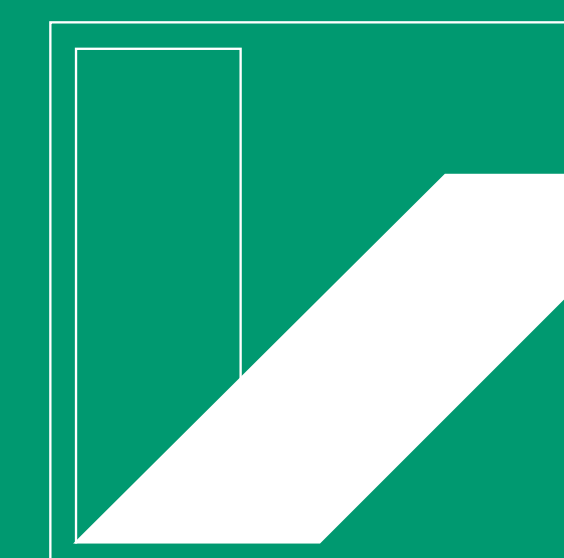


# Humic acids and HULIS as proxies for atmospheric organic aerosol



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## Introduction

The atmosphere is of utmost importance for the transformation of pollutants due to its oxidizing capacity and the availability of light > 290 nm enabling photoreactions. Besides this, it plays a crucial role for the dispersion of pollutants due to fast transport. Aerosols chemistry and physics are essential for understanding atmospheric transformation and transport processes because aerosols provide different surfaces (acidic, organic, dry/wet, etc.) for adsorption and heterogeneous reactions.

Investigation of atmospheric organic aerosol is a very recent topic in atmospheric research. Besides black carbon and soot, there is a fraction of organic macro molecules named HULIS which are of major interest because they are thought to participate in various atmospheric reactions and influence aerosol properties such as light scattering and hygroscopic growth.

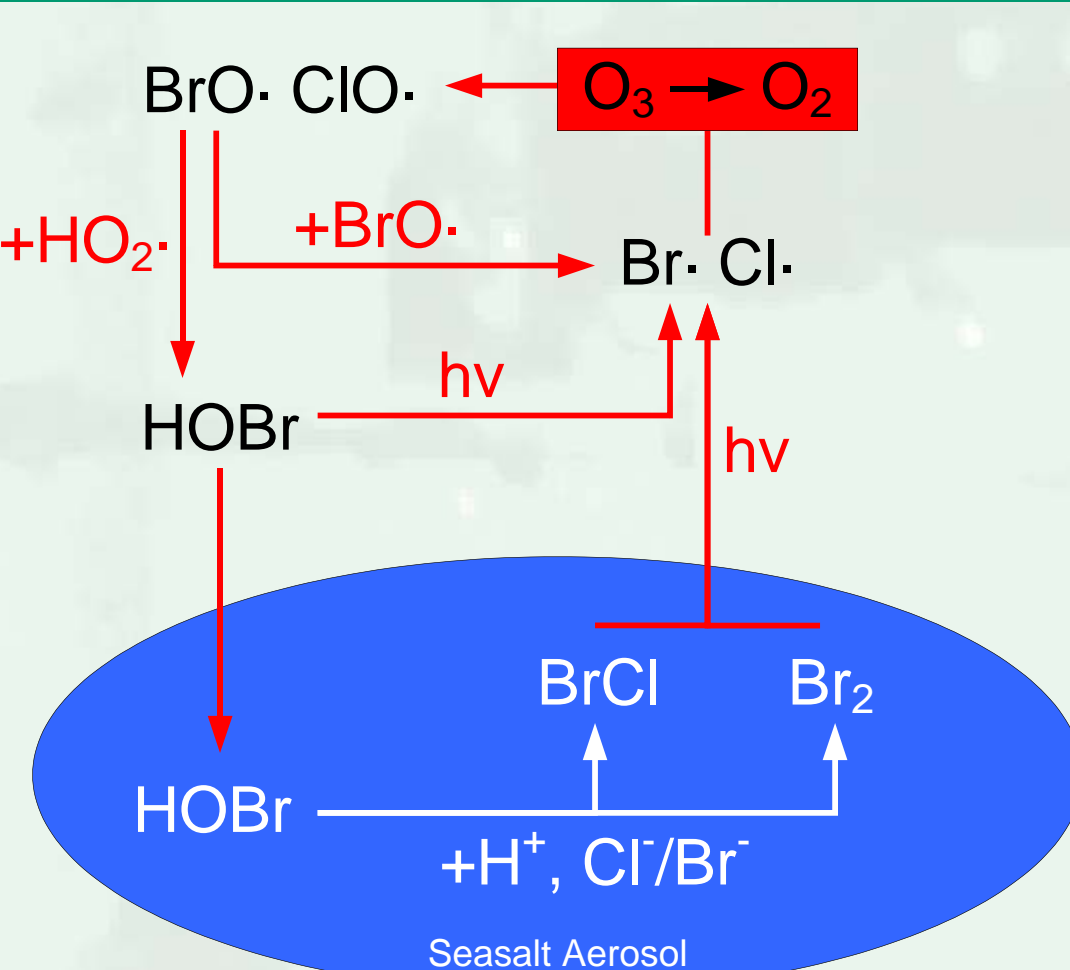
Actual projects in our laboratory aim to investigate the role of organic aerosols in halogen activation and formation of nitrous acid. During halogen activation organohalogen compounds may be formed which serve as reservoir for reactive halogens or are deposited to ecosystems. Nitrous acid (HONO) formation from NO<sub>2</sub> proceeds at humid surfaces (heterogeneously).

