Jean Baptiste Boussingault

Jaime Wisniak

Department of Chemical Engineering, Ben-Gurion University of the Negev, Beer-Sheva, Israel 84105
wisniak@bgumail.bgu.ac.il

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RESUMEN. Jean Baptiste Boussingault (1802-1887), un auto didacta que no tuvo una educación formal, es considerado el fundador de la química agrícola. Sus cuidadosos experimentos sobre suelos, cultivos, fertilizantes, la asimilación de nitrógeno atmosférico por las plantas, los cambios en la composición de semillas durante la geminación y la utilización de alimentos por los animales, aportaron la información fundamental que llevaría a la comprensión completa del ciclo del nitrógeno en la Naturaleza. También encontró una relación entre la enfermedad del bocio y el yodo y recomendó el uso de sal yodada para combatir los efectos de la enfermedad.

ABSTRACT. Jean Baptiste Boussingault (1802-1887), a self-trained scientist that did not have a formal education, is considered to be the founder of agricultural chemistry. His well-planned experiments on soils, crops, fertilizers, and assimilation of atmospheric nitrogen by plants, changes in composition of seeds during germination, and utilization of food by animals, contributed the fundamental information that would lead to the full understanding of the nitrogen cycle in Nature. He also found a relation between goiter and iodine, and recommended the use of iodized salt to fight the effects of the illness.

LIFE AND CAREER[1-7]

Jean Baptiste Joseph Dieudonné Boussingault (Fig. 1) was born in Paris on February 2nd, 1802, the second child of Charles Nicholas Joseph Boussingault (1760-1848), a Captain-General of the Royal Farms (army storekeeper), and Elizabeth Münch (1776-1836). He had two sisters, Colombe, which died of young age, Jeanette Elizabeth (1798-1859), and a brother Nicholas (1806-1836). His father, after resigning from the army, opened a small groceries and tobacco shop that provided the family with a minimal income; which was complemented by renting a room in their house.[6] Jean Baptiste did not receive an extensive formal education; he entered the usual *Lycée* (Louis-le-Grand) but quit it at the age of ten, a year before graduation, thus closing

Fig. 1. *Jean Baptiste Boussingault (1802-1887) (By permission of Edgar Fahs Smith Collection, University of Pennsylvania Library).*

cation in the sciences and his only contact with advanced education was the year he spent at approxi- Thenard (1777-1857) at the *Collège de France*. However, Thenard fired him after learning that he was working without his authorization. Twenty-five years later Thenard is said to have remarked: *"Ah, si j'avais pu prévoir!"* (if only I could have foreseen).[1] This short and unpleasant experience seems to be the one that opened Boussingault's appetite for science.

His autobiography gives no record of having entered any of the educational institutions of Paris as a regular student.[1] Nevertheless, his strong interest in science is illustrated by the fact that when aged ten to fifteen he attended the most popular free lectures that were open to the public at the *Collège de France, l'École Polytechnique, l'Université de Paris and the Muséum d'Histoire Naturelle*, on a wide range of scientific topics, i.e., chemistry, botany, crystallography, paleontology, and geology. To help him in his scientific endeavors his mother bought him Thenard's 4-volume treatise on chemistry.[8,9]

In 1817 Boussingault's parents allowed him to enter the recently opened *École des Mineurs* (School of Mines), a practical school for miners with little or no training in the sciences, at Saint-Etienne near Lyon, in Alsace, to begin the 2-year course. Classes were limited to eight or nine students in each of the two years of the course. Toward the end of his second year, after finishing with top grades the chemistry and mineralogy courses, Beaunier, the Director of the school, appointed him stuthat carried privileges such as access to the laboratory for his own study. The results were somewhat unusual: he got his first publication, at the age of 19 years, on the presence of silicon in steel and in a specimen of platinum, and during the experimental work set fire accidentally to the laboratory (see below).[10] His graduating class had only six students.[9]

In 1820 Boussingault went to work at the lignite mine in Alsace and became friendly with a local family, the Le Bels, who operated the Bechelbronn farm and on which asphalt and petroleum were mined. Boussingault's opportunity came in 1821 when Simon Bolivar (1783-1830), who had recently liberated Colombia and Venezuela (New Granada) from Spain, sent Francisco Antonio Zea (1770-1822), his vice President, to Paris to recruit technically trained young men to staff a new school of technology (*Escuela Nacional de Mineros*) in Bogotá for training civil and military engineers, as well as investigate the mineral and agricultural potential of newly liberated Colombia.[11] Simeon-Denisse Poisson (1781-1840) and Jean Baptiste Biot (1774-1862) gave him letters of introduction to Bolivar.[4,5] Boussingault received a four-year contract as professor and, an appointment in Bolivar's army, which he kept until he left South America 10 years later with the rank of lieutenant colonel.[9]

Boussingault went to South America not only to teach, but also as part of a scientific expedition organized by Alexander von Humboldt (1769-1859) to do geological, geographic, mining, and surveying studies of the area. Another member of the team was the physician-naturalist François Désiré Roulin (1796-1874). During his stay in Venezuela, Boussingault taught at the school of mines during 1823 and part of 1824 and also surveyed mining sites, particularly for gold and other precious metals. After concluding his teaching appointment Boussingault worked for sometime for the Colombian Mining Company, which was finding and working former Incan gold mines.[9]

