Modular Script System: Atmospheric Chemistry and Air Pollution
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Historical overview in recognizing the atmosphere: From the antiquity till industrial revolution

1. Introduction

Humans were dealing with and fascinated by the properties of our atmosphere already in antique eras. The term *atmosphere*, however, derived from Greek ατμόσ = vapour (in German: *Dunst* or *Dampf*) and σφαιρα = sphere (in German: *Raum*)[1] was not used before the beginning of the 19th century. In ancient times atmospheric observations (weather) were closely associated with astronomy, and all above the Earth was the heaven or aether. The Greek world metéron (or metéora) was in use already more than 600 years BC. It means "a thing in air". The world "air"[2] is derived from Greek αέρας and Latin aer.

Nowadays the terms air and atmosphere[3] are used as synonyms. From a chemical point of view it is possible to say that *air* is the substrate with which the *atmosphere* is filled. This is in analogy to the *hydrosphere* where *water* is the substance. The term "sphere" is related to the whole space where air is present. Thus, the term "atmosphere" should used as the more general one, including all physical, chemical and biological aspects occurring in air. Thus, before the 19th century it was spoken of "atmospheric air" to distinguish different kinds of air (the word "air" was also used for all kind of vapours and gases produced by alchemists – see later in this text).

To our present understanding of atmospheric processes it was a long way. Before discovering chemical components in air at the end of the 18th century, atmospheric air was regarded as a uniform matter. In discovering the atmosphere we may distinguish the following epochs:

- Antiquity (about 600-300 BC): air phenomenology and Earth philosophy
- Middle Ages and Renaissance (15th – 17th century): understanding the air as a body, first meteorological measurements
- Reconnaissance (18th/19th century): identification of air composition and cycling of matter between bio- and atmosphere, establishment of scientific disciplines like chemistry, meteorology, geography
- Industrial era (since 1850): discovery of trace species in air, understanding of air pollution, biogeochemistry, Earth science

[1] In old German publication the term "Dunstkreis" also was used instead of "Atmosphäre"; additionally in the 19th century the terms *Luftmeer*, *Luftozean* had been used in analogy to the sea.
[2] In German "Luft"; it is not known what the root of this word is (the term *Lufft* already was used in Middle Ages).
[3] English dictionaries define atmosphere as "the mixture of gases surrounding the Earth and other planets" or "the whole mass of an aeriform fluid surrounding the Earth".

You see, between the big time of Greek philosophers, who recognized the atmosphere only by visual observations and reflection, generalizing it in philosophic terms, and first instrumental observance were running almost 1500 years. Romanian Emperors were not interested in the continuation of Greek doctrines, however, they maintained it. After the decline of antiquity in about the 5th century the occident forgot the antique scientific heritage and replaced it by only one doctrine, the bible. Only in the orient *Aristoteles*[4] doctrine remained and came first to Europe in the 12th century, probably to Sicily, where famous alchemistic laboratories had been established. In that time any meteorological (i.e., weather) observation was linked with astrology. The idea that the motion of stars influences all processes on Earth and in the atmosphere inhibited any development of natural sciences.

In ancient times, the motivation in observing the atmosphere was clearly the urge in understanding the nature. Thus, first *Aristoteles* described in his Meteorologica a number of weather phenomena and the water cycle. Later, especially in the Middle Ages, when the belief dominated that all "heavenly" things are based on god (but that was the belief of all people in the world, creating the idea of the existence of special gods for many atmospheric phenomena), probably monks were the first to observe weather and make records, only by interest though.

Agricultural aspects and the understanding of the plant growth (i.e., the beginning of commercial interests) initiated chemical research with the 17th century. Chemistry, as a science first established by *Robert Boyle* around 1650, despite of many findings and describing chemical substances, remained so long as a non-scientific discipline (alchemy); alchemy never was a systematic approach and because of its "secrets", no public communication, essential for scientific progress, existed. However, physics, established a long time ago as a scientific discipline, made progress in mechanics due to better manufacturing of instruments with the 16th century. Thus, astronomers observing the object of their discipline through the atmosphere, also began to discover the Earth' atmosphere.

With the co-renaissance in the 18th century the interest in natural processes generally expanded. Travellers and biologist were interested in describing the climate and its relation to culture and biota, and chemists began to understand the transfer between solid, liquid and gaseous matter in the late 1700s. Fundamental interest in biological processes, such as plant growth, nutrition, animal breathing among others, stimulated the study of the water cycle, the gas exchange between plant and air, mineral input from air, and a first understanding of matter cycles.

With the stormy industrial development in the middle of the 19th century, a new atmospheric aspect, *air pollution* came into the interest of researchers - more exactly, air pollutants impacts (forest decline, human health, corrosion) were first the objects of research. Already in the latter 1900 some impacts have been related to individual air pollutants (cause-receptor relationship). However, the techniques to measure trace species were still very limited. Despite of missing quantified relationships, legislative acts on air pollution were passed in the 19th century. Nevertheless, air pollution remained a local problem only until the 1950s. Then, with *acid rain* (despite the fact it had already been described in England in 1852 by *Smith*[5]) the first regional environmental problem aroused in Europe. Only in the 1980s global problems were recognized in relation with *climate change* due to a changing global chemical air composition. Locally, even catastrophic environmental events like the smog in London and Los Angeles, initiated the *atmospheric chemistry* as a new discipline with the

[4] In English, the name is often written as *Aristotle.*
[5] Robert Angus Smith ( ) English chemist.

beginning of the 1950.

For structuring this contribution I am not going along the historic time scale (this contribution will not consider the history of air pollution and the development after 1900) but I am considering different aspects regardless of increasing interlink between them with historic development:

1. Earth view in antiquity
2. Weather and climate (history of meteorology)[6]
3. Composition of air (history of atmospheric chemistry)
4. Biosphere-atmosphere interaction

2. Air in antique view

Before the 6th century BC air was identified with emptiness. Greek nature philosophers named air to belong to the four elements (primary matter). *Thales of Milet* (624-546 BC) was the first trying to answer the question, by which the universe is made not simply „by gods and demons". He defined water as a primary matter and regarded the Earth as a disc within the endless sea. *Pytagoras* (about 540-500 BC) was probably the first to suggest the Earth be a sphere, but without explanation (only based on aesthetic ideas). *Parmenides* from Elea (about 540-480 BC), however, explained the spheric Earth due to observations of driving ships on sea. He was a scholar of *Xenophanes* from Kolophon (about 570-480 BC), the founder of eleatic philosophy. *Xenophanes* again was a scholar of *Anaximander* from Milet (about 611-546 BC). With *Anaximander*, a scholar of *Thales*, and *Anaximenes* (from Milet, about 585-528 BC) the cycle of pre-Socratic philosophers has been closed. *Anaximenes* assumed – in contrast to *Thales* – air to be a primary element (root or primordial matter) which can change its form in dependence of its density: diluted into fire which may condense to wind and by further condensation into water and finally into soil and rocks. This was very likely the first "poetic" description of the idea that all material on Earth is subject to cycling, where "dilution" and "condensation" are driving processes.

