STUDIES ON THE CHEMISTRY OF ATMOSPHERIC DEPOSITION IN THE EIGHTEENTH AND NINETEENTH CENTURIES

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1. INTRODUCTION

This paper examines the development of research on the chemistry of atmospheric deposition in Europe in the eighteenth and nineteenth centuries, stressing both the theories underlying the research and the development of research methods.

Such research was motivated by a variety of theories and cultural contexts.¹ The earliest studies were directed at the cycle of the Aristotelian elements (Boerhaave, Musschenbroek), then at the theory of transmutation of the elements (Boyle, Lavoisier), the parallel between the chemical composition of meteorites and solutes (Zimmermann), subsequently leading to the source of nitrogen and nutrients used by plants (Liebig, Boussingault), a topic which was also of great practical interest. The last-mentioned subject was of central importance during the last century, partly because of the establishment of agricultural research stations throughout Europe. Other studies related the chemical composition of deposition to the growth of towns and the resultant pollution and to urban heating and industrial activity, such as the smelting of pyrites.² The theoretical evolution behind these research initiatives was accompanied by progress in analytical methods and instrumentation, with much lively debate about the relative merits of each method of analysis. The existence of the agricultural stations and the establishment of measurement networks made it imperative to consider questions such as the precision of measurements and the comparability of data produced by different laboratories.

2. EARLY STUDIES

Since atmospheric deposition, rain in particular, is part of our everyday life, it should come as no surprise to learn that the ancients too were interested in rain as an object of study. In the second book of the Meteorologica, for example, Aristotle described the salinity of the rain as the deposition of residues produced by combustion and by vegetal and animal growth. He stated that rainfall from the South and in early autumn is saltier, due to the fact that the southern winds in Greece are the warmest and blow from hot, dry regions, and therefore contain less moisture.³ Up to the seventeenth century, however, the composition of rainwater seems to have been a marginal subject and one which was largely dealt with in relation to commentaries on Aristotelian treatises.

For example, in his 'Commentaires' to the four books of the Meteorologica, the Ferrarese Jesuit Nicolò Cabeo (1585–1650) described rain as part of the

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perpetual circulation in which vaporous spirits and earth flow to the atmosphere through the agency of heat, then fall back to the Earth. Cabeo's treatment of the subject is interesting because it seeks a rational explanation for observed phenomena; in the case of rain with the appearance of blood mentioned by earlier commentators. For example, he ascribed the colour to chemical reactions.

2.1 Rain in the Treatises of Boerhaave and Musschenbroek

The research of the eighteenth century, as shown by two treatises, *Elementa Chemiae* by Boerhaave and *Introductio ad Philosophiam Naturalem* by Musschenbroek, was more developed. Boerhaave's theory—distantly echoing Aristotle—was that rain had a place in the cycle of matter between earth and atmosphere. In this scheme of things, substances and corpuscles emitted from natural and anthropogenic sources are diluted by the element air and transformed through the action of the element fire. Boerhaave stated that even earth and metals may end up in the air: 'Think of it, minerals in the atmosphere! It is as if one were to paint deer in the air and dolphins in the forests!' Rain then was to be thought of as a true cleanser (lixivium) of the atmosphere insofar as it collected all the various kinds of particles dispersed in it. Boerhaave connected the quality of the precipitation with the seasons, with whether or not it came during thunderstorms, and with the proximity of large towns. His only actual analytical observation was referred to almost in passing: that rainwater collected in perfectly clean jars during thunderstorms showed traces of nitrous fumes.

Musschenbroek followed the general lines of Boerhaave's theory but introduced original examples, and made his own comments. In his manual, he devoted twenty-three sections to listing sources of natural and anthropogenic emissions, including carbon dioxide and other spirits emitted by plants, the fetid vapours produced by steeping flax and hemp, the acid fumes released by ants, bees and bugs, the miasma produced by boiling whale blubber, and the explosive gases from mines, particularly coal-mines.

He summed this up thus: 'Many substances of different kinds are exhaled by the earth, rising and mingling with the air; they are the cause and the matter of the aqueous atmospheric events. It is necessary to know these substances, otherwise nothing may be known about these events... It will be of great value to list those things we know today, leaving to posterity the task of adding others.' And again, since the quality of the rain depends on a large number of factors, 'to understand precipitation events it would be well to observe them in their own regions, without drawing general conclusions, as they are different in different regions.' He cited the discovery of sulphate in rainwater by Grosse (1724, in Paris) and by Hellot in 1735: 'During some exceptional thunderstorms in 1735, Hellot collected rainwater smelling of sulphur which precipitated oil of calcium in the form of clots similar to those obtained by adding diluted oil of vitriol (sulphuric acid). Claude Grosse dissolved salts of tartar (potassium tartrate) in rainwater collected during a cloudburst to purify
it and obtained (by evaporation) vitriolated tartrate (potassium sulphate).11 Later treatises on physics, such as those by Dalla Torre12 and Poli,13 contain brief summaries which are obviously derived from Musschenbrock and Boerhaave. The Encyclopédie Méthodique gave several examples of extraordinary rains (of stones, blood, etc.) but also cited Boerhaave: the rain that falls during hot seasons, accompanied by a strong wind and in the vicinity of towns, is richest in dissolved substances.14 Eller’s approach was original: he noted that rainwater and dew collected in summer and put in stoppered glass bottles form a slimy sediment, which when analysed yielded an acid spirit that he ascribed to the vapours from decomposing animal and vegetable matter absorbed by precipitation.15 The works cited show how investigations into rainwater developed in the eighteenth century: there was a gradual progression from mere description of the phenomena to the rational interpretation of them. The context changed from that of the commentaries on Aristotelian physics to that of the new science of chemistry with its specific problems. And of these problems, one in particular—the transformation of water into earth—was prominent, as in the case of Eller referred to above.

2.2 The Transformation of Water into Earth and Rain

In fact, the idea of transformation had a long and respectable history, which sometimes coincided with research on rain, as is apparent from experiments performed in 1666 by Boyle (1627–91). To test the validity of the transmutation theory, after slowly evaporating rainwater in a clear glass vessel, he observed on the bottom a tasteless whitish deposit, which he identified as ‘fine earth’.16 Boyle repeated the experiment several times, first allowing the coarser particulate in the rainwater to sediment, and then repeatedly evaporating the clear liquid, every time obtaining the fine white sediment.

What, to our knowledge, was the first clear identification of chemical components in rainwater on record is contained in the work of another researcher who followed the same line—Olaus Borrichius (1626–90), physician to Frederick III and Christian V of Denmark. Around the middle of the seventeenth century he had distilled 900 lb. of rainwater and 100 lb. each of snowmelt water and hail, thus obtaining an earth which on being washed released in its turn a small part of sea-salt, while the residue, when heated, revealed traces of sulphur.17 Marggraf (1709–1802) also worked on transformation by sampling rain and snow in Berlin from December 1749 to May 1750.18 He used glass jars washed with distilled water, placing them in a suburban garden away from buildings and trees. In the residue he found common salt, calcareous earth and ‘nitric acid’.

