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Esssay

Atmosphere/soil exchange processes of importance for molecular soil sciences

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Abstract

Globally the atmosphere/soil exchange can be interpreted as part of the biogeochemical cycles describing the transport of main chemical elements and their gaseous compounds between the compartments of the geosphere. Approaches to monitor and analyze these transport processes are described. The paramount role of Earth's life, the biosphere, in these processes is emphasized.

INTRODUCTION

Soil, geoderma, is the »skin» of Earth and the central organizer of the terrestrial ecosystems *(1)*. Through Earth's history soil has been formed by erosion of its mantle in interaction with existing bio- production/destruction of life forms and by deposition of particulate or gaseous matter from the atmosphere. In discussing their interaction we must be aware that both the soil and Earth's atmosphere are strongly influenced and can be considered a result of life. Every soil contains some water and organic material and plenty of life will be found in it too. Earth atmosphere which originally was hydrogen and helium later through volcanic activity and extraterrestrial impacts got nitrogen (N_2), carbon and sulfur dioxide (CO_2 and SO_2) along with water vapor which after cooling most have ended in the seas leaving an anoxic atmosphere of nitrogen, hydrogen and carbon dioxide. The early atmosphere composition might have resembled to the today volcanic gases *e.g.* from Kilauea summit [2] containing (in %) H_2O 37.1, CO_2 48.9, SO_2 11.8, H_2 0.49, CO 1.51, H_2S 0.04 and HCl 0.08. There is also a probability that much of the water on Earths came from one or more ancient comet impacts. Early life forms within their metabolism released methane (CH_4), ammonia (NH_3) and hydrogen sulfide (H_2S) until later new ones discovered photosynthesis and started to convert great amounts of carbon dioxide (CO_2) into oxygen and the atmosphere into an oxidative state as we know it today. Microbes (Bacteria) are still the most abundant form of life on Earth – even in our body there are ten times more then we have cells – and are irreplaceable in most vital processes. Atmosphere is the oxidizing medium in global biogeochemical cycles that, of course, involve also the soil and life therein. acting as the reducing medium (http://en.wikipedia.org/wiki/Biogeochemical_cycle) From the Earth's surface, either soil or water, natural and human produced gases enter the atmosphere where they react and get oxidized with hydroxyl and other oxygen radicals, singlet oxygen, peroxides, ozone or oxygen itself ending up in oxidized gaseous or aerosol form to be deposed again to the surface. Thus, the atmosphere, soil and hydrosphere, all in strong interaction with the life forms of the biosphere, are reservoirs of gaseous compounds on Earth and are important for their fate. There are actually two more possibilities, one to get them buried into the lithosphere (wherefrom they can eventually recover by erosion) and the other, as *e.g.* some helium or hydrogen, to get lost into the space. However, there is from the space also fallout of material which deposits over the time on the surface and in seas.

Soil and atmosphere are compartments of different phases and their interaction would call for a dividing solid/gaseous interface through which the exchange processes will take place. However, it is a property of soils to contain pores, cavities partially filled both with water and air, where actually, because of dynamic equilibrium between them, the exchange reactions take place. When water enters the pores it displaces some of the air. The composition of such soil air differs from that in atmosphere especially because of its higher water and CO_2 and lower oxygen content as consequence of metabolic activity; it also does not mix well with air above the soil. Clearly, the most important exchanged »gases« water and CO_2, along with sunlight are the main partners in the photosynthesis/respiration processes. Gases enter the soil either as dry or wet deposition, but the former always contains some part of the later. Interesting example is the atmospheric N_2 cycle. Soil bacteria absorb N_2 and reduce it to ammonia and into ammonium (NH_4^+) to create proteins and other nitrogen nutrients. Plants are eaten by animals, and dead plants, animals and animal wastes come into the soil where some bacteria turn them into ammonium and some others into nitrite (NO_2^-) and nitrate (NO_3^-). Finally, again bacteria turn them all into nitrogen (N_2), nitric oxide (NO) and nitrous oxide (N_2O) released to the atmosphere as products of denitrification *(3, 4)*. The last is source of NOx radicals in the stratosphere and along with CO_2 and CH_4 important greenhouse gas *(5)*. The importance of biological processes in the exchange of greenhouse gases between soil and atmosphere is obvious *(6)*. Thus, other important gases emitted from the soil into atmosphere are CO_2, CH_4, CO, COS, CH_3SCH_3 and H_2S *(7)*. From the atmosphere these are CO_2, SO_2, NH_3, CO, O_3, H_2O_2, nitrogen »oxides« (NO_2, NO, N_2O, HONO, HNO_2, HNO_3, NO_3^-), hydrogen, volatile organic compounds (VOCs, excluding methane) *(8)* and numerous compounds which we consider pollutants as organic chlorine compounds ($CHCl_3$, CCl_4, CH_3CCl etc., from pesticides) *(9, 10)*, PAHs *(11)*, PCBs *(12)* and other persistent organic pollutants (POP) and among others also mercury *(13, 14)*. Many of them enter the soil by deposition as fine particles or adsorbed on their surface.