Empedocles of Acragas (495-435 BC) introduced the four elements soil, water, air and fire, which have been extended by *Aristoteles* (384-322 BC) by another one, the aether (explaining the heavenly, in Greek αιθέρας). These views remained for nearly 1500 years as the doctrine of the occident. *Aristoteles*, the big Ionian philosopher, teacher of Alexander the Great, who wrote the textbook "Meteorologica" (The Rainbow)[7] and described the water cycle as follows[8]:

Während die Erde ruht, strömt die Feuchtigkeit ihrer Umgebung, durch die Sonnenstrahlen und die sonstige Wärme von oben verdampft, aufwärts; und wenn nun die Wärme, die alle Feuchtigkeit nach oben geführt hat, diese wieder verlassen hat, ... dann tritt der durch Entzug der Wärme abgekühlte Dampf wieder zusammen und verwandelt sich aus Luft in Wasser zurück, das als Regen wieder auf die Erde herabfällt. Die

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6 without going into details on atmospheric physics

7 Aristoteles. Meteorologia. Eleganti Iacobi Fabri Stapulensis Paraphrasi explanata. Commentarioque Ioannis Coclaei Norici declarata ad foelices in philosophiae studiis successus calcographiae iamprimum demandata. Nürnberg, F. Peypus, 1512. First printing in Germany of this valuable edition by the great French humanist *Jacques Lefevre d'Estaples*. It contains three sections on geophysics, astronomy, hydro- and climatology, which were the main sources of knowledge for the idea of nature at the turn from medieval to modern times.

8 Ernst Grumach (Ed.): Aristoteles, Werke in deutscher Übersetzung, Berlin 1959

Verdunstung des Wassers ist Dampf, die Verdichtung der Luft zu Wasser ist Wolke, und Nebel ist das, was bei der Rückverwandlung in Wasser zurückbleibt. (The earth is at rest, and the moisture above it is evaporated by the sun's rays and the other heat from above, rising upwards; but when the heat which causes it to rise leaves it, … then the vapour cools down and condenses again as a result of the loss of heat and the height and turns from air into water. The exhalation from water is vapour. The formation of water from air produces clouds.)[9]

After the great times of ancient philosophers (600-300 BC), 300 years later, only *Heron of Alexandrien* (10-75), who mainly worked as mathematician (as mathematics was focused in that time on all heavenly things) showed by pneumatic experiments (relationship between water, steam and air in constructions to open and close temple doors) that air is a body.

3. Weather and climate

A long time before dealing with atmospheric phenomena, we have to assume that man – in his early days as hunter and food gatherer – heavily depended upon the weather, more than on any other factor. Climate and weather play a dominant role in determining a nations' history and shaping its culture.

More than 100 years before *Aristoteles*, the Greek philosopher *Anaxagoras* (500-428 BC.) of Klazomenai came to Athens as a young man. Questioned, what he was born for, he answered: "To observe sun, moon and heaven"[10]. His philosophy is based on the Eleats and *Empedokles*. With his doctrine that meteorological phenomena are caused by sun activities he was in contradiction to the volubly meaning. First written notes on meteorological phenomena came down from *Aristoteles*. From his Meteorologica we know that he believed that weather phenomena were caused by mutual interaction of the four elements (fire, air, water, earth), and the four prime contraries: hot, cold, dry, and moist. *Aristoteles* freqently argued against ideas which were closer to the truth than his own, for example[11] he presented the view of *Anaxagoras* in considering the cause of hail:

Some think then, that the cause of the origin of hail is as follows: when a cloud is forced up into the upper region where the temperature is lower ... the water when it gets there is frozen, and so hailstorms occur more often in summer and in warm districts because the heat forces the clouds farther up from the earth.[12]

Anaxogoras´ theory is amazingly correct but *Aristoteles* wrote:

The process (hail) is just opposite on what Anaxagoras says it is. He says it takes place when clouds rise into the cold air: we say it takes place when clouds descend into the warm air, and is most violent when the clouds descend the farthest.

Aristoteles, however, contributed to many accurate explanations of atmospheric phenomena.

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[9] English version from R. A. Anthes, H. A. Panofsky, J. J. Cahir and A. Rango (1975) the atmosphere. Charles E. Merril Publ. Comp., Ohio (USA) p. 5

[10] after Diogenes Laertius: "Leben und Meinungen berühmter Philosophen", translated and explained by Otto Apelt, Felix Meiner, Leipzig 1921

[11] cited from: R. Anthes, H. A. Panofsky, J. J. Cahir and A. Rango (1975) The atmosphere, Merril Publ. Comp., Ohio

[12] Aristoteles: Meteorologica, engl. translation by G. D. P. Lee, Harvard Press, Cambridge, 1952, p. 81

The description of the water cycle (reasons for rain), as presented in the previous chapter, could have been taken from a modern textbook. *Archimedes* of Syracuse/Sicily (287-212) indirectly contributed with his buoyancy principle to the design of the hot-air balloon, an invention which contributed much to our knowledge of the vertical structure of the atmosphere, and to the basis for theoretical investigation of the buoyant rise of cumulus clouds. *Theophrastus* (about 372-287 BC), the successor of *Aristoteles* in the Peripatetic school, a native of Eresus in Lesbos, compiled a book on weather forecasting, called the *Book of Signs*. His work consisted of ways to foretell the weather by noticing various weather-related indicators, such as a ring around the moon, which is often followed by rain.

Gervasius of Tilbury (author of the Ebstorf World Map), wrote "Otia Imperialia" as a conception of the world between 1209 and 1214 dedicated to the emperor Otto IV:

> Ventus autem nihil aliud est quam aer commotus et agitatus. vende aeris fluctus dici potest. (Well, wind is not different from air, which is moved and driven; therefore it also can be named flow of air.)

However, all "philosophies" from the Middle Ages[13], were based on ancient philosophers, no new observations and conclusions had been added, in contrast, due to non-scientific approaches ("alchemy") it no made progress, despite the findings of several empiric relationships (see later in connection with *Paracelsus*).

Although weather records had been kept for different locations as early as the 14th century, meteorology did not become a genuine natural science until the invention of weather instruments; after *Hellmann*[14] this is called the 2nd period in the history of meteorology. Probably in the middle of the 15th century (before having instruments) first systematic (i.e., day-to-day observations) were started by an unknown monk in Italy. In Germany first regular weather observation were made between 1513 and 1520 by the mathematician and astronomer *Johann Werner* (1468-1522) of Nuremberg. In that time only astronomers made regular weather observations: the Danish *Tycho Brahe* (1546-1601) in Uraniaborg between 1582 and 1597, as well as the German *Johannes Kepler* (1571–1630) since 1604 in Prague and 1628 in Sagan. However, these astronomers concluded that (astro-meteorological superstition) the positions of planets determine the weather.