Transformation was still an important open question around 1769 when Lavoisier (1734–94) began to work on it, condensing the results of his research into two memoirs. The first is a historical treatment of previous research, while the second includes the results of his analysis of rainwater samples.19 Interestingly, though Lavoisier’s subsequent revolution would involve a simplification of the concept of atmosphere, reduced from a chaotic mixture
of molecules and particles to a mere three gases and aqueous vapours,\textsuperscript{20} this
did not seem to stimulate research into rain. However, in an article on
"Chimie" in the \textit{Encyclopedia}, Fourcroy (1755–1809) wrote: 'Precipitation
chemistry should be considered a branch of chemistry, because this part of
human knowledge, up to now regarded as being entirely included in physics,
cannot be properly explained or understood or even perfected without the
help of chemistry.'\textsuperscript{21} This new departure suggested by Fourcroy should be
understood as a simplification of the concept of 'aqueous atmospheric events'
in the light of Lavoisier's new chemistry.

Indeed, although there were still some champions of transformation theory,
interest in it seemed to decline after Lavoisier's work. Wallerius (1709–85)
held that the atmosphere was a sort of reservoir of oily, inflammable, watery
and saline particles, the last of which were present in small quantities: 'It
should be observed that there can be no great abundance of these (particles),
as it is difficult to find in rainwater traces of these saline particles... as for those
who claim that the air is full of nitre, sulphur, and other solid particles, saline
or sulphurous, they are quite mistaken, as bodies of this kind cannot even exist
in substance.'\textsuperscript{22} Bergman (1735–84) was apparently more interested in purely
analytical aspects. He noted the presence in snow of a minute portion of
calcareous sea-salt (calcium chloride) and slight traces of nitrous acid, and that
rainwater was ordinarily adulterated by the same substances, absorbed from
the atmosphere, but in larger quantities. He further observed that when it had
rained or snowed for several days, the rainwater and the snow were much
purer.\textsuperscript{23}

At the end of the century Chaptal, when the debate on the transformation
of water into earth was in decline, made reference to the effect of the sea and
wind on the quality of the rainwater. 'I observed in Montpellier that the
rainwater falling during storms had more impurities than that of undisturbed
rainfall; that the first water to fall is less pure than that which has fallen for
several hours or after several days of rain; that the rain blown by the south wind
contains some small quantity of sea-salt, while that blown by the north wind
does not contain one atom (of sea-salt).\textsuperscript{24}

3. THE NINETEENTH CENTURY
3.1 Plants and Rain

About the middle of the nineteenth century, there was a sharp increase in the
number of publications on chemical analyses of rainwater (Fig. 1\textsuperscript{25}).

Studies performed at this time dealt primarily with compounds of nitrogen
(nitrate and ammonium), and were largely carried out in the field of
agrochemistry. The major problem in this area, and one which occupied the
most prominent chemists of the time, was that of plant nutrition. Rainwater
analysis was one way of verifying the various theories under consideration. It
will therefore be useful here to make a brief digression on the various plant
nutrition theories, to show the links among them, research on the atmosphere
and research on precipitation.
Opinions diverged on the function of saltpetre (potassium nitrate) which had been found in plants by Glauber (1604–70): some regarded it as quite useless, while others viewed it more positively. After 1700, English researchers concentrated on the practical side of the question, while the French preferred to develop the theory. 25 Louis Lemery (1677–1743) was the first to show that the saltpetre in the soil was of organic origin. Nitrification was an important topic for both agriculture and the military (saltpetre being used in making gunpowder) for over a century, and attracted the attention of eminent researchers like Lavoisier and Gay-Lussac, 27 leading eventually to the work of Liebig and Boussingault, which, as will be seen, was connected with rainwater analysis.

As for the mechanics of nutrition, it was towards 1690 that Homberg (1632–1715), basing his conclusions on the thousands of plant analyses performed by Claude Bourdelin (1621–99), declared that plants take up a volatile acid from the soil and synthesise volatile urinous acid (ammonium carbonate) and fixed lye (potassium carbonate). At the same time, Mariotte (1620–84) put forward the hypothesis that all plant nutrients are derived from earth and rain. 28 At the beginning of the eighteenth century, Hooke (1638–1703) portrayed plants as

![Graph showing the number of papers published on deposition chemistry and the number of years of studies.]

Fig. 1. Number of sampling years and of published papers on the chemistry of atmospheric deposition.
having two types of root, one type reaching into the earth, the other (the leaves) into the air, with both types having the function of absorbing food. Wallerius put forward the theory that plants which grow on bare rocks and which are rich in resinous matter, such as pines and firs, take this substance from the air. Saussure (1767–1845) pointed out that some mineral components are necessary for plant growth. Around 1810, Davy (1778–1829) summarised the situation as follows: 'There is no one principle that is responsible for feeding vegetal life, neither carbon, nor hydrogen, not nitrogen, nor oxygen alone, but all of them together in various states and in various relationships.' During the first decades of the nineteenth century, Thaer (1752–1828), once the physician of George III of Great Britain and later a Prussian minister of agriculture and professor in Berlin, pronounced his 'humic' theory, the substance of which is that plants take their food from the humus of the soil. Around 1820, his pupil Sprengel (1787–1839) stated his belief that certain elements are essential for plant life and raised the question of their origin.

It should be noted that research into plant nutrition at this time often refers to the wider theme of the circulation of elements through the atmosphere, a widely-held idea in the eighteenth century. Cabeo, for example, had stated that the circulation of substances was the perpetual state of flux through which everything in the atmosphere was generated and destroyed; and Stahl (1661–1734) had suggested that there was a continuous movement of matter between minerals, plants, animals and atmosphere which was independent of divine intervention. In 1819 Gmelin adopted this idea in speaking of inorganic compounds transported by water and wind on the surface of the earth and taken up by plants. In the 1890s, the atmosphere would be once again indicated by Boussingault (it was no coincidence that he was to play a prominent part in rainwater analysis) and Dumas as the link between the vegetal world, with its reducing action, and the oxidising animal world.

These theories of plant nutrition and the global circulation of matter formed the background for research performed in Germany in 1820–27 by Liebig and Brandes on the chemical composition of precipitation.

3.2 Meteors, Meteorites and Nitrates

This was the research focus of the investigations into the origin of atmospheric particles performed by W. Zimmermann (1780–1825), professor of chemistry at Giessen who was interested in whether there was a relationship between meteorites and precipitations. The thread of his argument may be summarised as follows: if atmospheric particles and meteorites have a common origin, then their chemical composition must be similar. Since analyses of meteorites revealed high concentrations of iron and nickel, the same elements should be found in the particles washed down by rainwater.