For the simple exchange of gases between atmosphere and soil two mechanisms are important: (i) convection of air *i.e.* the moving force given as total gas pressure gradient forces the mass of air from the zone of higher pressure into that of lower and (ii) diffusion where not the air as a whole but each gas moves in the direction determined by its own partial pressure gradient (Fick's Law). Mass flow of air is except in layers at or very near to the surface much less important than diffusion.

By entering or leaving the soil pores, sorption and desorption of the gas bound with the surface either by van der Waals forces and hydrogen bonding (20 kJ/mol), or much stronger, chemically with some active site (200 kJ/mol) happens. At dynamic equilibrium and isothermal conditions the classical models of Langmuir (limited to monolayer), Freundlich (valid for heterogeneous surface) or Brunauer, Emmett and Teller (BET, with many existing variations) isotherms are developed. More recently instead of modeling the adsorbing surface as planar, with cylindrical pores, as slit-like etc., for soil and soil compounds with no Euclidean geometry structure their surface complexity is suggested to be captured by a single number – their fractal dimension *(15)*.

Concerning the rate of exchange besides diffusion calculations chamber methods, static *(16, 17)* or dynamic *(18)* are the most commonly used techniques for estimating the rate of soil/atmosphere exchange. Chambers are a great variety of bottomless, transparent or opaque, containers placed on a ground area of 0.1 to 1 m^2 and equipped with sensors, analyzers and devices. Their systematically underestimated exchange rates are addressed and discussed *(19, 20)*.

The most sophisticated method to get a handle on the number of specific molecules moving either from the atmosphere to the ground or *vice versa* is given by the eddy correlation (covariance) technique. See *e.g.* *(21)* for details. It is based on flux measurement *i.e.* of the number of entities (eddies) which in unit time move through a unit area in up or in down direction. Namely, horizontal airflow is basically turbulent containing eddies which can move orthogonally to airflow up or down. Counting the number of such eddies by fast micrometeorology equipment at times t_1 and t_2 it can be found which of them are more and if at the same times a fast response monitoring exists for specific gas molecules in that mass of air then their number (concentration) moving towards or from the surface can be determined. Thus, *e.g.* for ozone and NO_2 eddy correlation shows that ozone at night time deposits more readily to soils rich in organics and at daytime to plant surfaces (leaves), but NO_2 prefers to stay in the atmosphere

The fast monitoring requirement is difficult to meet because most gases are in very low concentrations and monitoring methods are rather slow (tunable diode laser absorption and fluorescence techniques are used). Also important is to locate the sensors at some height and ensure that the surface below is flat and homogeneous in all directions for at least hundred times that height *(22)*

Very important findings from monitoring and modeling of biosphere/atmosphere exchange of gases and aerosols over Europe *(8)* and quantifying biosphere/atmosphere exchange of nitrogen species *(4)* resulted from multi-institutional scientific cooperation in joint European projects (BIATEX, NEU)

CONCLUSION

In conclusion, looking at the concerted actions taking place between soil and atmosphere, two in all respects different terrestrial compartments, actions exercised by complementary life forms that exist above and below Earth's surface, we need be very concerned about disturbing them. Our accelerated demand for more space, energy and food impacts both compartments in many respects quite irresponsible.

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