Boussingault journeyed at length through Colombia, Venezuela, Ecuador, Peru, and Chile and summarized his findings and observations in the areas geology, chemistry, medicine, and climatology in twenty-five papers that he sent to the *Académie des Sciences* in Paris.[4,5] and platinum, and his foreign experience and many papers published while overseas earned him a doctorate and a post as professor of chemistry at Lyon. Shortly thereafter he was elected Dean of the Faculté des Sciences in Lyon. Two years later he replaced Dumas as substitute of Thenard at the *Faculté des Sciences* de Paris and accepted a concurrent post at the *Conservatoire des Arts et Métiers*. In 1839, after the death of the veterinarian Jean-Baptiste Huzard (1755-1838), a member of the *Académie des Sciences*, Boussingault was elected to succeed him in the section *Économie Rurale* (rural economy); making him one of its youngest members of the Academy. In the following year he became one of the editors of the Annales de *Chimie et de Physique*, the journal in which he had published most of his South American work. In 1845, André Thouin (1747-1823), Professor of Agriculture at the *Conservatoire des Arts et Métiers*, passed away and the *Académie des Sciences* elected Boussingault as his successor. This appointment did not involve much work and enabled Boussingault to spend considerable time in Paris. He lost the chair in the political unrest of 1851 as the Republic was shifting to a dictatorship and an Empire, but got it back again as a chair in Agricultural Chemistry, which he kept until the end of his life. In 1849 Boussingault was elected president of the *Académie des Sciences*.[22]

In 1833 Boussingault traveled again to Alsace and there he married Adèle Le Bel, about 10 years his junior, and sister of a fellow student at St. Etienne. Four children were born, three daughters, the first one born shortly after birth, then Berthe Gabrielle (1836-1890), and Alice (1839-1928), and one son, Joseph (18421925).

By this marriage Boussingault became, together with his brother-in-law, Louis Frédéric Achille, joint proprietor of the estate at Bechelbronn (today, Pechelbronn). His brother-in-law was the father of the Joseph Achille Le Bel (1847-1930) who later achieved fame for his research in stereochemistry (Wisniak). After his marriage Boussingault established a private laboratory at the farm and a life-long series of studies connected to the application of chemistry and physics to, as well as performing both field and laboratory experiments. This laboratory has modern sense. From the time of his marriage on Boussingault spent about half of the year in Alsace and the other half in Paris.[3]

In the elections for the *Assemblée Nationale* in April 1848, after the revolution, Boussingault became of the fifteen representatives of the Department of Bas-Rhin, all of who were members of the socialist Louis Blanc's (1811-1882) party, the *Société Centrale des Ouvriers*. While a member of the *Assemblée*, Boussingault was elected in April 1849 to the *Counseil d'État*, an advisory body, which also had executive powers except in financial matters. He kept this post until 1851. His political ideas led to his being considered anti government and intent to dismiss him from his post at the *Conservatoire*. Upon hearing about this decision his colleagues threatened to resign in a body, a move that made imperial government to reconsider and give him back his professorship.[22] Interesting enough, his anti government ideas did not prevent his being appointed to the *Legion d´Honneur*.

The Franco-Prussian War of 1870 and the subsequent Treaty of Frankfort (1871), where Alsace was transferred to Germany, forced Boussingault to lose his Bechelbronn farm. He left Alsace to initiate a series of investigations on iron and steel at his son-in-law's, Jules Gustave Holtzer (1834-1876), factory, (Jacob Holtzer et Cie at Unieux, Loire, near Saint-Etienne). His first paper was related to the nature of a platinum silicide, which he had prepared in 1821. In addition to the main research on steel he tried to make a platinum-carbon alloy, or platinum carbide, analogous to steel, by heating thin leaves of platinum with wood charcoal in a clay crucible. The results were almost disastrous, as can be learned from a letter to his father in Paris: "*Since my last letter...I have set fire to the school and I have melted a metal (platinum) which was believed to be infusible...The cause of the fire was that the flue had not been constructed for a fusion furnace...As soon as the fire was extinguished I went to look for my crucibles and had the satisfaction of seeing that my platinum had melted; in another crucible I found that the platinum had combined with the carbon and formed a casting similar to an iron casting...Since then I have...succeeded in making plati-*

other done in 1875 on the cementation of steel in which he attempted to determine the difference between blister steel an iron, that is, to determine the nature and amount of the substances lost and produced during the process of cementation.[11,12] In spite of all his efforts, Boussingault did not succeed in elucidating the true nature of steel.

From 1834 on Boussingault applied organic analysis in field and laboratory research in his farm at Bechelbronn, Alsace, to problems of soil fertility, crop rotation, plant and soil fixation of nitrogen, ammonia in rainwater, and nitrification, in order to determine the sources of plant nitrogen. In his 1837-1838 nitrogen fixation experiments, he suggested that legumes might fix nitrogen from atmospheric sources. Afterwards he also showed that legumes, when grown with cereals in initially exhausted soil, restored to soil far more nitrogen than could attributed to fertilizers; that both herbivores and carnivores could obtain their nitrogen from plants; and that the nitrogen of all plants, except legumes, could be accounted for by organic fertilizers.