From 3 May 1821 to 31 December 1823, at Giessen, Zimmermann took 280 samples of rainwater in five different places and at different heights from the ground. He then made a series of qualitative tests on the sample residues,
identifying among other elements chloride, sulphate, iron, manganese and, only in some samples, nickel (Table 1). His exposition was clearly linked with the treatises of Natural Philosophy of the eighteenth century, as may be understood from the following statement: "One slowly became used to viewing the atmosphere only as a mixture of the three well-known gases and water vapours. Since, in the air, the precipitations were able to incorporate only gas, not earth or salts, one gradually became used to seeing, through this hypothesis, that this part of natural history was completed."\(^{30}\) At the same time Brandes published in Schweiggers Journal für Physik und Chemie, of which both he and Liebig were members of the editorial committee, the results of the analysis of 90 rainwater samples collected throughout 1825 in Salzufeln (Germany).\(^{40}\)

Brandes began his work by recalling the theme of the circulation of matter: "The fact that all forms of life are connected with the circulation of the mixture of vapours formed by the atmosphere encourages us to broaden our knowledge of the latter." Farther on, referring to the origin of the substances, he added: "We know so little about many of the components found in the air, apart from oxygen, nitrogen and carbon dioxide; where these substances come from, whether they are created in the atmosphere through some unknown cause, or if they originate on the earth."\(^{41}\) Brandes favoured the latter hypothesis, taking up a position in contrast to that of Zimmermann. He divided the substances identified into 'organic' and 'mineral' and recalled that the former had previously been observed by Marggraf as blackening of the

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residue during ashing), Hermbstädt (1760–1833) and Dobereiner (1780–1849), whose research had been undertaken following suggestions by Goethe (1749–1832). Brandes was particularly careful about collecting the samples: every morning and evening when it rained he removed the receptacle from its position on the roof of his house, washing the fresh one with distilled water and checking for the absence of chloride with silver nitrate solution. To avoid contamination, he wore gloves when handling the equipment, never using his bare hands. Brandes quantitatively determined a series of substances, weighing the residue of the rainwater collected monthly. He believed that the substances present in rainwater derived essentially from the earth's surface (in particular from the soil), from seawater and from anthropogenic emissions (for example, from factories). Brandes thought that the substances present in rainwater could explain how mosses and lichens were able to grow on bare rock, in the absence of humus, and in general could throw light on the usefulness of the substances in the economy of plants.

The different nomenclature adopted by Brandes and Zimmermann (see, for example, the pairs of terms in Table 1: potash-potassium chloride; lime-calcium sulphate; iron-iron oxide) illustrates how the two authors referred to different paradigms, by this time on the two opposing sides created by Lavoisier's revolution. This is also reflected in the different levels of care they devoted to experimental procedures. While they both paid great attention to the causes of contamination during sampling, Zimmermann still used 'old-fashioned' analytical procedures (for example, the blowpipe) and, unlike Brandes, was interested solely in qualitative results.

3.3 Liebig

On appointment to the University of Giessen, Liebig did not devote himself only to organic chemistry, but also, for as long as two and a half years, to rainwater analysis. Liebig (1803–73) did not believe that rainwater could contain iron, manganese and nickel, and on his appointment as professor at Giessen, where he was of course also Zimmermann's colleague, began a lengthy series of studies to prove it. In an abstract published in 1827, he reported analysing the residue of seventy-seven rainwater samples which he collected personally, as well as fifty which he inherited on Zimmermann's death. He found nitrate only in the samples collected during thunderstorms, using an old qualitative test based on the crackling sound nitrate makes when thrown onto burning coals.

The presence of nitrate in rainwater was already known to Marggraf, and Cavendish (1731–1810) had also shown that electrical discharges (and therefore probably also lightning during thunderstorms) produced nitrate in moist air. Liebig however thought that nitrate of meteorological origin could explain the presence of nitrate in spring water, in the absence of decomposition (nitrification) of plant or animal matter. Thus, Liebig was already interested in problems of plant nitrification and nutrition early in his career. It was no coincidence that the title of his dissertation, written in 1823, was
"Ueber das Verhalten der Mineralchemie zu Pflanzchemie."\textsuperscript{45}

Liebig resumed and developed these ideas in 1840 in his \textit{Die organische Chemie in ihre Anwendung auf Agricultur und Physiologie}, where he states confidently: 'The primary source of plant nutrition is essentially inorganic in character'.\textsuperscript{46} And in a note he wrote himself for a review of the same text for the English press, he recalled the analysis of ammonia in rainwater that he had carried out at Giessen: 'Dr Liebig has discovered the hitherto unknown source of the nitrogen in plants, from which derives gluten, the most important animal nutrient. He has found in it rainwater and demonstrated that it is the exact equivalent of the nitrogenous substances of fermented urine and animal excrement.'\textsuperscript{47}

Liebig collected rainwater at a spot 600 paces from Giessen, to the southwest, upwind. He distilled several hundred kilograms, first acidifying the water with hydrochloric acid; to identify the ammonium ion in the residue he precipitated it with platinum chloride. He also found ammonium in snow. His enquiries led him to conclude that rainwater always contained ammonium, in greater concentrations in summer than in winter, and on the first day of rain more than on subsequent days. Furthermore, his strict adherence to his hypothesis meant that he did not consider the presence of sulphur in rainwater, believing it to be assimilated by plants solely from the soil.

3.4 Boussingault and the Nitrogen Question

Liebig's theory of the meteorological origin of the nitrogen taken up by plants received a severe blow with the failure of his patent chemical fertiliser containing no nitrogen compounds.\textsuperscript{48} However his theory of the source of nitrogen in plants aroused much controversy which had the corollary of stimulating several series of rainwater analyses after 1850.\textsuperscript{49}

A decisive stimulus to this research, however, came from the work of Boussingault (1802–84), who in 1838 began to devote himself to the topic, accurately determining the nitrogen content of plants with the method recently devised by Dumas.\textsuperscript{50} Boussingault was cautious about the sources of nitrogen: 'In some circumstances certain substances are able to take nitrogen from the air; but in what circumstances, and in what state is the nitrogen that is fixed by the plants? This is a topic on which we are still ignorant. The nitrogen may enter the plants through aerated rainwater, which is absorbed by plants. Finally, it is possible, as some doctors think, that there exists in the air an infinitesimal amount of ammonia vapour.'\textsuperscript{51}

For Liebig, on the other hand, the solution was simple: the sought-for source was the ammonia present in the air. Subsequently, in 1840, Boussingault seemed to look favourably on Liebig's theory: 'Monsieur Pelouze has told me of your discovery of ammonium carbonate in rainwater.... I am in agreement with your opinion and I also see here the most important source of nitrogen for crops, a source I have previously sought in vain.'\textsuperscript{52} All the same, it was not until a decade later that analyses of ammonia in rainwater were performed, and then only after Peligot (1811–90), a pupil of Gay-Lussac (1778–1850).
perfected a fast, accurate volumetric technique for determining it. The technique used a basic solution which on distillation yielded ammonia, which was then made to bubble in water and titrated with sulphuric acid. With this method, from May to November 1853 Boussingault determined ammonia in seventy-seven rainwater samples collected on his Liebenfrauenberg estate near Bechelbron in the Vosges. From July 1856 to November 1857 he examined the nitrate content of ninety precipitations (rain, snow and hail) and found a mean value of 0.05 mg N-NO₃ 1⁻¹.

