journal of Historical Geography* 31, January 2005, 134–148.
- Wells, C., 1977: Diseases of the maxillary sinus in antiquity. *Medical and Biological Illustration* 27, 173–178.
- Withhöft, H., 1989: Das Maß der Arbeit an Sole und Salz. In: C. Lamschus (Editor), *Salz – Arbeit und Technik. Produktion und Distribution im Mittelalter und Früher Neuzeit. Förderkreis Industriedenkmal Saline, Lüneburg*.

Chapter 2

Modelling Air Pollution in Sixteenth Century Lüneburg

Peter Brimblecombe

As part of the workshop the students were presented with an exercise concerned with estimating the concentration and deposition of air pollutants around the salt works of Lüneburg during the sixteenth century.

We began with a short exercise that allowed students to reflect on issues that concerned late medieval Lüneburg from the perspective of influential civic groups (mostly merchant's guilds). Students were divided into groups representing urban guilds of: (1) saltmakers, (2) doctors and surgeons, (3) carters and haulers, (4) butchers, (5) bakers, (6) mayor and other elites. They discussed and ranked issues of concern to their guild considering issues such as: wood, food, trade, water, smoke, war and health or plagues.

During an excursion to the German Salt Museum at Lüneburg with an original boiling house from medieval times the students convinced themselves of the severe working conditions in the small rooms containing the boiling pans made out of lead. Figure 2.1 gives an impression of these working conditions, clearly indoor pollution was an important topic those days not because of incomplete combustion of the fire wood but also because lead from the pans entered air in considerable amounts.

Later in a computer laboratory they were provided with copies of SCILAB (similar to MATLAB) and two programs and their linked functions to model pollution. This allowed atmospheric dispersion of the pollution from the salt works to be modelled. Two approaches were adopted:

1. The average deposition flux of large particles was determined by considering the fall rate of the particles along with their dispersal by wind – (deposition model).
2. The concentrations in the air was estimated from a simple Gaussian plume models – (plume model).

The results gave a picture of air pollution in Lüneburg when it was a great salt producing town.

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Fig. 2.1 Worker at a lead pan in a salt boiling house. Photographic reconstruction of the medieval working conditions (Photo provided by Lüneburg Marketing)

2.1 Emissions

The models required that we estimate emission from the salt works Q_p from the fuel use. This was available from historical data for the annual firewood use and overall salt production (Withhöft 1989; Lamschus 1993). Emission factors were required for relevant pollutants to determine emissions. These were taken as:

- Soot from wood 12 g/kg
- Particulate matter from wood 15 g/kg
- NO_x from wood 0.2 g/kg
- PAH from wood 41,000 ng/kg
- Benzo(a)pyrene 1,200 ng/kg
- PCB from wood 550 ng/kg
- PCDD/PCDF from salt production 130 ng/kg – this has been enhanced tenfold over typical values for wood to allow for the large chloride concentration in the salt works

2.2 Deposition Model

In the case of long term deposition of particulate material we calculated the particle deposition around the sources using the early Bosanquet et al. (1950) model for the dispersion and deposition of large particles about a point source. This allows the flux of particles to the ground to be determined from as:

$$F_{\text{bosanquet}} * F_{\text{wind}} * Q_p * a * p * p / \text{He}^2$$

Input, along with some initial guesses of values, includes:

- x = distance from source
- Q_p = source strength in g/s
- $r = 25$; particle radius in μm
- $\rho = 1$; particle specific gravity
- $H_e = 10$; emission height in m
- $p = 0.05$; dispersion factor
- $u = 4.6$; average wind velocity in m/s
- f_i = the wind probability along eight compass points. N, NE, E, etc.
- v_f = fall velocity this includes Stokes settling plus the Cunningham correction with radius, mean free path (La , 0.065) in μm , i.e.,
- $vf = 1.210^{-4} * \rho * r * r * (1 + La/r * 1.26 + .4 * \exp(-1.1 * r/La))$

There are also two functions to be executed in SCILAB,

1. The Bosanquet function treats the fall of the particles to the ground and utilises the gamma function (Γ) available in SCILAB:

$$F_{\text{bosanquet}} = (v_f/p * u) * (H_e/p * x) (2 + v_f/p * u) * \exp(-H_e/p * x) / \Gamma(1 + v_f/p * x)$$

2. F_{wind} which determined wind direction in 45° sectors at each point on the grid from an averages from a year's modelled meteorological data.

The calculations, although not especially difficult, can be rather tedious, particularly if we need to determine the concentration and deposition at a range of locations and do this for many salt-pans (49 were used in the modelling exercise). SCILAB allowed these to be done rapidly for multiple pans and for many deposition points and then plotted out as contoured deposition fields, using one of the numerous plotting functions available in SCILAB.

2.3 Plume Model

The concentration of pollutants downwind from the salt works is determined using a simple plume model (e.g., Pasquill and Smith 1983). As the emission height is very low with little plume rise so a ground level source approximation was adopted (although this simplification was not possible under the deposition model).

$$c = Q_p / (\pi \sigma_y \sigma_z U) * \exp(-y^2 / (2 * \sigma_y^2))$$

c is the concentration and the whole expression has to be multiplied by a conversion factor to go from g m^{-3} to more comprehensible units such as from $\mu\text{g m}^{-3}$ or ng m^{-3} .

y is the distance off the plume axis in metres, z is the height above the plume axis in metres, σ_y and σ_z are measures of dispersion in the cross-wind and vertical