A dexterous chemist, Boussingault performed, in addition to his researches concerning nitrogen life, diverse researches such as the extraction of oxygen from air by baryta and the composition of air retained by vegetable soil. In his study about the functions of leaves, he established that the volumes of carbon dioxide absorbed and oxygen released under light were almost identical. In his remarkable studies of growing vegetables in the dark, he demonstrated by elemental analysis and dosimetry of the most important organic components that plants in the absence of light behaved like animals and that there respiration involved starch and sugar.[7,13]

Boussingault was one of the founders of the Institute Agronomique de France. He received many honors from foreign governments and from scientific societies both at home and abroad. In 1878 the Royal Society awarded him the Copley Medal, "for his long-continued and important researches and discoveries in agricultural science". [22]

Boussingault died in Paris at his daughter Berthe Holtzer house, on May 11, 1887, and was buried at the *Père Lachaise* cemetery. As a former colonel of the Colombian forces of

SCIENTIFIC ACTIVITIES

Boussingault's publications include more than 140 papers and the books *Économie Rurale*, in two volumes;[14] *Agronomie, Chimie Agricole et Physiologie*, in eight volumes;[15] *Études sur la Transformation du Fer en Acier par la Cémentation*;[12] and his autobiographical *Mémoires*, in five volumes. [1]

Afterwards, it will be described some of his most important contributions.

Nitrogen role and nitrogen cycle

When Boussingault began his researches at the Bechelbronn farm, the state of knowledge regarding nitrogen and living organisms was much undeveloped. Milk casein, clotted blood fibrin, egg-white, gelatin, and the coagulum formed on heating blood serum, were considered to be distinct chemical substances, but nothing was known about their chemical nature. Gerardus Johannes Mulder (1802-1880) observed that these substances had about the same percentage composition of carbon, hydrogen, nitrogen and oxygen, as well as sulfur and phosphorus, which suggested the existence of a radical of some sort, which he named *protein* (from the Greekprwteioz, primarius). According to Mulder animals seemed to draw their most essential nutrient ingredients directly from the plant kingdom and the plant protein contained sulfur and phosphorus in a different relation from that in the animal protein. Herbivores could then be considered not different from carnivores; they were both nourished by protein.[22]

The chemistry and fertility of soils have been of concern to humans since ancient times. According to McCosh[6] during the nineteenth century, much research was done in Europe trying to determine the interdependence of plants, soil, and the atmosphere. Central to these studies was the very practical question of whether mineral fertilizers alone would maintain soil fertility, or whether their action must he increased by additional by nitrogenous sources.[22] Louis Lémery (1677-1743) had shown that saltpeter (potassium nitrate) was of organic origin and should not be considered a mineral. He had also described the slow production of KNO_3 in the superficial layers of the soil and recognized the reciprocal relationships that charac- *aërial* matter.[16] According to Lémery the nitre principle originated from dead animals and plants and its accumulation in the soil could be explained by their slow transformation. In 1804 Nicolas Théodore de Saussure (1767-1845) recognized the importance of nitrogen in the life processes of plants and declared that they obtained this *partie esentielle des végétaux* (essential part of vegetables) from solutions of *principes extractifs* (extractive principles*)* absorbed from the soil.

It was generally understood that plants take at least part of their carbon and oxygen from the atmosphere, but there was no evidence that this was so for nitrogen. Physiologists like Joseph Priestley (1733-1804) and Jean Ingenhousz (1730-1799) believed that there was a clear absorption of nitrogen during growth; they had tried to resolve the question of the possible absorption of nitrogen through vegetables, but had obtained conflicting results. In 1804 Saussure repeated Priestley's and Ingenhousz's experiences using more precise eudiometric methods and established that no absorption of nitrogen took place, on the contrary, there seemed to be a slight *exhalation* of this gas.[17] Claude Louis Berthollet (1748-1822) found nitrogen in plant gluten and demonstrated that the volatile alkali (ammonia) is produced during the decomposition of animal material[18]; in 1785 he discovered the presence of nitrogen in both plants and animals. Priestley, Ingenhousz, Jean Senebier (1742-1809) and Saussure worked out the main paths of the oxygen and carbon dioxide cycles, as they are known today.

In 1806, Louis Nicolas Vauquelin (1763-1829) and Antoine-François Fourcroy (1750-1809)[19] showed by numerous analyses of barley, peas, and beans that the legumes were richer in "*animal matter*". In 1816, François Magendie (1783-1855) established that food not containing nitrogen was unable to sustain animal life; dogs could not survive on a diet of non-nitrogenous food alone.[20] His studies indicated that the nitrogen, which is found in the animal economy, is in great part extracted from the food.[22] In 1833 Joseph-Louis Gay-Lussac (1778-1850) reported that all vegetable seeds contain nitrogen and Anselme Payen (1795-1871) showed that the younger vegetable tissues are also the richest in analysis of animal albumin and found it to contain about 16 % of nitrogen. It was also known that the decomposition of nitrogen substances in the soil liberated ammonia .[7]