Boussingault found that fog contained concentrations of ammonia that were much higher than those of rain. For example, 'a particularly dense, odorous and persistent fog covering the Rhine Valley between the Black Forest and the Vosges from 14 to 16 November 1853 was found to contain 50 mg of ammonia per litre.' On the 19 December 1857 in Paris he analysed fog water which was amber in colour, smelled of smog and gave a basic reaction, and contained 10 mg 1⁻¹, while a fog of 23 January 1854 yielded as much as 138 mg 1⁻¹. In his view, these concentrations were enough to account for the irritation of the respiratory tract produced by breathing in the fog, and showed the importance for hygiene of this kind of work.

In 1850 Ville (1824–97) had suggested that atmospheric nitrogen was assimilated by Leguminosae. To resolve this question, Boussingault conducted a long series of experiments in which plants were grown in controlled conditions, culminating in the summer of 1854 in a test before an arbitrating committee. In Boussingault's view the data showed that the nitrogen in the air was not assimilated, but the committee considered the question still largely open.

In 1856, with the aim of testing the absorptive properties of soils for manure, Way conducted some experiments which further complicated the puzzle of the source of nitrogen in plants. In fact, he revealed that agricultural land in Rothamstead lost much more nitrate through drainage than it gained from rainfall. Way also noticed that while the ammonia concentration in the rainfall of large towns was more or less comparable, Barral had found in Paris (see Table 2 below) a nitrate concentration which was strikingly different from that of London (around 0.2 mg NO₃ 1⁻¹). He therefore made the observation that 'unless there be some cause connected with the difference of fuel employed in the two capitals (one being coal and the other wood), I should be inclined to think that M. Barral's determinations of nitric acid were in error from the faultiness of the method to which he was compelled to have recourse.' Boussingault was of the opinion that the ammonia concentration found at Rothamstead was rather higher than that measured at Liebenfrauenberg in 1857 because that year was particularly wet. The fact that the ammonia concentration was much higher in Paris 'could be explained by the circumstances which tend to develop ammonia in a place where there is a large conglomeration of population.' Significantly, Boussingault said nothing about the discrepancies regarding nitrate. The high value found by Barral certainly appeared to lend more support to Liebig's hypothesis, which was that
the load of atmospheric nitrogen was an adequate source for the cultivation of crops.

Also in 1856, Boussingault's attention was attracted to a discovery by Bineau who had noticed that analyses of ammonia in rainwater samples repeated after the interval of a few months gave much lower values and at the same time algae had developed in the samples. He then inoculated an ammonium solution of known concentration with these algae; after ten days he found that the ammonium had decreased by three-quarters in the samples exposed to light, and by half in those kept in the dark. Boussingault initiated a series of studies which by 1860 had led him to suspect that micro-organisms in the soil were able to fix nitrogen. His pupils Münz (1846–1917) and Schloessing (1824–1919) continued working in the same direction and in 1877 put forward “nitric ferment” (micro-organisms) as the agent of the nitrification of the soil. It was about 1886 that Hellriegel and Willfarth finally identified the nitrogen-fixing bacteria in Leguminosae. One result of solving the problem of the source of nitrogen was a decline in research into the chemistry of rainwater shown in Fig. 1.

3.5 Other Nineteenth-Century Researches

In 1834, at Freiberg in Saxony, Lampadius (1722–1842) quantitatively determined oxygen, nitrogen and carbon dioxide, and qualitatively nitrate, sulphate, sodium and calcium chloride and organic substances in 213 samples of rainwater, snow and hail. He was working on the possible influence of rainwater on the composition of spring water in the Erzgebirge. In his opinion the main cause of the pollution (Verunreinigung) of rainwater was the washing away of dust particles floating in the air, which in turn reflected the type of land surface it came from. The conclusions of his research may be summed up as follows: (a) the particulate found in rain did not come from meteorites (as Zimmermann thought) but from the ground; besides, he had never found any trace of nickel (an indicator of meteoric origin of the particulate); (b) the sea-salt was from an oceanic source and, for this reason, it was measurable, especially when the wind was blowing from the west; (c) the organic substances present in rain can contribute to the formation of humus in the soil and would explain the presence of vegetation in barren areas covered with sand or rock; (d) the precipitation which followed long periods of drought contained the greatest quantity of particulate. Lampadius found that significant quantities of sulphurous and sulphuric acid, and traces of arsenic, were present in rain samples taken near metallurgic factories where locally extracted lead and silver ores were processed. He noticed that these depositions caused considerable damage to plants, except for cabbages, cauliflower and turnips, which were quite unaffected.

During the second half of the nineteenth century chemical analyses of rainwater were performed principally at the agricultural research stations which were being set up at that time, mostly in Germany, creating an environment in which Liebig's theories were discussed and tested. The first of
a series of Agricultural Research Stations (Landwirtschaftlichen Versuchsstationen) was established on 28 December 1852, in Möckern (Saxony). By 1871 they were to number as many as fifty-one. In the three years from 1864 to 1866, a research project was carried out by some Prussian agricultural stations to test the nitrogen content of rainfall. The Central Commission for chemical-agricultural research in the field (Central Komission fuer das Agricultur-chemisch Versuchwesen), created for the occasion, brought together several Agricultural Research Stations and Agricultural Colleges, and had two objectives: (1) to evaluate the deposition (flux) of nitrogen carried annually by the rain to the ground, (2) to verify if the amount of deposition varied from year to year and from region to region. The results of the first series of tests, in 1864–65, showed great variability both in ammonium and nitrate values, with the highest deposition value about thirty times higher than the lowest value. The commission discovered that an important source of error probably lay in the concentration of the samples and suggested evaporating them without boiling; it was subsequently decided to continue the research in 1865–66. On this occasion the results of five stations showed nitrate concentrations in the range 0.6–1.9 mg N-NO₃ per litre.

In England, Lawes (1814–1900) from 1834, and later Gilbert (1817–1901), a pupil of Liebig’s, were beginning to work with agrochemicals at Rothamstead. Their first analyses of ammonium in rainwater date from 1853–54; further analyses, extended to include nitrate, were made by Way (1821–84) in 1855–56. Research on ammonium in rainwater at Rothamstead was not resumed until 1877 and then continued until 1916 (with a break from 1885 to 1887); nitrites were determined from 1866, chlorides from 1877, and sulphate every three months from 1881 to 1887. For nitrate analysis, Schloessing’s method was initially adopted, with the subsequent use of the reduction from nitrate to nitrite through zinc-copper; the analyses were normally performed on monthly samples. This last detail led to the supposition that the nitrogenous compounds, kept for such a long period, might have been consumed by bacteria and/or algae, as Bineau demonstrated at Lyons in those very years, explaining thus the particularly low concentrations of these compounds found at Rothamstead. Other analyses focused on chloride in rainwater for agricultural purposes and the health risks produced by the polluted atmosphere in towns, leading to the finding that the air was acid and the rain basic.

Another research in the medical field was that of Bence-Jones, who in a footnote to one of his works on physiology describes some qualitative determinations of nitrate in rain collected in London and the surrounding area.