The new instruments[15] gave scientists data, so that the physical laws could be tested. Italian physicist and astronomer *Gallileo Gallilei* (1564-1642) made evidence for the weight of air and invented a crude thermometer in the late 1500s. Italian mathematician and physicist *Evangilista Torricelli* (1608-1647), a student of Galileo, produced a vacuum for the first time and discovered the principle of a barometer in 1643. *Torricelli* also proposed an experiment to show that atmospheric pressure determines the level of a liquid (he used mercury). *Torricelli´*s scholar *Vincenzo Viviani* (1622-1703) finally carried out this experiment successfully and *Blaise Pascal* (1623-1662), a contemporary French scientist, carried out very careful measurements of the air pressure on Puy de Dome near Clermont in France. He realised the decrease of pressure with altitude and concluded there must be a vacuum in high

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[13] For example *Albertus Magnus* (Albert der Große), the most prominent German philosopher and theologian of the Middle Ages (1193-1280) wrote four books "Meteorum" fully identical with Aristoteles books.

[14] Johann Georg Gustav Hellmann (1854-1939) Prof. for meteorology at Berlin University, 1907-1922 Director of the „Preußisches Meteorologisches Institut" (later German Weather Service)

[15] The oldest meteorological instrument is the wind vane already used by Greeks and Romanians. The poet *Terentius Barro* (185-159 BC) used it on his estate. Only *Ignacio Denti* put several wind vanes combined with a wind rose in the 1570s in Bologna and Florence to exactly show the incoming wind direction.

altitudes. In 1667 *Hook*[16] invented an anemometer for measuring wind speed. In 1714 *Fahrenheit*[17] worked on the boiling and freezing of water, and from that work he developed a temperature scale. In 1780 *Horace de Saussure*[18] invented the hair hygrometer for measuring humidity[19]. *Benedetto Castelli* (1578-1643), a friend of *Gallileo*, used the first rain gauge in 1639 to measure the rain height.

Before inventing the thermometer, human skin, which is very sensitive to the temperature, could have served the purpose of a thermometer (most people can estimate the temperature within a range of 3°C). Measurement of temperature needs a scaling which was suggested by *Celsius*[20] in 1742 on the base of phase transfers of water (boiling and freezing). In english spoken countries the scaling (based on different "typical" temperatures, e.g., human body temperature) proposed by *Fahrenheit*[21] around the same time has remained until today. *Fahrenheit* established his scale after meeting that by *Roemer*[22] making a misunderstanding due to fixing the normal human body temperature (in the *Roemer* scale 22.5°) whereas Roemer already used as fixing point the boiling temperature of water (60°), Middleton (1966).

The 3rd period of developmental history in meteorology began around the middle of the 17th century with systematic instrumental observations. The Grand Duke *Ferdinand II* of Toscana (1610-1670) together with Prince *Leopold de Medici* (1617-1675) founded in Florence the Accademia del Cimento in 1657. *Ferdinand II* also founded the first meteorological stations network belonging to the Accademia (in Northern Italy, Germany, France, Poland and Sweden). The Accademia (and the network) lasted only until 1667 and marked the "beginning of modern physics," according to Ornstein (1963). Between 1780 and 1790 the Societas meteorologica Palatine (Pfälzer meteorologische Gesellschaft)[23] in Mannheim (Germany) established an international network of 39 stations including Northern America and Greenland. In this network for the first time only the same instruments (produced and controlled in Mannheim under the auspice of the director and founder *Hemmer*[24]) were used at same times (so-called "Mannheimer Stunden").

Von Buch[25], *Wahlenberg*[26] and *Humboldt*[27] concluded from these annually published first

[16] Robert Hook (1635-1703) English scientist, assistant to Robert Boyle

[17] Gabriel Daniel Fahrenheit (1686-1736) German glassblower and physicist, born in Danzig and later working in Holland

[18] Horace-Bénédict de Saussure (1740-1799) Swiss geologist and meteorologist

[19] After Umlauft (1891) the Grand Duke Ferdinand II of Toscana (reigned 1621-1670) invented the first hygrometer (Torricelli was the court mathematician).

[20] Anders Celsius (1701-1744), Swedish professor for astronomy, suggested specifying the boiling point of water at 0° and the melting point at 100° - only after his death it was decided to turn the scale upside down.

[21] Fahrenheit divided the 22.5 degrees of the Roemer scale into four subdivisions (in total 90 degrees) and thus ascertained 90° as body temperature. In 1717 he moved this to 96°. According to his thermometer, Fahrenheit measured the temperature of boiling water with 212°, that is, a few degrees more than it should have been using the body temperature as a reference. After his death this point was rectified to 98.6°, and the 212° for boiling water were taken as a reference.

[22] Olaus Roemer, Danish astronomer, in 1701 used a thermometer with two fixed points, which mit zwei Fixpunkten, which comply with the body temperature of a healthy human (37°C) and the temperature of melting ice (0°C). However, this scale soon fell into oblivion. He fixed the zero point to the temperature of a salt-ice-mixture, the by him assumed lowest possible temperature. His scale therefore ranged from 0 to 60, whereas the melting point of ice was noted at one eight of the scale, and the body temperature at four eight of the scale.

[23] Being a part of the „Kurpfälzische Akademie der Wissenschaften" (electoral Palatine academy of sciences), founded by Elector (Kurfürst) Carl Theodor von der Pfalz (1742-99) in 1763 at Mannheim.

[24] Johann Jacob Hemmer (1733-1990) a former Jesuit and court chaplain who was interested in physics and meteorology

[25] (1774-1853), studied at the mining academy in Freiberg together with Alexander von Humboldt, a life-long friend

[26] George (Göran) Wahlenberg (1781-1851) Prof. for Linnaeus at the University of Upsala (Sweden), botanist, pioneer in homeopathy

[27] Alexander von Humboldt (1769-1859) German natural scientist in Berlin, deeply interested in discovering

synoptic observations (called “Ephemeriden”) on many relationships to their own disciplines.

In that time the term “meteorology” not longer was used in an *Aristoteles* sense as the discipline of *all* nature phenomena but only for atmospheric processes; consequently the term “atmospherology” (in German: Atmosphärologie) was introduced, although forgotten nowadays. In 1820 *Brandes*[28] used the Palatine´s obervations from 1783 to reconstruct the first weather map of Europe. Typical weather cards, however, could only be established after the introduction of the telegraph (in 1833): 1851 at the London World Exhibition an only two month old weather map was shown. First in France (1863) weather maps with isobars have regularly been published (this was stimulated by the big accident during the Crimea War in 1851, were France lost a ship in storm and afterwards it was found that this storm had already been forecasted). In Germany the first weather maps were produced by the “Deutsche Seewarte” in Hamburg (German Sea Observatory). By 1860, about 500 stations were reporting the weather worldwide and forecasting based on more than local observations became possible. In 1873 in Vienna the first non-governmental International Meteorological Organisation (IMO) had been founded (which in 1949 lead to the World Meteorological Organisation WMO).

Lampadius[29], a fellow student of *Humboldt*, wrote the first textbook on meteorology, entitled

Systematischer Grundriß der Atmosphärologie (Systematic Compendium on Atmospherology), Freiberg, 1806.