Justus von Liebig (1803-1873) outstanding position in the scientific community helped persuade scientists by 1840 that plants could be produced from carbon dioxide, water, ammonia, and certain minerals, the ultimate products of the decay of plants The putrefaction of animal and vegetable material occurring everywhere on the earth's surface constantly renewed this ammonia, and in addition, plants also assimilated nitrogen from ammonia that was washed down automatically from the air in the rain. His theory overturned the older agricultural ideas that plants utilize complex, soluble organic compounds released during the breakdown of manures. Liebig later found ammonia in plant sap, and came to believe that as it was also present in the atmosphere it must be absorbed by plants aerially like carbon dioxide in amounts sufficient to meet their full needs for nitrogen. According to Liebig, certain minerals, such as gypsum, had the remarkable property of fixing in the soil the ammonia of the atmosphere and of retaining it by changing the ammonia coming down in solution as a carbonate into a soluble sulfate. Liebig's view led to the establishment of the *mineral theory*, according to which soil fertility could be maintained by the mineral constituents of artificial fertilizers that lack nitrogenous components.

Boussingault's experiments during the middle years of the nineteenth century led him to view the soil as the site of many complex chemical reactions (today, it is enough to look at the part of the nitrogen cycle that takes part in the soil to understand how correct Boussingault was).[21] Soil was a chemical dynamic system, capable of supplying all the nutritional needs of plants.[4,5] He demonstrated that most of the soil nitrogen did not have an immediate effect on plant nutrition and that the assimilable fraction, occurring as ammoniacal salts and nitrates in the soil, not only accumulated in time but did so beyond the residual sources. Boussingault believed that "*it is the soil and not the plant that fixes the nitrogen*" and was then left with the question as to trates.[22] To test this possibility he set up a plant nutrition experiments in which he sought to eliminate any possible sources of nitrogen in the soil. His research method was based on comparing the elemental composition of seeds with that of plants grown in soils supplied with only water and air. He used as substrate cooked clay or silica sands previously cleaned of organic matter by calcination. The soil was moistened with distilled water and sowed with a known weight of seeds. Samples of the seeds were dried, weighed, and analyzed for carbon, hydrogen and nitrogen by the combustion method. The pots were put inside a closed pavilion under the action of the sun during the full day. These precautions were taken to avoid any possible nitrogen contribution from atmospheric dust. The plants were collected in their grown state and their elemental analysis and cinder content determined. Thus it was easy to determine the proportion and nature of the elements (carbon, hydrogen, oxygen, and nitrogen) assimilated during growth.[7] Boussingault's experiences proved that growth did take place without the aid of nitrogen, but under the unfavorable conditions used the original grains did not reproduce. The nitrogen present in the original grain simply distributed itself in the vegetable and led to a stunt and incomplete grown plant.[23] As the above experiments show, Boussingault was not aware of soil organisms and the deleterious effect calcination had on them.

Boussingault remarked that in nature plant growth did not take place in the presence of only of water and atmosphere; the roots that anchored the plant to the soil provided an important part of its nutrition. Development of the plant took place as the combined contribution of the foods that the roots took from the soil and of the gaseous elements that the leaves took from the air. Since the nourishment provided by the soil was nitrogenated, then one had to consider that the fertilizer was the principal source, probably the only one, of the nitrogen found in vegetables. This seemed to confirm Sigmund Frederick Hermbstädt's (1760-1833) conclusions that cereals cultivated under the influence of highly nitrogenated fertilizers were the ones that contained the most gluten, meaning that plants took all

Boussingault also found that during their growth the peas, lucerne (alfalfa, *Medicago sativa*), and red clover showed a marked increase in nitrogen content over that of the original seeds; with wheat and oats, however, no nitrogen had been added to what was originally present in the seed. The extra nitrogen in the legumes must have come from the air and not from the soil, or so it seemed. The final explanation of these phenomena by the discovery of nitrogen-fixing bacteria in the nodules of the roots of legumes, came about 50 years later when Hermann Hellriegel (1831-1895) and Hermann Wilfarth proposed that nodules on the roots of legumes were induced by soil bacteria, that these bacteria fixed atmospheric nitrogen, and that legumes without nodules behaved like non-legumes in using nitrogen compounds in the soil rather than atmospheric nitrogen.[22]

In his book about crop economy[14] Boussingault concluded: "*clover and peas grown in a soil absolutely deprived of manure, acquire, besides carbon, hydrogen, and oxygen, a substantial amount of nitrogen and... wheat and oat, cultivated under the same conditions, also takes on from air and water, carbon, nitrogen, hydrogen, and oxygen, but in comparison with the vegetation of these cereals, there was been no gain in nitrogen... My results seem to indicate that under many conditions, certain plants are able of drawing air nitrogen, but we do not know in which state this element in being fixed in vegetables*".[23,24]

In 1855, Boussingault made his case conclusively that although there was not enough ammonia in the rain to satisfy the nitrogen needs of plants, it was necessary to know how much it contained. For this task, he first developed his own analytical method for the accurate determination of small amounts of ammonia in water, and then proceeded to analyze a large number of water samples taken from rivers, wells springs, and rain from different regions of France, as well as fog, dew, and snow.[25] Boussingault also used his findings and analytical procedures to categorically oppose Georges Ville (1824-1897) contention that plants were able to assimilate the free nitrogen of the air (Ville, 1854). Boussingault's experiments published in 1854-1855 as his *Recherches sur la Végétation*[26,27] had the effect of draw-