On 20 February 1852, a memoir on the collection and analysis of rainwater from July to December at the Astronomical Observatory of Paris was presented at the Académie des Sciences by Barral (see Table 2). Barral’s memoir was enthusiastically approved by the secretary of the Académie, Arago. He had found that the composition of the atmosphere was well established as regards
nitrogen and oxygen, whereas the situation was very different with regard to the other components. Barral had been the first to demonstrate—and in this he corrected Liebig—that nitrate was always determinable in rainwater. In Arago’s view these field experiments were important, as ‘the atmosphere (is) comparable to a great laboratory in which reactions occur over long periods, reactions which it would be scarcely possible for scientists to reproduce otherwise in their laboratories;’ furthermore these experiments were of interest for the fields of hygiene, agriculture, meteorology and physics.69

Arago was conscious of the limitations of Barral’s research, which derived from the fact that he had had to use a wooden rain-gauge, leaving himself open to criticism (by Bineau for one) as to the possibility of sample pollution. To rectify this drawback, he asked the Académie to provide funds for a rain-gauge made of platinum. Barral was able to have the use of this apparatus within a short time.70 However, a comparison between the results obtained with the new and the old methods did not reveal any differences.

It is likely that the favourable reception given to Barral’s work helped to instigate a series of réclamations de priorité by Chatin, Marchand, and Meyrac, who had previously sent to the Académie memoirs of their own on the determination of nitrogen compounds in rainwater. Meanwhile,71 in 1851, at Caen, Pierre determined chloride, ammonia and sulphate.72

In 1854 at Marseilles, Martin successfully quantified chloride, but was forced to admit failure in the case of nitrate.73 J. F. Heller had regularly found nitric acid both in the air and the rain in Vienna in 1852.74 Chatin hypothesised that

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<th>Author Site</th>
<th>Pierre75 Caen</th>
<th>Barral76 Paris</th>
<th>Marchand77 Paris</th>
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<tr>
<td>Sodium Chloride</td>
<td>4.4</td>
<td>3.6</td>
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<td>–</td>
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<tr>
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<td>0.3</td>
<td>2.1 (*)</td>
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<tr>
<td>Calcium chloride</td>
<td>0.2</td>
<td>6.5 (**)</td>
<td>–</td>
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<tr>
<td>Sodium sulphate</td>
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<td>–</td>
<td>10.07</td>
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<tr>
<td>Potassium sulphate</td>
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<td>0.7</td>
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<tr>
<td>Magnesium sulphate</td>
<td>0.6</td>
<td>–</td>
<td>trace</td>
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<td>Ammonium</td>
<td>–</td>
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<td>–</td>
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<td>Organic substances</td>
<td>–</td>
<td>–</td>
<td>24.88</td>
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<tr>
<td>Nitrate</td>
<td>–</td>
<td>12.6</td>
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<tr>
<td>Chloride</td>
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<td>–</td>
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<tr>
<td>Ammonium bicarbonate</td>
<td>–</td>
<td>–</td>
<td>1.74</td>
</tr>
<tr>
<td>Ammonium nitrate</td>
<td>–</td>
<td>–</td>
<td>1.89</td>
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(*) Expressed as MgO  
(**) Expressed as CaO
goitre was due to a deficiency of iodine, and (successfully) sought it in precipitation.\textsuperscript{74} His results were however contradicted by De Luca\textsuperscript{79} and MacAdam.\textsuperscript{80} Active in the fields of hygiene were Bobierre\textsuperscript{81} at Nancy, and De Luca (1820–80), who from 1860 to 1891 sampled rainwater at various heights in Pisa, making use of the Leaning Tower.\textsuperscript{82}

Bineau, in Lyons, also considered the question of urban pollution. From 1851 he determined ammonium and nitrate concentrations in rainfall, finding winter maxima and summer minima, contrary to the findings of Liebig. Bineau’s conclusion is significant: ‘I need not go back over the facts, often quoted in this memoir, which testify to the power with which the influence of the city of Lyons makes itself felt in the various fields studied. These facts show the enormous variations exerted by great centres of population, both within themselves and towards the outside, as regards ammonia and organic compounds dispersed in the atmosphere, and as regards the same compounds which are found in precipitation.’\textsuperscript{83}

Unlike Barral, Bineau did not measure nitrate in rainwater. This gave rise to a dispute during which Barral was persuaded to state explicitly that: (a) the quantity of dissolved substances in rainwater depended on where the sampling was performed; (b) Bineau’s rain sampler was smaller in diameter than the one used in Paris (which had a surface area of about 0.5 m\textsuperscript{2}), and so his results could have been less exact; (c) the conversion of ammonia to nitrate, a hypothesis put forward by Bineau to explain the high nitrate values found in Paris, was possible both with samplers made of wood (Paris) and metal (Lyons); and (d) the concentration of substances in rain water had a marked seasonal trend, and therefore the results of Lyons and Paris, which referred to different seasons, were not comparable.\textsuperscript{84}

Different again was the approach of Goppelschröder (1837–1919), (a pupil of Schönbein (1799–1868)) in Basel around 1870. In his opinion, the study of rainwater could not be reduced to a mere catalogue of the substances it contained, but there also had to be an inquiry into the chemical processes occurring during the water cycle. Goppelschröder was to perform an extended series of analyses, mainly of nitrate in rain, river, lake and spring water.\textsuperscript{85}

In 1882 Boussingault made what was probably the first litmus paper measurement of acid snow, during the event sampled at 2100 m a.s.l. on the Combe glacier (Val d’Aosta, Northern Italy).\textsuperscript{86} Other components were also attracting the attention of researchers. Struve and Emil Schönbe, exploiting research by Schönbeim and Meissner, were looking for hydrogen peroxide. Schönbe’s researches at Moscow are interesting because they place the accent for the first time on possible cyclical trends of this chemical species. He found seasonal maxima in July and minima in winter; daily maxima were around midday, with minima during the night. With the aim of evaluating whether there were gradients over the whole surface of the earth, he suggested that there should be a survey ranging from the tropics to the poles.\textsuperscript{87}

To evaluate the load of phosphate to agricultural land, Barral determined it in rain, noting that all the elements essential for the development of micro-
organisms, as shown by Pasteur's studies, were in this way present in the atmosphere. Chambrier observed in 1871 that there was an excess of nitrate over nitrite if the precipitation fell during a thunderstorm, whereas there was in general an inverse relationship in other kinds of precipitation.

The mass of accumulated data was such that the first syntheses, by Ville and Reichardt, appeared in the 1860s. Figure 2 provides an overview of the research performed to this point; the relevant bibliographic references are given in Table 3.