With *Humboldt* and *Lampadius* began the modern “science or a treatise on the atmosphere” (*atmospherology*). Remarkable, how broad natural scientists at the beginning of the 19th century defined their interest, as shown in the preface to the book by *Lampadius*:

„Bald nach meiner Ankunft in Freyberg wurde die Atmosphäre ein Gegenstand der Unterhaltung zwischen unserem vortrefflichen Mineralogen Hrn. Bergrath Werner und mir. Dieser würdige Gelehrte hatte schon stets in seinen Vorträgen, von der Nothwendigkeit die Atmosphäre als viertes Naturreich zu betrachten, gehandelt, und munterte mich auf - besonders als Beyhülfe für das geognostische Studium - über die Atmosphäre zu lehren." (Soon after my arrival in Freiberg the atmosphere became part of the discussions between the excellent mineralogist Mr. Werner and me. In his talks, this dignified scholar had always already been dealing with the necessary to regard the atmosphere as the fourth nature preserve, encouraged me – especially with aid of geo-gnostic studies – to lecture about the atmosphere.)

In that time “meteorologists” still came from chemistry[30] (persons who were interested in air chemical composition) and geography, esp. geographical climatology (weather discription in different geographic regions of the world). *Alexander v. Humboldt´s* numeros contributions to the institutionalisation of meteorology in Germany were finally finished in 1847 with the

natural interrelationships, treats of chemical problems and of phenomena like the atmosphere, the climate, the light etc. One of the founders of modern scientific geography.

[28] Heinrich Wilhelm Brandes (1777-1834) German astronomer, physician and mathematician, 1811 Prof. for mathematics in Breslau, 1826 Prof. for physics in Leipzig

[29] Wilhelm August Eberhard Lampadius (1772-1842) Professor in Freiberg, founder of modern metallurgy

[30] After the establishment of thermodynamics in the middle of the 19th century, physicists began to theoreticall study the atmosphere. In 1800 Humboldt was elected as member of the Royal Academy of Sciences at Berlin for “chemistry”; later he put himself into “mineralogy and geognosy”.

foundation of the “Preußisches Meteorologisches Institut” in Berlin, with *Mahlmann*[31] being the first director who soon died. In 1849 *Dove*[32] became the 2nd director but he was already known world wide as meteorologist (in the issue of April 10, 1879, the English journal “Nature” named him “Father of the Meteorology”). Soon after the foundation of the German Weather Institute, the “Physikalisches Hauptobservatorium St. Petersburg” (1849)[33] with its first director *Kupfer*[34] and the “Centralanstalt für Meteorologie und Erdmagnetismus in Wien” (1851) were founded.

With the beginning of the mathematical description of atmospheric dynamics and thermodynamics in the middle of the 19th century (the names *Ferrel*[35], *Helmholtz*[36], *Bezold*[37], *Hann*[38], *Margules*[39] and many others should be noted), the theoretical understanding of the atmosphere was possible and meteorology became a scientific discipline on its own.

3. Chemical composition of air

Before the discovery of nitrogen and oxygen as the main constituents of air in the late 1700s, it was recognized as a uniform matter[40]. The English physicist *Robert Boyle* (1626-1691) was the first to combine chemistry, before only conducted as alchemy, with the exact natural science of physics while investigating gases and esp. the relations between gas mass, pressure and temperature. Beside the scientific introduction of the terms element, chemical compound and chemical reaction, he wrote that air seems to be a "*confused aggregate of effluvium*" (Brimblecombe, 1996). *Boyle* wrote the book “*Memoirs for a General History of the Air*” suggesting production and investigation of different kinds of air, but nothing is

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[31] Wilhelm Mahlmann (1812–1848) German meteorologist, died on an official journey to Silesia.

[32] Heinrich Wilhelm Dove (1803–1879) physicist, first full professor for meteorology at Berlin university,

[33] Main Physical Observatory; renamed in Main Geophysical Observatory “Главная Геофизическая Обсерватория им.Воейкова” in 1924 and added by the name A. I. Voeykov in 1949

[34] Adolf Yakovlevich Kupfer (Купфер, Адольф Яковлевич; Adolph Theodor Kupffer) (1799-1865) Russian-German from Kasan, Prof. for physics, mineralogy and chemistry in St. Petersburg

[35] William Ferrel (1817-1891) Mathematician. Born in a farmers family in Pennsylvania (USA), after finishing a college he became a school teacher. Fascinated by an eclipse event he studied copies of works from *Bernoulli*, *Euler* and *Laplace*. From these studies Ferrel concluded .... *that the action of the moon and sun upon the tides must have a tendency to retard the earth's rotation on its axis.* This conclusion contradicted that which *Laplace* had come to and Ferrel decided that Laplace had made an error in neglecting second order terms. In 1853 Ferrel moved to Nashville Tennessee where he set up his own school. As well as research on tides Ferrel studied currents and storms. In 1882 he was moving to the United States Army Signal Service, but this is much more obvious when we realise that at the time it ran the national weather service, and that it became the U.S. Weather Bureau under civilian control in 1891. After working for four years Ferrel retired at the age of seventy. Among his works published during the last ten years of his life were *Popular Essays on the Movements of the Atmosphere* (1882), *Temperature of the Atmosphere and the Earth's Surface* (1884), *Recent Advances in Meteorology* (1886), and *A Popular Treatise on the Winds* (1889).

[36] Hermann Ludwig Ferdinand von Helmholtz (1821–1894), Prof. für Physik, Anatomie und Physiologie in Berlin, Königsberg, Bonn und Heidelberg

[37] Wilhelm von Bezold (1837-1907) was Professor of Meteorology in Munich as well as Director of the Prussian Meteorological Institute. His main interest as a scientist was the physics of the atmosphere and he contributed much to the theory of electrical storms.

[38] Julius von Hann (1839-1921) 1874 bis 1897 Prof. der physikal. Geographie, Univ.Wien; 1897/00 Prof. der Meteorologie in Graz, anschl. bis 1910 wieder in Wien

[39] Max Margules (1856-1920) Austrian meteorologist. Born in Brody (Ukraine), 1885-1906 belong „Zentralanstalt für Meteorologie“. Was dealing esp. with tides, established a theory on polar fronts and air pressure waves.

[40] This statement must be limited to the “gaseous” fraction of air; water, vapor, dust, meteorits etc. where known since antique, but not identified as chemical substances.

reported on its execution. *Ramsay*[41] believed that the composition of air would be discovered hundred years earlier carrying out those experiments.