Boussingault's thoughts about nitrogen were as follows: "*Nitrogen is an essential element for the existence of every living organism…If it is searched what can be the source of this principle in herbivores it is found very naturally in all manure from animal sources because plants to survive must receive nitrogenated food through their roots. In this manner, it can be concluded that it is the vegetables the ones that provide nitrogen to animals, and that the latter return it to the vegetable kingdom when they die. In few words, organized living matter obtains its nitrogen dead organic matter. This last conclusion tends to establish that living matter is restricted to the surface of the Earth and that its limit is bound by the amount of nitrogen in circulation in living entities. But the question must be put in a more general context by asking about the origin of the nitrogen that enters in the composition of the total of organic matter. If we examine the deposits of nitrogen and put aside organized entities or their debris, there remains only one pool, which is the atmosphere. Hence it is extremely probable that living entities have taken their nitrogen from the atmosphere.*"[24]

As mentioned before, Boussingault grew clover and wheat in the presence of soil and air only and analyzed the composition of the original seeds and the ones cropped, for oxygen, carbon, hydrogen, and nitrogen. He also analyzed the plants during different stages of their growth. The analytical method employed did not allow determining the particular nature of the products formed during growth, but did allow calculation of the gross elements that had been acquired or eliminated, independently of their state. In the first stages of germination, the analysis proved that with the help of air carbon dioxide was always formed, jointly with the absorption of oxygen. In this initial stage the grain lost carbon and also oxygen, but the latter loss did not express itself totally as water. It was very probable that oxygen had combined with carbon, forming with the elements of water a non-gaseous compound. The plant took from the air and water, carbon, oxygen, and hydrogen. Interesting enough, the relative increases in weight of hydrogen and oxygen were in the precise ratio as they appeared in water.[23] According to Antoine Becquerel (1788-1878) firmed the presence of acidity by growing seeds over a sheet of litmus paper. It was clear then that a germinating grain loses part of its carbon, in addition to forming carbon dioxide with the oxygen of air, and that the oxygen present in the grain enters in the composition of the acetic acid formed. Since all the elements of the grain that contributed to the formation of this acid were detected using eudiometric methods; hence, it was probable that all nongaseous volatile products (such as acetic acid) could dissipate as gases during the drying of the germinated grain.[23]

Boussingault concluded that during germination clover and wheat did not gain or lose nitrogen, and that their grains lost carbon, hydrogen, and oxygen in amounts that depended on the germination stages. During the growth period of clover, in a soil absolutely deprived of fertilizer and under the influence of water and air alone, the plant picked up carbon, hydrogen, oxygen, and an appreciable amount of nitrogen, while wheat, grown under the same set of conditions, took out from water and air, carbon, hydrogen, and oxygen, and showed no gain or loss of nitrogen. [23]

Role of nitrates and minerals

It was well known that the nitrates of sodium and potassium contributed vigorously to the development of plants, and hence it was important to learn the way of their action. Boussingault examined the effects of various salts on the growth of plants, again by the use of sterile soil to which inorganic salts were added and found that the addition of a mixture of calcium phosphate and potassium nitrate produced excellent growth, while by omitting the nitrate, by use of a mixture of calcium phosphate and potassium bicarbonate, the growth rate was almost as poor as that in sterile soil. [23] Ville found that although mineral salts and nitrates alone produced little effect on growth, however, when they were used together the difference was remarkable, the greatest development occurring when the mineral salt employed in conjunction with a nitrate was a phosphate. [26,27]

According to Boussingault, the only reasonable explanation about the action of nitrates was the one advanced by Charles Frédéric Kuhlsorbed by the plant was transformed in the soil to ammonia. Hence, to obtain the high utility of nitrates it was necessary that they be put under the deoxidation action of putrid fermentation where the definite result was ammonium carbonate. [30,31] Boussingault believed that it was necessary to examine if the presence of putrescible organic matter in the soil was really indispensable for the assimilation of the nitrogen by the plant. If assimilation took place in the absence of the element then it was not necessary for the nitrogen of the nitrate to be converted into ammonia previously to become fixed by the vegetable, and hence nitrates did not behave as salts based on potassium or sodium.[31]

Once again Boussingault's experiments consisted in cultivating a plant in a sand substrate made sterile by calcination, containing a known amount of alkaline nitrate and cinders, and accompanied by irrigation with pure water. If the plant developed, then the nitrate absorbed was calculated by analytical determination of the nitrate remaining in the soil. These experiments were carried out with lupin, sunflower, and watercress and their results indicated that alkaline nitrate acted on plants with the same pace and slightly more energy than ammonia salts. In the absence of potassium nitrate sunflower hardly developed. The clear influence of nitrates on the development of the vegetable organism confirmed the opinion given in a previous memoir that the decomposition of carbon dioxide by the leaves was in a certain way subordinated to the prior absorption of a fertilizer operating like farm manure. It was important that the nitrogen added be assimilable so that it could contribute to the formation of nitrogenated tissue in the plant. The demonstration of this fact, (that saltpeter acted very favorable on vegetation thanks to its direct absorption and without the participation of substances capable of putrefaction) allowed understanding why certain waters exerted such remarkable effects (even if they contained traces of ammonia) because these waters normally contained nitrates that competed like ammonia to the vegetable production. [31]