4. Development of Analytical Techniques and Their Influence on Rainwater Analyses

Research into rainfall in the nineteenth century owes much to the development of methods of chemical analysis. This was a rapidly evolving field, especially from 1800 on, with the union between scientific and manufacturing interests which created the distinction between pure and applied chemistry and to which the profession of "chemist" may ultimately be traced. Examples of how theoretical preconceptions can prevail over technical-analytical means are provided by the history of determinations of sulphate and nitrogenous

![Map of Europe with sampling stations](image)

Fig. 2. Sampling stations of atmospheric deposition in operation in Europe. Numbers refer to Table 3.
compounds in rainfall. Analytical methods for determining sulphate were already fairly accurate and sensitive enough for this purpose around the middle of the nineteenth century, but sulphate was hardly ever determined in precipitation, because it was not considered important. Liebig, for instance, stated that the only source of sulphate for plants was the earth, this probably helped to inhibit research on this chemical species in rainfall. On the other hand, during this period the determination of nitrogenous compounds, nitrate in particular, was still imprecise and difficult, but the determinations were nonetheless extensively used because of the importance of the scientific problems associated with the compounds. The development of analytical methods in this latter case was extremely important, and it was perhaps the volumetric technique which made the greatest contribution. Gay-Lussac in

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<td>1 Paris91</td>
<td>Barral, Albert-Ley,</td>
<td>22 La Guardia112</td>
<td>Miller</td>
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<td></td>
<td>Anonymous</td>
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<td>Martin</td>
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<td>5 Marseille95</td>
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<td>6 Lyon96</td>
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<td>30 London120</td>
<td>Bence-Jones</td>
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<td>7 Pic du Midi97</td>
<td>Eriksson</td>
<td>31 Western Alps121</td>
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<td>8 Feldkirch98</td>
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<td>9 S. Michele all’A-</td>
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<td>34 Pavia124</td>
<td>Cossa</td>
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<tr>
<td>10 Florence100</td>
<td>De Luca</td>
<td>35 Scandicci125</td>
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<td>11 Pisa101</td>
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<td>14 Rothamstead104</td>
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<td>15 Kollin105</td>
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<td>21 Copenhagen111</td>
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particular is to be credited with a fundamental role in spreading information about the new technique and its development. In fact, he published a long series of eminently practical instructions which, together with his personal prestige, greatly increased the popularity of titrimetric techniques. The refinement of volumetric determinations of nitrate and ammonia, especially by Pelouze, Gay-Lussac’s pupil and his successor at the Ecole Polytechnique of Paris, made the analyses of these species in rain water considerably easier.

Analytical methods were also used for rhetorical purposes, insofar as discussion of their precision and reliability was sometimes subordinated to other aims, such as upholding or discrediting a theory. Liebig, for instance, discussing the research performed at the German agricultural stations, treated the data selectively, choosing those which confirmed his hypotheses and ignoring criticism of the analytical methods used. No less important was the existence of specialist reviews such as the Zeitschrift für Analytische Chemie, first published in 1862 by R. Fresenius (1818–97). They played an important role in publicising and testing analytical protocols. In short, chemists were now confronted not only with alternatives among different explanations or research projects, but also among different instruments and techniques.

The considerable discrepancies that emerged between analytical results brought the question of the validity of analytical methods to the forefront of scientific debate. Between 1862 and 1882 there were at least five bibliographic reviews treating nitrate determination alone. In rain water and natural water problems arose essentially from the extremely small concentrations present. Eder, for example, estimated losses of around 10% in the determination of 50 mg of nitrate (a much greater quantity than is usually found in 1 litre of rainwater) with errors increasing exponentially with decreasing quantity. Martin, in a test which was often quoted at the time, failed in his attempt to determine nitrate in rain water concentrated 100 times, using Pelouze’s method developed for gunpowder.

The fact that different scientists, within such a short space of time, should propose such a large number of variations of analytical methods suggests that the methods used were unsatisfactory. The problem was actually that they took a long time and required skilled operators, due to the rather complicated experimental apparatus involved. A further reason was the establishment of agrochemistry as an autonomous branch of science, in which analytical methods originally used in the chemical field had to be adapted to new purposes. Boussingault, for example, in 1857 developed a method for determining nitrate in rainwater based on a reaction, discovered by Liebig, between indigo in sulphuric acid and nitrate.

In determining ammonium, the gravimetric method with platinum chloride, used by Liebig, was very slow and therefore unsuitable for routine analyses, requiring as it did the concentration by evaporation of large quantities of samples. It was largely superseded by Pelouze’s method (1847–48). This consisted of making the sample basic, distilling its ammonium in a solution of sulphuric acid of known normality, and back titrating with caustic
soda. Knop’s method for ammonium determination was apparently applied only in Prussian agricultural stations. It involved transforming the ammonium into gaseous nitrogen through the action of bromine in caustic soda and the gas-volumetric determination of the evolved nitrogen. Nessler’s method was not introduced until later; originally it was not a colorimetric technique but involved precipitating the ammonium as an iodomercurate complex, separating this by filtration, dissolving it and reforming the ammonia, and finally distilling the ammonia with a final titration.

Lastly, as regards the collection of the samples, the risk of contamination by birds, insects and dry deposition was realised early; Boussingault devised a series of mirrors to keep birds away from the pluviometer.

5. The End of the Century

After Hellriegel (1831–95) satisfactorily resolved the problem of the source of nitrogen around 1886, there was a drop in the number of investigations, but rainwater analyses continued to be used to calculate the nitrogen budget of crops. Some series of analyses went on at Rothamstead and in Paris at the

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Fig. 3. Sampler of atmospheric deposition used by Boussingault. The apparatus was around 1 m high and 1.2 m in diameter. Nails and dangling mirrors were used to discourage birds.
Montsouris observatory under Albert-Levy, who studied precipitation in the thirty years from 1876 to 1906. From 1889 to 1891, Petermann and Craffin determined ammonia and nitrate in rain, snow, hoarfrost and fog, at the Belgian Agricultural Station of Gembloux; they found on average a deposition of 10.3 kg N ha⁻¹, very close to the mean in studies at German and Italian agricultural stations (11.3 kg N ha⁻¹) but much higher than the Rothamstead data (only 7.36 kg N ha⁻¹). However, they considered these differences to be unimportant, preferring to emphasise the fact that in all the studies the ammonia percentage in the total nitrogen was practically constant (around 78–76%). Chemical studies had started in Italy in 1860; as Basile observed in his paper of 1895, they were not few, but they lasted only for short periods. A contribution was made to these studies by De Luca, who had assisted Barral in his work on rain at the Paris observatory. Much of the Italian work too was carried out at agricultural stations established from 1871 on the German model.

Towards the end of the century rainwater analyses were being performed in practically every part of the earth from the tropics in 1889 to the Antarctic in 1911. At this time the possibility that changes in the chemistry of the atmosphere could have consequences for human health was beginning to be suggested. As early as 1901, Casali at Bologna presumed that there had been an increase in ammonia concentration due to anthropogenic activity, anticipating the hypotheses made (and argued more forcefully) by Crowther regarding the English city of Leeds. Casali did not regard this as a wholly negative fact, insofar as the increase in ammonia was 'an effect of human industry assisting nature by supplying new quantities of nitrifiable nitrogen, entirely to the advantage of agricultural production and therefore to the existence of all life.' The disadvantages derived from the presence in smoke of fossil carbon of compounds of the aliphatic and aromatic series (the latter certainly poisonous) which, when transformed in the atmosphere, could continue to develop micro-organisms damaging to crops. He therefore suggested 'the judicious application of new apparatus for the elimination of smoke.'