3.1 Gases

The term *gas* was first introduced by *Helmont*[42], deduced from the world *Chaos*[43], used by *Paracelsus*[44,45]. *Helmont* studied carbon dioxide, *gas sylvestre*, and showed that it is formed in fermentation processes, coal combustion, limestone burning and by addition of hydrochloric acid to potash (K_2CO_3). He also knew, but only very impure, hydrogen, methane and sulfuric dioxide (without knowing the names). Thus, in (al)chemical experiments gaseous substances have been observed, named Fumes ("Dünste"), Vapours ("Dämpfe") and Airs ("Lüfte"). To separate it from the conditions of formation (cold and hot), *Helmont* called substances not simply formed by heating (fume) *gas*; he wrote in his (posthumously edited) book "Ortus medicinae" (Amsterdam 1648):

> "Halitum illum GAS vocavi non longe a Chaos veterum secretum" (I have named this breath GAS because it is not far from the Chaos of the ancients).[46]

Georg Ernst Stahl (1660-1734) was a German chemist who developed the theory that objects burn because they contain a combustible substance, *phlogiston* (meant in Greek language "flammable"). Substances rich in phlogiston, such as wood, burn almost completely away. Metals, which are low in phlogiston, burn less well. The phlogiston theory was the first attempt of a rational explanation for combustion and what we would call *oxidation*. However, they bring a lot confusion in understanding the chemistry of phase-transfer processes and solid-gas reactions. Chemists spent much of the 18th century evaluating *Stahl's* theories before these were finally proved to be false by *Antoine Lavoisier.*

Before discovering atmospheric chemical composition, air was separated into "different" air (types), see Table 1. However, just in the time before *Stahl*′s phlogiston theory was published, *John Mayow*[47], a forgotten chemist showed that air contains a gas which is a special agent for combustion and respiration and is fixed from calcified metals (it is carbon dioxide). Modern chemistry might be said to have its beginning with the work of *Stephen Hales* (1677-1761), who early in the 18th century began his important study of the elasticity of

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41 William Ramsay (1907) Die Gase der Atmosphäre und die Geschichte ihrer Entdeckung. Halle, Verlag W. Knapp

42 Johann Baptist (Jan) van Helmont (1577-1644) physicist and alchemist in Brussels; believed that all substances may be reduced to air and water.

43 The Greek world „χαως" denotes emptiness, the endless blank space. It was not put on a level with nonentity; the world was born from the Chaos according to the Greek phiilosophers.

44 Theophrastus Bombastus Philippos von Hohenheim (later named *Paracelsus*) 1493-1541, Swiss physician (1516 "Doctor beyder arzneyen"), alchemist, theologist and philosopher; stated that science must be based on observations and experience

45 *Paracelsus* used the term Chaos in sense of atmospheric space, later named airspace ("Luftraum") and air ("Luft").

46 Helmont left out the "o" in "Chaos" and because Dutch pronunciation of "Ch" is like "G", what remains is "Gas". Due to dominantly written propagation of the word gas, the relation (only latent in Dutch) to Chaos was lost (J. Egli, Geschichte des Wortes Gas. Das Mosaik. Kunst Kultur Natur 2/4, 1947, p. 125). The word „gas" now exists in all languages. It appeared in dictionaries in France in 1690 (gaz), in England 1692 and in Germany 1727. In the ordinary language it has been widely used only end of 19th century with its introduction for illumination. In World War I it became the synonym for chemical weapons (poison gas).

47 (1643-1679), English chemist and physiologist; cited from A. Mangin (1866) das Reich der Luft. Berlin, p. 113

air. He pointed out, also, that various gases, or "airs," as he called them, were contained in many solid substances.

Table 1. Nomination of gases and "airs"

English	*German*	*Formula*
phlogisticated (nitrous) air	phlogistierte (salpetrige) Luft	NO
acid air	saure Luft	HCl
alkaline air	alkalische Luft	NH_3
vitriolic air	vitriolische Luft	SO_2
reduced fixed air	reduzierte fixe Luft	CO
fixed (*and*: mephitic) air	fixe Luft	CO_2
good (*and*: vital) air (dephlogisticated air)	gute Luft (Dephlogiston)[b]	O_2
inflammable (non-combustible) air	verdorbene Luft	N_2
flammable air	brennbare Luft	H_2

[a] "acide crayeux" (charc acid ; in German « Kreidesäure ») after *Lavoisier*
[b] „Feuerluft" named after *Scheele*

The careful studies of *Hales* (see also chapter 4) were continued by his younger confrere, *Joseph Black* (1728-1799), a Scottish chemist, whose experiments concerning the weights of gases and other chemicals were the first steps in quantitative chemistry. *Black* made valuable studies on carbon dioxide which he named *fixed air* and found that candle lights do not burn in this gas, creatures cannot exist, and that it is a product of respiration.

In the 2nd half of the 18th century air was found to consist of two different constituents, maintaining respiration and combustion and not keeping it (*Woodward* and *Senebier* were famous scientist in beginning to understand the atmosphere-biosphere linkage, see chapter 4). It is accepted to account the discovery of nitrogen[48] to *Rutherford*[49], who wrote his dissertation in 1772, entitled

"Dissertation Inauguralis de aero fixo dicto, aut mephisto",

17 years after *Black´*s dissertation on "fixed air" (CO_2). Just before *Priestley´*s discovery of "good air" (O_2), *Rutherford* made experiments where he removed oxygen from air by burning substances (i.e., charcoal) and afterwards carbon dioxide by absorption with lime; the rest (nitrogen) he denoted as "phlogisted air", despite it was not flammable. *Joseph Priestley*[50] spoke 1771 about the *goodness* of air (air quality in modern terms) and noted that *injured* or *depleted* air will be *restored* by green plants. In 1772 *Priestley* started his studies on air using mercury for locking of gases. After a break he systematically began in 1776 to investigate different kinds of "air": nitrous (salpetric) air (NO_x), acid (muriatic[51]) air (HCl), alkaline air (NH_3). He stated that these "kinds of air" are not simple modifications of ordinary (atmospheric) air. He wrote down his observations in a book called "*Observations on different Kinds of Air*" (1772)[52]. By heating of red mercury oxide, he produced dephlostigated air (O_2) in 1774.

Most clearly the facts on air composition were expressed by *Carl Wilhelm Scheele*[53] in his

[48] see comments to Cavendish later in text
[49] Daniel Rutherford (1749-1819) born in Edinburgh, physicist
[50] Joseph Priestley (1733-1804) English scientist; due to his sympathy with the French revolution he moved to USA (Philadelphia) in 1794
[51] anhydrous hydrochloric acid gases; in German: "Salzsäure"
[52] In: Philosophical Transactions of the Royal Society. Vol. 62. London, Lockyer Davis, 1772, pp. 147-264
[53] Carl Wilhelm Scheele (1742-1786) born in Stralsund/Pomerania (Sweden in that time), druggist in Gothenburg, Malmö and Stockholm, member of the Royal Academy of Sweden (1775)

booklet "*Abhandlung von der Luft und dem Feuer*“ (Treatise on Air and Fire), which was published 1777 (from laboratory scripts it is now known that *Scheele* discovered oxygen – dephlogisticated air – earlier than *Priestley* in 1773 by similar methods: heating of silver carbonate, red mercury oxide, saltpetre and magnesium nitrate). *Scheele* also discovered chlorine (Cl_2); he named the ingredients of air “Feuerluft” (O_2) and “verdorbene Luft” (N_2). *Scheele* found evidence that one volume of oxygen produces one volume of carbon dioxide and defined that

Feuerluft (O_2) = Phlogiston + fixe Luft (CO_2);

which was wrong and should be written (in the old terms): carbon = fixe Luft + phlogiston, i.e., when carbon is burning, it is transformed into carbonic acid (CO_2) while releasing “phlogiston”.