Boussingault continued this work by following the growth of sunflowers in open air and protected from rain, using a basic substrate had been washed with distilled water. Three series of experiments were carried out: (a) with nothing added to the soil, (b) by addition of basic calcium phosphate, vegetable ashes, and potassium nitrate, and (c) by addition of calcium phosphate, vegetable cinder, and an amount of potassium bicarbonate containing the same amount of potassium as in series (b). The relative crops obtained; 3,6 kg for experience (a); 198,3 kg for experience (b), and 4,6 kg for experience (c); clearly demonstrated the influence of a nitrogenated fertilizer. In order to contribute actively to the vegetable production, the basic calcium phosphate and alkaline salts had to be associated with a substance capable of providing assimilable nitrogen. Manure, a fertilizer by excellence, provided exactly this type of association. It was then clear that calcium phosphate and alkaline salts, added to a soil without the cooperation of a nitrogenous fertilizer, did not contribute sensibly to the development of the organism. When phosphate and potassium nitrate were associated they acted with the energy of manure.[23]

To investigate this matter further, Boussingault performed another series of experiments using a substrate made of calcined sand supplemented with calcium phosphate and potassium salts and controlled amounts of sodium nitrate that is, containing different doses of assimilable nitrogen. The results provided another clear demonstration of the importance of assimilable nitrogen. While the blank test led to a production of 0,397 g of dry matter, addition of 0,003 3; 0,006 6, and 0,0264 g of assimilable nitrogen increased the weight of dry matter to 0,720; 1,130, and 3,280 g, respectively.[23]

Boussingault concluded that calcium phosphate and alkaline and earth salts, although indispensable for the constitution of plants, did not exert any action on vegetation except when they were joined by materials capable of providing assimilable nitrogen. Atmospheric materials containing assimilable nitrogen but in the absence of a nitrogenated manure, had a minimal participation in producing an abundant crop. Saltpeter associated to calcium phosphate and potassium silicate acted like a complete fertilizer.[23]

Boussingault also studied the influence of calcium phosphate on the production of vegetable matter. quartz, to which he added saltpeter or ammonium carbonate, in the complete absence of phosphate. Since the cultures took place in free air, it was necessary to determine the part contributed by nitrogenated principles present in the atmosphere, by cultivating in a terrain deprived of organic matter, the same species that were cultivated under a controlled regime of nitrate of ammonia salt. Again, this was done by studying the gradual development of sunflower in detail. Six series of growth experiments were performed using: (1) a substrate of calcined quartz sand containing calcium phosphate and vegetable ashes, (2) the same substrate without calcium phosphate and containing potassium nitrate, (3) the same substrate, without calcium phosphate and addition of ammonium carbonate, (4) hemp growth, in a soil deprived of organic matter and containing calcium phosphate and vegetable ashes, (5) the same as (4) with potassium nitrate added; and (6) hemp growth, in a soil containing only ammonium carbonate.[23]

The results indicated that in free air and in a soil absent of phosphates mixed with other mineral salts, a plant would grow with a certain vigor only during the first state of vegetation, as long as the nitrogenated substance present in the seed sufficed for the formation of organs. Beyond this state the plant languished.[32]

According to Boussingault, he had previously shown that calcium phosphate did not operate favorably on plants unless it was associated with substances that could contribute what he called *assimilable nitrogen* (to differentiate it from atmospheric nitrogen that plants do not assimilate directly). In this new work he had shown that a substance rich in assimilable nitrogen functioned as a fertilizer only with the help of phosphates. Although in the absence of phosphates the plant became more voluminous than the one grown in the presence of phosphate alone, it never achieved a normal development.[23]

Crop rotation

Crop rotation was practiced in ancient Roman, African, and Asian cultures. During the Middle Ages in Europe, a three-year crop rotation was practiced by farmers rotating rye or winter wheat in year one, followed by spring oats or barley in the century, when it became known that addition of legumes to the cycle would maintain the yield of a succeeding crop, the practice was replaced by a four-year sequence involving a string of wheat, barley, turnips, and clover. This new cycle was implanted as a consequence of experience, without understanding the reason for it.