6. Conclusions

While necessarily incomplete, our examination of deposition chemistry research in the eighteenth and nineteenth centuries highlights the remarkable variety of theories and contexts which gave rise to such work. It is difficult to reconstruct the historical course of the actual arguments developed by researchers into rain, since it is not possible to disentangle the different theories from the controversies and personal interpretations which accompanied them. However, allowing for these limitations, the researches we have looked at raise a number of general issues such as: the stimulus given to scientific practice by certain institutions; the constraints on scientific practice deriving from experimental methods; the changes in definition of scientific problems according to how the subject is viewed; the rhetorical use of analytical methods, insofar as they were often employed by researchers to
sustain their own hypotheses or to disparage those of their rivals. Furthermore, research into rain has made a major contribution to the development of the environmental disciplines, if we think about the enormous importance of the nitrogen cycle for vegetation, and the wider application of some theories, such as that of the limiting element, otherwise known as 'Liebig's Law'.

Eighteenth and nineteenth-century researches on deposition, such as those by Marggraf, Lavoisier or Liebig, cannot be regarded as 'primitive' because they are analytically inadequate by present-day standards; nor can they be admired as expressions of a 'classical' epoch of chemical thought. To understand and evaluate them properly, there must be an appreciation of the environment in which they were conducted and the problems they were trying to solve. Many of the problems which were then considered important—a prime example being the transformation of water into earth—are no longer even a part of current chemical thinking. In this sense any historical study of rainwater chemistry must embrace a field which is different from, and wider than, that of present-day chemistry. It is not even correct to speak of one history, but rather of many histories.

A view of research that is restricted to quantitative considerations excludes qualitative studies, but also does not recognise the fact that the data of the past were scientifically valid and acceptable for the aims for which they were intended. Examples of these aims are the evaluation of the differences in precipitation between town and country or the circulation of nitrogen in the biosphere. It is hardly reasonable to expect them to be equally valid if they are used to answer other questions, like the evaluation of long-term trends of nitrate concentrations in rainfall. It is no coincidence that responding to this last question becomes easier if we consider the data collected after 1850. At that time, long series of determinations began to be conducted in the agrochemical sector, where careful quantification was all-important. However, the considerable differences in concentrations measured at the various European stations led to an almost desperate search in the analytical chemistry of the time for the more controllable, analytical sources of error; witness Eder's reviews. At this stage of research, nutrient loads from the atmosphere to forest or agricultural land were considered a positive contribution to the growth of vegetation and a factor of crucial importance to the whole ecosystem. A parallel development, which started in England in the seventeenth century, involved studies on acidity and its negative effects on the environment, but considered mostly local situations of industrial or urban pollution. At the beginning of this century, these studies were reinforced by work in an important sector dealing with the general chemistry of the atmosphere and the atmospheric circulation of chemicals. It was not until after the Second World War that loads from the atmosphere began to receive serious attention as a vehicle for the re-deposition of pollutants, with widespread negative effects and serious economic repercussions. Nowadays, investigators largely concur that atmospheric pollution and re-deposition through precipitation is an important, if not the main, cause of the
deterioration of vegetation. The excessive load of nitrogen from the atmosphere is seen as a cause of environmental imbalance severe enough to necessitate international agreements to reduce nitrogen emissions to the atmosphere, following similar agreements for sulphur emissions. Thus there has been a fundamental reversal in the perception of atmospheric deposition: from beneficent source of indispensable elements for ecosystem development, to vehicle for the re-deposition of potentially harmful pollutants.

There has rarely been sufficient contact and exchange of knowledge between the two main fields of study, agriculture-forestry and acid deposition. Thus, bibliographic reviews of acidification often do not recognise the importance of research in the agronomic field. The possible use of these data for a better understanding of the evolution of the phenomena has only been partially explored. Of course, this must be done only after a careful consideration of methods of sampling and analysis, which are both important factors in determining the results. The geographic variability of the chemical characteristics of deposition is also crucial, so that any investigation of trends must consider stations in a restricted, homogenous geographical context. Lastly, it should be borne in mind that only in some fortunate cases have the results of research in any particular direction not been forgotten, but instead have been re-used in another context. This did happen with the data from the agricultural stations collected in the second half of the nineteenth century; but this is the exception rather than the rule. A great deal of material remains to be examined, and there are other data from the last century which are valid for comparison with data of recent decades. On the other hand, studies of rainfall in the eighteenth and nineteenth centuries cannot be considered merely as a source of numerical data, but also as useful sources for a critique of current theories and methodology.

ACKNOWLEDGEMENTS

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11. Ibid., p. 455.
13. G. S. Poli, Elementi di Fisica Sperimentale, Edizione seconda Veneta (Tipografia Pepoliana, A. Curri O. Giacomo, 1768), IV, p. 3.
16. R. Boyle, "The Origin of Forms and Qualities (according to corpuscular philosophy)" in C. Pighetti ed. (Torino: UTET, 1977), p. 979. Boyle makes a clear distinction between the saline and earthy substances conveyed by the rain (revealed by the residue left after the first evaporation) and the transmutation of water into earth (shown by the residue of subsequent evaporation).


27. S. Cloez, “Recherches sur la nitrification,” *Soc. Chim. Paris. Répertoire de Chimie appliquée*, 3 (1861), pp. 11-72. Military interest in the manufacture of saltpetre anticipated by at least a century any such interest from the agro-chemical sector, as witnesses the series of prize competitions promoted by the military academies of Europe. Consequently the old theory on the formation of nitre (which involved the supposed transformation of vitriolic acid into nitre) was discarded in favour of the theory that regarded the essential point of the preparation as the combination of the emanations of decomposing bodies with the vital air, or oxygen principle of Lavoisier, and in the subsequent fixing of the product with calcareous earth.


44. Liebig, *op. cit. (28)*, p. 331.


46. J. Liebig, *Die Organische Chemie in ihrer Anwendung auf Agricultrue und Physiologie* (Braunschweig, 1840, Vieweg Verlag, 1 Auflage, 1 (German Editions), 2a, 1841; 3a, 1841; 4a, 1842; 5a, 1845; 6a, 1846; 7a, 1862 (2 vol); 8a, 1865). Liebig originally intended to give his work the title "Die letzten Metamorphosen organischem Verbindung und ihre Einfluss auf das Leben". The term "metamorphosis" recalled Goethe's work "Metamorphosen der Pflanzen", and more generally one of the fundamental questions of physiology in the nineteenth century: how it was possible to explain the transformation of substances in the passage from one living species to another. (P. Munday, "Liebig's metamorphosis: from organic chemistry to the Chemistry of Agriculture," *Ambix* 38 (1991), 135-53. In his manual of 1840 (referred to in the text), Liebig did in fact deal with the flux of matter between the mineral, vegetable and animal kingdoms. In all of this the links with "Naturphilosophie" were evident. In this connection it should be remembered that Liebig attended the lectures of F. W. Schelling.


58. J. T. Way, "On the composition of the waters of land drainage and of rain," *J. Roy. Agric. Soc.*, 17 (1856), 123–62. For example, Barral in 1851 and Boussingault in 1853 had found about 3 mg of ammonia per litre in Paris; Boussingault about 0.5 mg/l in 1857 at Liebenfruentberg, and Lawes and Gilbert about 1 mg/l at Rothamstead in 1852–53; Way himself had measured concentrations around 10 times greater in the rain collected at his London home than at Rothamstead.