Lavoisier[54] founded his theory on combustion on these discoveries. *Priestley* reported him 1774 in Paris from his discovery (O_2) and said that he has no name for this gas. *Lavoisier* repeated the experiments of *Priestley* and dealt especially with the question of calcining caustic substances (metal oxides) as well as their reduction by charcoal. In “*Reflexions sur le Phlogistique*” (1783), *Lavoisier* showed the phlogiston theory to be inconsistent. He believed that this element (oxygen, denoted as *Dephlogiston*) is an immanent part of acids and gave him the name *Oxygéne* (from greek οξνς - acid). He also named the other element, called by *Scheele* "verdorbene Luft" (bad air, named by *Priestley* “noncombustable air”) by *Azote*, i.e. *Stickgas* or *Stickstoff* in German (nitrogen) and was the first who quantified the composition of air in 1778 (Table 2).

Another remarkable scientist was *Cavendish*[55], who had not published his results on air studies before 1783. Already in 1772 he privately told *Priestley* about his experiments with “mephistic air” (nitrogen); thus it seems likely that *Cavendish* already knew before *Rutherford* “inflammable air” (N_2). In 1781 he realized that water is produced in reaction of hydrogen (“flammable air”) with oxygen (“vital air”) and soon he noted that there are also acidic substances not containing any oxygen. In 1781 he sampled atmospheric air at different sites and analyzed it gravimetrically after sorption of water-soluble gases (CO_2, NH_3 and water vapour), see Table 2. *Cavendish* already treated to find whether airy nitrogen is a uniform matter and found that there is a small rest (novel gases). He did not conclude, however, that these remains are an element (Ar).

Blagden[56] reported *Lavoisier* on *Cavendish´*s experiments in 1781, and together with *Laplace*[57] they reviesed his experiments and he was able to invert the experiment, i.e. he decomposed water (by passing water vapour on red-hot iron wire) into hydrogen and oxygen. Only *Lavoisier* (*Cavendish* remained a conformer of the phlogiston theory until his death) gave a right explanation for the dissolution of metals in acids. Finally, in 1787, *Lavoisier*, *Morveau*[58], *Berthollet*[59] and *Fourcroy*[60] established in Paris a new chemical nomenclature, valid until today. *Lavoisier* wrote in 1793 the “*Traité élémentaire de Chimie*” (Elementary Treatise of Chemistry), the first modern textbook on chemistry, and presented a unified view

[54] Antoine Laurent de Lavoisier (1743-1794) French chemist in Paris (« Father of modern chemistry »), was executed using a guillotine
[55] Henry Cavendish (1731-1810) chemist and physicist in London
[56] Sir Charles Blagden (1748-1820) English physicist, Cavendish's assistant from 1782 to 1789
[57] Pierre-Simon (Marquis) de Laplace (1749-1827) French mathematician
[58] Louis Bernard Guyton de Morveau (1737-1816) French chemist
[59] Claude Berthollet (1748-1822) French chemist, introduced the term chemical affinity
[60] Antoine François de Fourcroy (1755-1809) French chemist

of new theories of chemistry, containing a clear statement of the Law of Conservation of Mass, and denied the existence of phlogiston. In addition, it contained a list of elements, or substances that could not be broken down further, which included oxygen, nitrogen, hydrogen, phosphorus, mercury, zinc, and sulphur.

Gay-Lussac[61] and *Humboldt* carried out air analysis from different sites and validated the ratio 21/29 for oxygen/nitrogen as a constant. In 1804, *Gay-Lussac* made several daring ascents of over seven thousand meters above sea level in hydrogen-filled balloons – a feat not equalled for another fifty years – that allowed him to investigate other aspects of gases. Not only did he gather magnetic measurements at various altitudes, but he also measured pressure, temperature and humidity, and took samples of air, which he later analyzed chemically. *Humboldt*[62] is also known for the first scientific definition of *climate* (see chapter 2). *Bunsen*[63] showed in 1846 that the oxygen content in air varies slightly between 20.84 and 20.95 % (measurement error was 0.03 %).

Lord Raleigh[64] was the first who observed (beginning of 1882 and ending of 1892) that oxygen and other gases, produced from different sources always showed the same density but not airy nitrogen. While "airy nitrogen" had a density of 1.2572 g l^{-1}, nitrogen from decomposition of organic substances showed a density of 1.2505 g l^{-1}. The difference of 7 mg was already away far from measurements errors. In his address on the occasion of receiving the Nobel Prize *Rayleigh* explained how he made his discovery, showing us the (from today's point of view) simple but accurate experiments and conclusions:

> *The subject of the densities of gases has engaged a large part of my attention for over* 20 *years. ... Turning my attention to nitrogen, I made a series of determinations ... Air bubbled through liquid ammonia is passed through a tube containing copper at a red heat where the oxygen of the air is consumed by the hydrogen of the ammonia, the excess of the ammonia being subsequently removed with sulphuric acid. ... Having obtained a series of concordant observations on gas thus prepared I was at first disposed to consider the work on nitrogen as finished. ... Afterwards, however, ... I fell back upon the more orthodox procedure according to which, ammonia being dispensed with, air passes directly over red hot copper. Again a good agreement with itself resulted, but to my surprise and disgust the densities of the two methods differed by a thousandth part - a difference small in itself but entirely beyond experimental errors. ... It is a good rule in experimental work to seek to magnify a discrepancy when it first appears rather than to follow the natural instinct to trying to get quit of it. What was the difference between the two kinds of nitrogen? The one was wholly derived from air; the other partially, to the extent of about one-fifth part, from ammonia. The most promising course for magnifying the discrepancy appeared to be the substitution of oxygen for air in the ammonia method so that all the nitrogen should in that case be derived from ammonia. Success was at once attained, the nitrogen from the ammonia being now* 1/200 *part lighter than that from air. ... Among the explanations which suggested themselves are the presence of a gas heavier than nitrogen in air ...*

This new gas was identified by *Ramsay*[65] in 1894 who made spectroscopic studies,

[61] Joseph Louis Gay-Lussac (1778–1850) French chemist
[62] Alexander von Humboldt (1799) Versuche über die chemische Zerlegung des Luftkreises und über einige andere Gegenstände der Naturlehre. Braunschweig, Vieweg
[63] Robert Wilhelm Bunsen (1811-1899), German chemist in Göttingen
[64] John William Strutt Lord Rayleigh (1842-1919) mathematician and physicist in Cambridge, Nobel Prize in physics 1904
[65] Sir William Ramsay (1852-1916) English chemist, Nobel prize in chemistry 1904

identified this gas as an element and named it argon (Ar), derived from Greek αργόν = slack. While investigating for the presence of argon in a uranium-bearing mineral, he instead discovered helium, which since 1868 had been known to exist, but only in the sun. This second discovery led him to suggest the existence of a new group of elements in the periodic table. *Ramsay* and his co-workers quickly (1898) isolated neon (Ne), krypton (Kr), and xenon (Xe) from the Earth's atmosphere.