Blue Mountains:  
The blue dust is caused by secondary organic aerosol (SOA) which was generated through oxidation and polymerization of organic molecules, emitted by evapotranspiration of plants and trees.



## Seasalt Activation

Seasalt aerosol, which is mainly formed through bubble bursting, is a very important natural source of atomic chlorine and bromine in the troposphere.



These halogens are best known to destroy ozone by intermediate halogen oxides, described in the atmospheric halogen cycles.

The release of reactive halogens from seasalt aerosol can be described as follows: HOBr is transformed to molecular Br<sub>2</sub> or BrCl, these gas phase molecules leave the aerosol particle and are photolysed. By destruction of ozone halogen oxides like BrO and ClO are formed. BrO reacts with the atmospheric hydroperoxyl radical (HO<sub>2</sub>) to form HOBr. HOBr is adsorbed by the seasalt aerosol and halogens are released again ("Bromine Explosion").

## SOA and HULIS

Gas to particle conversion forms so-called secondary aerosols. Secondary Organic Aerosols (SOA) are formed by reaction of Volatile Organic Compounds (VOCs), which are released by plants and trees. Gaseous isoprenoids like  $\alpha$ -pinene are oxidized by atmospheric reactants like ozone or hydroxyl radicals and form particles by nucleation and aggregation.



Glass fibre filter coated with SOA formed by the reaction of catechol with ozone and hydroxyl radicals at ultraviolet radiation.

A special class of SOA are so-called Humic Like Substances (HULIS). HULIS have similar structures to humic acids which are well known from soil chemistry. While HULIS are formed by short-time atmospheric oxidation and nucleation, humic substances are formed slower at dark conditions.