Boussingault's interpretation of the practice was different from that of Liebig, who Liebig argued "*cultivated plants receive the same quantity of nitrogen from the atmosphere as trees, shrubs and other wild plants; but this is not sufficient for the purposes of agriculture*". The distinguishing action of fertilizers was not in their nitrogen but rather in their inorganic constituents, the most valuable of which were the "*phosphates of lime and magnesia, carbonate of lime and silicate of potash*," and also common salt (sodium chloride). These minerals could be added to the soil in artificial form. According to Liebig, the nitrogen in fertilizers had the auxiliary task of assisting in the fixation of carbon from the atmosphere, but artificial replacement of the nitrogen removed from the soil by crops by fertilizers; would lead to its unnecessary accumulation in the soil, because a portion was added continually from the atmosphere as ammonia.[22]

According to Boussingault, the two important questions in agricultural were the theory of soil depletion by cultivation, and crop rotation. Albrecht Daniel Thaër (1752-1828) believed all the organic matter in plants originated from the soil and the depletion of the soil was proportional to the amount of nutritional material contained in the harvest. The soil contributed to the development of vegetables but so did air. Soil could be provided with an unlimited amount of fertilizers, without the need of crop rotation, but in the majority of agricultural exploits where it was not possible to previously add fertilizers, it was indispensable to follow a crop rotation policy, and the amount of products obtained yearly was limited. In order to return to the soil its normal fertility, it was necessary to add, after a series of crops, equal amounts of fertilizer. Looking at this condition from a purely chemical point, it could be said that the products, which might be produced without detracting from the fertility of the soil, could be reprematerial contained in the fertilizer. The latter, in one form or another, had to return to the soil in order to fertilize it again; it was a capital invested in the soil and the product marketed represented its interest. [24]

In another memoir, Boussingault tried to prove that the best regime of crop rotation was the one that removed from the atmosphere the largest amount of elemental material, and that it was this amount the one that had to be evaluated to judge the relative value of different crop rotation regimes. To this he was intent in comparing for a particular situation of soil and climate, the ratio that existed between the elementary material contained in a series of crops and the same material contained in the fertilizer employed for producing it. In other words, he was trying to evaluate by analysis the amount of organic substances taken from the atmosphere by each type of rotation. For this purpose he put up a one-hectare experimental plot and grew different crops during a period of ten years, using as fertilizer farm manure containing the organic matter to be consumed by partial assimilation in the collected crop. Boussingault believed that assimilation was partial because the total did not necessarily become part of the plants that were born; part of the fertilizer decomposed spontaneously or was carried away by the water. Another portion probably became inert with time and could not carry on its fertilizing action at the proper time of growth.[24] Boussingault performed an elementary analysis (carbon, hydrogen, oxygen, and nitrogen) of the crops (grains, straw, roots, and tubers) obtained from 14 different plants (wheat, rye, oat, wheat straw, rye straw, oat straw, potato, beet, turnip, artichoke, yellow pea, pea hay, red clover, and artichoke stems), as well of the fertilizer employed. Crop rotation was as follows: potato or beets, wheat, clover, wheat, and oat. Of the plants studied, artichoke showed the largest growth in the atmosphere and gave the largest amount of nutritive material with the least amount of fertilizer. [24]

The results of the work confirmed what was known empirically: the best crop rotation is the one that withdraws the largest amount of principles from the atmosphere. Hence this parameter can be used to meliorative action of legumes was due to their ability to restore nitrogen to the soil. "*Nitrogen is an element essential to the existence of all living things; it is kindred moreover to both the animal and the plant kingdoms…it is the plants that furnish nitrogen to animals when their existence is accomplished… organized living things take their nitrogen from dead organic matter… living material is therefore limited… by the quantity of nitrogen actually in circulation within living things*". [4,5,33]

Rating of foods and feeds by nitrogen content

Farmers were well aware of the fact that the most active manures were those originating from animal matter; their principal difference with the ones of vegetable origin was the amount of nitrogen they contained. According to Boussingault and Payen the most valuable fertilizers were the ones that not only contained the largest amount of nitrogen but also this content was larger than that of their non-nitrogenated organic substances.[34]

Boussingault analyzed the amount of nitrogen contained in different forages looking for a parameter that would best compare their relative nutritional value. Thaër and others had provided numbers expressing the ratio in which different forages can substitute one another. To Boussingault, these numbers should be considered true equivalents; they reflected, for example, the amount of hay or roots that could be replaced by an amount of leaves or grains that fed equally a cow or a horse. Unfortunately, the figures reported by different authors varied widely, an expected result since it was not possible to assure that the observations were based on the same experimental conditions. All vegetable substances used as feedstock for animal contain a certain amount of nitrogenous materials, and Magendie had already proved that food deprived of nitrogen could not support life. Vegetable flours contained a principle similar in nature to the nitrogenous materials of animal origin. This principle, discovered in wheat in 1754 by Jacoppo Beccaria (1716-), was designated vegetable gluten. Afterwards, Guillaume François Rouelle (1703-1770) had discovered that most vegetable saps contained a substance coagulable by heat, which he thought was similar to egg albumin. *Principle* and believed that this principle together with sugar, gum, and starch, constituted the nutritive portion of a vegetable. Based on this idea Einhoff had tried to compare the nutritive vale of certain vegetables based on the amount of the principle present in the plant. [35]

Boussingault believed that the nourishing property of forages resided in the nitrogenous matter they contain. Using this value as a parameter he classified 18 feeds and determined their nitrogen content using Dumas's method. Assigning the value 100 to wheat flour, he found for example, that the indexes for barley flour, corn, yellow peas, lentils, potatoes, carrots, and turnips were 119, 138, 67, 57, 613, 757, and 1 335, respectively.[23]