Table 2. Historic data on air composition (in Vol-%)

species	Lavoisier (1778)	Cavendish (1783)	Krogh (1919)[b]
nitrogen	79.19[a]	79.16[a]	79.022
oxygen	20.81	20.84	20.948
argon	-	-	0.94
carbon dioxide	-	-	0.03
hydrogen	-	-	0.003
helium	-	-	0.0005

[a] within these figures novel gases are

[b] A. Krogh (1919) The composition of the atmosphere. Det Kgl. Danske Videnskabernes Selskab. Math.-fys. Meddelser. I, 12, København

Ozone, the first atmospheric trace species, was discovered by *Schönbein*[66] while conducting electrolysis experiments with water in 1841. *Van Marum*[67], subjecting oxygen to electrical discharges in 1785, noted "the odour of electrical matter" and the accelerated oxidation of mercury. Thus, *van Marum* reported the odour of ozone but he failed to identify it as a unique form of oxygen. Its chemical composition (only consistent from oxygen), however, was proposed many years later by *Thomas Andrews* in 1856. The formula O_3 was proposed by *William Odling* 1861. Ozone as a natural compartment of air was found in 1866 (Andrews, 1867), despite the fact that the so-called Schönbein paper (ozonometry) had already been used in England in 1848 for atmospheric “monitoring”.

Other atmospheric trace gases where known from the experiments by *Priestley* around 1774 (HCl, NH_3, SO_2) but not yet identified in air. *Scheele* identifies that nitrogen is in “alkaline air” (NH_3); the formula was established in 1785 by *Berthollet*. *Scheele* found ammonia in air by observing that on the cork from the bottle containing hydrochloric acid a precipitation originated, identified as salt ammonia (NH_4Cl).

Hydrogen (H_2) was already known in 16th century to *Paracelsius* but often confused by other combustible gases. *Cavendish* separated in 1766 hydrogen from other gases and showed that it burned to water. In connection with *Lavoisier*´s discovery on the role of airy oxygen (1777) it became clear that water is a chemical compound. Only in 1901 *M. A. Gautier*[68], who was the first to proclaim the presence of hydrogen in atmospheric air, found that water was formed when perfectly dry air was treated with copper at a red heat. This was verified in 1902 by *Rayleigh*´s spectroscopic studies in air.

Beside ammonia (NH_3), nitric acid (HNO_3) was known since Middles Ages. Ammonia was found in the atmosphere by *Scheele* in 1786 and by *de Saussure* in the early 1800s. Still at 1900, it was stated that ammonia never exist free (i.e., gaseous) in air but only in compounds

[66] Christian Friedrich Schönbein (1799-1868) Swiss chemist in Basel
[67] Martinus van Marum (1750-1837) Dutch chemist
[68] Ann. de Chimie 22 (1901)

with carbonate and others[69]. Both *Lavoisier* and *Priestley* suggested the formula HNO_3 in the years 1784-1786 independently from each other. *Cavendish* (1785) and *Priestley* (1788) described the HNO_3 formation in moisture air under the influence of electric dicharges.

Only in the latter 1900 all theses gases (NH_3, HNO_3, HNO_2) have been directly identified in the atmosphere. It is remarkable that the ocean as ammonia source, which was controversially discussed before 1990 and is now generally accepted, already has been suggested by *Schloesing*[70], who found that in sea water 0.4 mg l^{-1} ammonia are dissolved (cited after Blücher, 1900). However, as mentioned above, ammonia already was considered in early 1900 as a natural constituent of air. The same was "known" for nitric acid (HNO_3)[71] as a result of thunderstorms and (without knowing details) life processes. Atmospheric H_2S was known from mineral springs and rottenness of organic material. "Hydrocarbon" (not yet specified as methane, CH_4) was known from marshes and swamps (called swamp gas) but many natural gas sources (from which it was partly already used for burning). This gas was feared by coal miners where it was called "*böses"* or "*schlagendes Wetter*" (firedamp) because it was the reason for dangerous explosions.

As natural sources of phosphurated hydrogen (phosphine PH_3) sewage sludge, swamps and human flatus have been identified. In the early 19th century phosphine (which is spontaneously inflammable) was also known from cemeteries where it sometimes burned with blue flames.

Hydrogen peroxide (H_2O_2)[72], an important gaseous species belonging to atmospheric oxidants, was first found in thundershower by the German chemist *G. Meißner*[73] in 1863 where *E. Schöne*[74] also found evidence for its existence as gaseous substance in air (in 1872).

3.2 Particulate matter: atmospheric aerosol

Dust (in history often called "solid bodies") has been observed since ancient times and with the beginning of the 19th century some chemical species (iodine, phosphorus), micro organisms and plant rests have been considered. In the 1850s *Pasteur*[75] sampled air at Arbois (France) to investigate the issue of so-called "spontaneous" generation and in 1862 wrote the booklet

> *Die in der Atmosphäre vorhandenen organisirten Körperchen, Prüfung der Lehre von der Urzeugung* (The in the atmosphere existing organized bodies, examination of the theory of abiogenesis.), Leipzig, Verlag von W. Engelmann

He found many different germs in collected dust which are able to germinate with different

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[69] H. Blücher (1900) Die Luft. Ihre Zusammensetzung und Untersuchung, ihr Einfluss und ihre Wirkung sowie technische Ausnutzung. Leipzig, Verlag von O. Wigand, 322 pp.

[70] Jean Jacques Théophile Schloesing (1824-1919) French professor for agriculturchemistry; member of the French Academy of sciences

[71] In 19th century terms nitric acid, sulphurous acid etc. were used in the same sense for dissolved species (nitrate, sulphite) as well as anhydrites (e.g. SO_2).

[72] discovered 1818 by French chemist Louis-Jacques Thénard (1777–1857), Professor in Paris

[73] Göttinger Nachrichten (1863) p. 264

[74] Ueber das atmosphärische Wasserstoffhyperoxyd. *Ber. Dt. Chem. Ges*. 7, 1693-1708

[75] Louis Pasteur (1822-1895) French scientist (chemist, physicist) who was celebrated for his studies and discoveries in fermentation, and also for his researches in hydrophobia, and his suggestion of inoculation as a cure

substrates. *Pasteur* also studied air from different sites (rural, urban) and different altitudes and found a decrease of air germ with height (up to 2000 m a.s.l. at Mt. Montauvert). Before *Pasteurs* findings, it was believed that in air are *miasmas*, foul smelling gases, transferring diseases.

Scientific understanding of dust in atmosphere began with *Graham´*s [76] definition of a colloid in 1861. First direct observations of finest dust particles[77] dispersed in air were made by *Tyndall*[78] (1870) and *Aitken*[79] (1880). *Aitken* also found that the presence of fine particles is necessary for the formation of rain. Lord *Rayleigh* had shown that these dust particles, by their scattering action on the small waves of light at the violet and of the spectrum are the cause of blue sky. Beside fines dust particles, soot and coarse particles have been known. At the end of the 19th century it was known that the coarse fraction was soil dust and organic matter (with the latter up to 1/3). *Tissandier*[80] first stated that dust partly is of cosmic origin[81].