59. Boussingault, *op. cit.* (55), p. 242. It was well-known that the ammonia concentration decreased as the volume of precipitation increased: Boussingault himself had shown this but only considering single meteoric events.


63. W. A. Lampadius, "Fortgesetzte Beiträge zur näheren Kenntniss der Quellwasser des Sächsischen Erzgebirges, so wie der atmosphärischen Wasser," *J. Prakt. Chem.*, B VI, 7–8 (1835), 363–82. These observations predate by at least thirteen years Smith's identification of sulphuric acid in Manchester, commonly regarded as the first record. A. Smith, "Some Remarks on the Air and the Water of Towns," *The London, Edinburgh and Dublin Philosophical Magazine and Journal of Science*, 30 (1847), 478–82. Lampadius had subdivided spring waters into acid, basic and neutral according to their reaction to tincture of litmus. He did not apply this test to measure the acidity of rainwater, probably because his procedure required large quantities of sample. On the basis of the substances he found in rainwater, he considered as unfounded Berzelius' claim that only the volatile salts could be found in rain; J. J. Berzelius, *Trattato elementare di chimica teorica e pratica*, tr. A. Frisiani (Milano: 1826), 1, p. 456.


65. W. Eichhorn, "Bericht der Central-Kommission für das agrarische Versuchsweisen über die in den Jahren 1864–65 ausgeführten Messungen, der mit dem Regenwasser niederfallenden Ammoniak und Salpetersäure Mengen, an den Minister für die Land-
wirtschaftlichen Angelegenheiten Hermann von Selchow,"Ann. Landwirthschaft, 24 (1866), 97–141. The Commission suggested the methods for analysing ammonia and nitrate proposed by Knop (W. Knop and W. Wolf, "Untersuchung über das Vorkommen und Verhalten des Ammoniaks in der Ackererde," Landw. Versuchs. Stat., 3 (1861), 109–27). Not all the stations took up the suggestion; for example, the station of Proskau adopted a different method because it thought that Knop's 'left much to be desired in the way of precision.' In their 1861 work (which was the model for the Commission's methods), Knop and Wolf engaged in controversy—albeit cautiously—with Liebig. In fact, after stating (echoing Liebig) that carbon dioxide, water and ammonia are the result of the decomposition of vegetable and animal bodies, and repeating that the animal kingdom is nourished by plants, which are nourished by the mineral kingdom and by the atmosphere, they posed the question (in opposition to Liebig) of whether nitrate may not also have as essential a function for the earth as ammonia. This respect, then, though not openly stated, was probably also one of the aims of the Commission. That the Commission's aims were not only those cited is also suggested by the fact that ammonia concentrations in rain were no longer a problem. Knop and Wolf themselves had summarised the knowledge of ammonia concentration thus: rain contained about 1–3 mg NH₃·L⁻¹; rivers and ponds had lower values, and in spring water it was normally absent. W. Eichhorn, "Berichte der Central-Kommission für das agriculchemischen Versuchsanstalten über die in den Jahren 1865–66 ausgeführten Messungen der mit dem Regenwasser niederfallenden Ammoniak und Sulfursäure Mengen," Ann. Landwirthschaft, 25 (1867), 249–78.

65. At the beginning of the 1860s Lawes and Gilbert became convinced, in sharp contrast with Liebig, that the quantity of nitrogenous compounds of atmospheric origin were quite inadequate for crops. They later confirmed these findings (J. B. Lawes and J. H. Gilbert, "On the amounts and methods of estimating ammonia and nitric acid in rain water," Rep. Brit. Assoc. Rothamstead Memoirs I, N. 6 (1854)). J. B. Lawes, J. H. Gilbert and E. Pugh, "On the sources of the nitrogen of vegetation: with special reference to the question whether plants assimilate free or uncombined nitrogen." J. Chem. Soc. (London) N. S., VII (1863), 100–86.


69. G. A. Barral, "Premier Mémoire sur les eaux de pluie recueillies à l'Observatoire de Paris," Compt. Rend., 34 (1852), 283–4. F. Arago, "Rapport sur un travail de M. Barral intitulé: Premier Mémoire sur les eaux de pluie recueillies à l'Observatoire de Paris," Compt. Rend., 34 (1852), 924–34. Arago had noted, commenting on Barral's work: 'possiility will only have to find out if, in the centuries to come, the composition remains constant, and whether the causes of the gradual disappearance of a portion of oxygen, such as combustion and respiration, are exactly compensated by the well-known opposite causes which daily emit these gases into our atmosphere.'


71. Arago, op. cit. (69). Arago pointed out at the Académie that these authors had not actually determined nitrate, which was what he considered the particular merit of Barral.


86. J. B. Boussingault, “Recherches sur la présence de l’acide nitrique et de l’ammoniaque dans les eaux et les neiges recueillies dans les Alpes par M. Civiale,” *Comp. Rend.*, 95 (1882), 1121–28. The paper was only published in 1882, though the research had been performed in 1866.

87. E. Schöne, “Zur Frage über das Vorkommen des Wasserstoffhypoxids in der Atmosphärischen Luft und den Atmosphärischen Niederschlägen,” *Ber. Deut. Chem. Gesells.*, Berlin, 36 (1893), 3011–27. In 1893 Schöne engaged in a controversy with Ilosvay, who questioned the presence of ozone in rain and considered the methods used by Schöne to be unsuitable. The argument re-focused attention on the possibility that rainwater might contain species held to be incompatible, such as hydrogen peroxide and nitrates.


94. Ibid.

95. Martin, *op. cit.* (73).


100. E. Bechi, *Saggi di esperienze agrarie* (Firenze: Tofani, 1870).


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105. Miller, op. cit. (104).
106. Ibid.
107. Ibid.
109. Boussingault, op. cit. (51); Boussingault, op. cit. (53).
110. Goppelsröder, op. cit. (83).
111. Miller, op. cit. (104).
112. Ibid.
114. Miller, op. cit. (104).
116. Zimmermann, op. cit. (38); Liebig, op. cit. (28).
117. Eichhorn, op. cit. (64).
118. Arago, op. cit. (69).
120. Bence-Jones, op. cit. (68).
121. J. B. Boussingault, op. cit. (86).
122. Brimblecombe, op. cit. (2).
123. Miller, op. cit. (104).
128. Eichhorn, op. cit. (94).
129. Ibid.
130. Ibid.
131. Ibid.
132. Ibid.
133. Eriksson, "Composition of Atmospheric Precipitation. II.," op. cit. (1).
134. Heller, op. cit. (74).
135. Schöne, op. cit. (87).
144. Martin op. cit. (73), p. 84.
145. Boussingault, op. cit. (55), p. 244. The method was further refined by K. H. F. Marx.

146. Way, op. cit. (57), p. 151. This method is still in use today and yields results comparable to modern instrumental methods; Ulrich and Williot, op. cit. (136), p. 35.


154. Petermann and Grafitiau, op. cit. (92), p. 711. They observed that the trend of the nitrogenous compounds in rain was cyclical, with minima in July-August and maxima in February, while the quantity of wet deposition followed an opposite trend.

155. Busile, op. cit. (103), 5-45.


159. Casali, op. cit. (127), 842.