Boussingault and Payen tried to define the nutritional value of fertilizers applicable to cultivated soils that contained the residues of previous crops, which were poor in nitrogen but rich in ternary organic matter. For the fertilizer to be able to provide to the nutrition of the plant, it had to contain all the organic and inorganic elements, which without being taken from the atmosphere, would be assimilated during the life of the plant and retained in the harvest. Under these requirements, the proper fertilizer had to vary according to the nature of the soil, the climate, the season, the species being cultivated, the slope of the terrain, and finally, the influence of the subsoil and the residues of previous crops. Under these conditions the composition of the ideal fertilizer would be so complex and variable that it was impossible to give general rules for defining it. [36]

Boussingault and Payen divided fertilizers into inorganic and organic, described the general characteristics of the most common ones, and provided two comparative tables for 94 classes of manure, reporting the amount of water in the normal state, nitrogen content of the dry material, and the fertilization value or nutritional equivalent, relative to common farm manure assumed 100. For example, the fertilization value (based on dry material) of wheat bales, flax meal, beet pulp, acacia sawdust, cow droppings, and residue of bone glue, were 207,4; 32,5; 154,7; 513,1; 84; and 213, 8, respectively.[36]

Boussingault extended these studies to the case of animal feeding. For this purpose he fed cows a diet results indicated that cows fed *ad libitum* would lose weight, that is, animals were unable to use atmospheric nitrogen to supplement inadequate protein in the rations, for the synthesis of nitrogenous animal matter. [37]

Goiter[38-40]

During his stay in Venezuela, Boussingault noticed that the local population was seriously affected by goiter and cretinism; even dogs were affected by the illness. He observed the same phenomenon in Bogotá but learned that some families avoided the problem by drinking water from a particular source. He hypothesized that some water had a noxious substance in it that caused goiter, and initially thought that drinking rainwater would prevent goiter. [9,40]

In 1824 Humboldt described the occurrence of goiter in Colombia, and stated that the native Indians knew of a salt deposit that they believed to be remedial for this disease. Roulin, who had learned in Paris the work of the Swiss physician Jean François Coindet (1774-1834) on the therapeutic use of iodine, secured samples of this salt source (and others) and asked Boussingault to analyze them. [22]

Boussingault published two papers on his findings about goiter and iodine.[39,40] Boussingault connected goiter in the cordilleran mines to the possibility that mine water and the salt made from it might contain iodine. The salt used then was a by-product of silver mining. Common salt, required for the extraction of silver from its ores was obtained by the evaporation of salt streams or marshes. His chemical analyses indicated that although the salt from the mines in Antioquia seemed to contain only traces of iodine, the oily mother liquor (*aceyte de sal*) left after the salt had crystallized contained noticeable amounts of the element. The aceyte de sal itself did not react with starch but addition of a few drops of sulfuric acid led to the appearance of an intense violet color, fact that Boussingault interpreted as iodine being present in the form of a iodide. He wrote: *"the reason why goiter does not occur in Antioquia is because all the inhabitants of this province take every day, with the salt that they consume, a certain amount of iodine"*.[38-40]

In his paper of 1831 Boussingault wrote that the authorities would do a deposit of iodized salt, were the citizens could buy the salt necessary for their consumption. This measure would not only help prevent the illness but also provide an additional economic activity by the establishment of industries devoted to the preparation and export of this particular salt. He added: *"...it is true that the revenue of the mines run by the State might suffer but I write in the interest of the health of the citizens and not in the interest of the Treasury...In New Granada, this question...is of the highest importance because goiter not only disfigures people but it exerts the most deadly effects on their intellectual faculties."*

Boussingault distinguished between the use of iodine itself, which could lead to *"very serious accidents"*, and the *"use of iodized salt, used as seasoning on food, which is always followed by happy results"*. Sixty-five years were to pass however, before Eugen Baumann (1846-1896) in 1896 discovered the presence of iodine in the thyroid gland, thus affording a scientific basis for the importance of this element in physiology and medicine; and about one hundred years were to pass before the use of iodized salt for the prevention of goiter was to be placed on a firm foundation and supported by medical authority. [22]

In 1851, Boussingault was appointed to a committee of the *Académie des Sciences* to evaluate a report by a Dr. Grange. Grange had essentially discarded most of the proposed causes of goiter and concluded that it had something to do with a change in the character of the soil and that goiter was basically caused by too much magnesium in the diet or in the water. Grange prepared a geographic table of the localities affected in France and limiting countries, particularly Switzerland, Savoy, and Piedmont, and concluded that while towns located by the sea were exempted of the illness, the most badly affected regions were those in the mountains and regions were the soil was not rough. Goiter and cretinism appeared usually together and were endemic illnesses proper to certain localities. Foreigners, who came to inhabit these regions, became affected only after a long time. Grange believed that one of the main reasons for the appearance of goiter and cretinism was the geological constitution of the soil, such as saltiness and presence of

The committee's response was to adopt Grange's hypothesis in part, to thank him and encourage him to continue his studies. The committee thought that the best way to prevent goiter would be to change the drinking water or, if this was not practical, to give people slightly iodinated salt. Of real interest is that Boussingault now mentions; that in 1835, or 3 years after he had left, the government of New Granada did in fact distribute iodized salt from Antioquia to the population in goitrous areas and that *"this trial was followed by an incontestable success"*.[9]

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