Table 3 summarizes the milestones in discovering the atmosphere.

Table 3. Milestones in discovering the atmosphere

Jan van Helmont (1577-1644)	introduction of the term "gas"
Robert Boyle (1626-1691)	physical treatment of gases
John Mayow (1643-1679)	combustion – CO_2
Georg Ernst Stahl (1660-1734)	Phlogiston theory
Josef Black (1728-1799)	discovery of carbon dioxide
Stephan Hales (1677-1761)	dew and rain chemistry
Daniel Rutherford (1749-1819)	discovery of nitrogen
Jean Senebier (1742-1809)	CO_2 exchange by plants
Joseph Priestley (1733-1804)	discovery of oxygen, HCl and NH_3
Carl Wilhelm Scheele (1742-1786)	discovery of oxygen, ammonia, chlorine
Antonne Laurent de Lavoisier (1743-1794)	first air analysis
Henry Cavendish (1731-1819)	air analysis
Joseph Louis Gay-Lussac (1778–1850)	air sampling and analysis, gas laws
Alexander von Humboldt (1769-1859)	air sampling and analysis, climatology
Christian Friedrich Schönbein (1799-1868)	discovery of ozone, H_2O_2
Justus von Liebig (1803-1873)	nutrients from air
Julius Adolf Stöckhardt (1809-1886)	"Rauchschaden" by SO_2
Louis Pasteur (1822-1895)	germs in air
Robert Angus Smith (1817-1884)	acid rain
Sir William Ramsay (1852-1916)	discovery of argon in air
John William Strutt Lord Rayleigh (1842-1919)	discovery of other novel gases in air
John Tyndall (1820-1893)	scattering of aerosol particles
John Aitken (1839-1919)	first observation of finest aerosol particles

[76] Thomas Graham (1805-1869) born in Glasgow, Scotland; professor for chemistry in Glasgow and London
[77] called in German in 19th century "Sonnenstäubchen"
[78] John Tyndall (1820-1893) professor for physics in London
[79] John Aitken (1839-1919) Scotch physicist and meteorologist
[80] Gaston Tissandier (1843-1899) French balloonists, dirigible builders, and aeronautical historians
[81] Gaston Tissandier : *Observations métérologiques en ballon*. Paris, Gauthier-Villars, 1879. 51 p.

3.3 Hydrometeors: rain, fog, clouds, dew

Hales was the first who analysed dew and rain (in 1772), noted that *"the air is full of acid and sulphurous particles"*. Nitrogen in rainwater (as nitrate NO_3^-) was first found by the German chemist *Marggraf* [82] from Berlin in 1774 and soon later confirmed by the Swedish chemist *Torbern Olof Bergmann* (1735-1784)[83]. *Smith* (he probably was a scholar of *Liebig*) noted 1873 in his book[84]

> *"Acid Rain – the Beginning of a Chemical Climatology, published in London 1872 (Longmans, Green, & Co)*

three types of areas as one moved from the city to the surrounding countryside:

> *"that with carbonate of ammonia in the fields at a distance, that with sulphate of ammonia in the suburbs and that with sulphuric acid or acid sulphate, in the town".*

The longest measurement series in the world exists from Rothamsted Experimental Station (beginning about 1880)[85]. Analyses of rain water when collected 1850 at the Paris Observatory made by the French chemist *M. Barral* show a residuum of 0.0228 g l^{-1}; he found nitric acid (nitrate), ammonia (ammonium), chloride, lime (calcium) and magnesium. All these substances have been attributed in the Middle of the 19th century to natural sources and esp. biological activities.

4. Biosphere-atmosphere interaction

Hales[86] made many careful measurements (1738) of the absorption of water and its transpiration to the atmosphere. He understood that air and light are necessary for the nutrition of green plants. First *Woodward*[87] (1733) suggested the mineral nutrition of plants. But it was not before the composition of air from different gases became known that their significance for plant nutrition was studied.

Senebier[88] discovered that the regeneration of air is based on the use of "fixed air" (carbon dioxide) or – in modern terms - he demonstrated that green plants consume carbon dioxide and release oxygen under the influence of light. In 1804 *Saussure*[89] discovered that the

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[82] Andreas Sigismund Marggraf (1709-1782) German chemist, a pioneer in analytical chemistry. Born in Berlin, studied chemistry, physics and pharmacy at Caspar Neumann (1683-1737) in Berlin (Collegio Medico Practico), later in Frankfurt, Halle and Freiberg. 1738 member of the "Königliche Societät der Wissenschaften" (Royal Society of Sciences), after renaming into "Akademie der Wissenschaften" he became its director in 1767. Discovered 1747 sugar in beetroot and the element zinc in 1772.

[83] cited after G. Torstensson (1954) Stickstoff- und Schwefelverbindungen aus der Atmosphäre und ihre Bedeutung für die Pflanzen. Sitzungber. Dt. Akad. der Wiss., Berlin, Vol. III, Heft 18

[84] Most remarkable is the first use of the term "Chemical Climatology" which was only used again after 1950 at the Meteorological Institute of the Stockholm University. Nowadays, most but not all scientists consider the "climatology" as the discipline to describe the long-term physical and chemical atmospheric status and its statistics.

[85] The world's oldest and England's most important agricultural experiment station. It was founded in 1843 by John Bennet Lawes on his estate at Harpenden, in Hertfordshire, where he had been experimenting with fertilizers.

[86] Stephen Hales (1738) Vegetable Statics, 3rd ed., London

[87] John Woodward (1665-1728) Professor at Gresham College in London

[88] Jean Senebier (1742-1809) Swiss botanist and naturalist, priest in Geneve

[89] Théodore de Saussure (1767-1845) Swiss botanist and naturalist from Geneve

plants'' increase in weight cannot solely be caused by the uptake of carbon and minerals, but is based on the binding of the water components, too, and accompanied by the release of oxygen during photosynthesis. In 1838, *Boussingault*[90] conducted an elegant series of experiments and showed that legumes had higher nitrogen levels than cereals and, based on some crop rotation studies over 5 years, concluded that the atmosphere was the source of this nitrogen (it could have been particulate matter, nitrogen gas or ammonia - he did not specify which). In 1848, *Liebig*[91] argued, with no new evidence, that it was ammonia and this was accepted because of his reputation. Already in 1840 *Liebig* published a book entitled "*Die organische Chemie in ihrer Anwendung auf Agricultur und Physiologie*" (Organic Chemistry in its Application to Agriculture and Physiology). A strong dispute between *Liebig* and his colleagues (esp. *Lawes* and *Gilbert*) on the mineral fertilizer theory initiated soon many studies on chemical composition of rainwater (see previous chapter).

In the 1880s, *Schloesing* and *Muntz*[92], two German scientists, discovered that nitrification is biological, proving *Pasteur's* hypothesis from years before. The phenomenon of nitrification, i.e. the formation of nitrites and nitrates from ammonia and its compounds in the soil, was formerly held to be a purely chemical process.

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