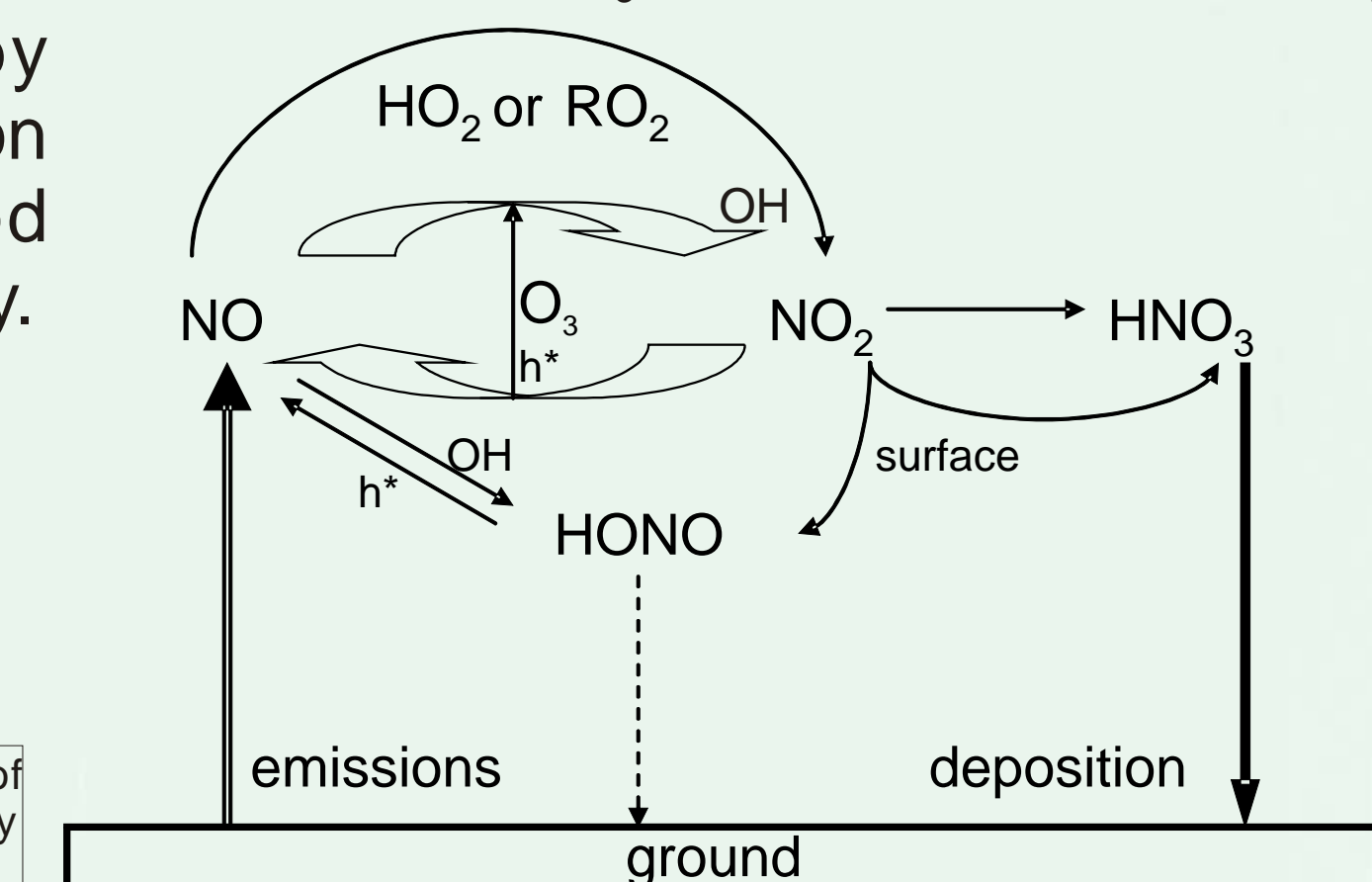
SOA and HULIS play an important role in atmospheric chemistry. They are very important reactants in atmospheric trace gas reactions.

Mechanisms of heterogeneous atmospheric reactions of SOA and HULIS are hardly known.

## Atmospheric NOx Chemistry

NO is mainly emitted by combustion processes (traffic, biomass-burning) and by microorganisms in soil. In the atmosphere NO is oxidized by O<sub>3</sub> to NO<sub>2</sub> which undergoes further oxidation to HNO<sub>3</sub> and heterogeneous reaction (see schema) forming HONO and HNO<sub>3</sub>. In the presence of Volatile Organic Compounds (VOC) the oxidation of NO to NO<sub>2</sub> proceeds also via oxidation by HO<sub>2</sub> and RO<sub>2</sub> producing additional O<sub>3</sub> from NO<sub>2</sub> photolysis depending on the ratio of VOC/NOx.

The heterogeneous reaction of NO<sub>2</sub> with surface adsorbed water forms HONO and HNO<sub>3</sub> which are effectively deposited by wet deposition due to good water solubility.



Simplified schema of 'daytime'-NOx-chemistry

## Natural organic halogens

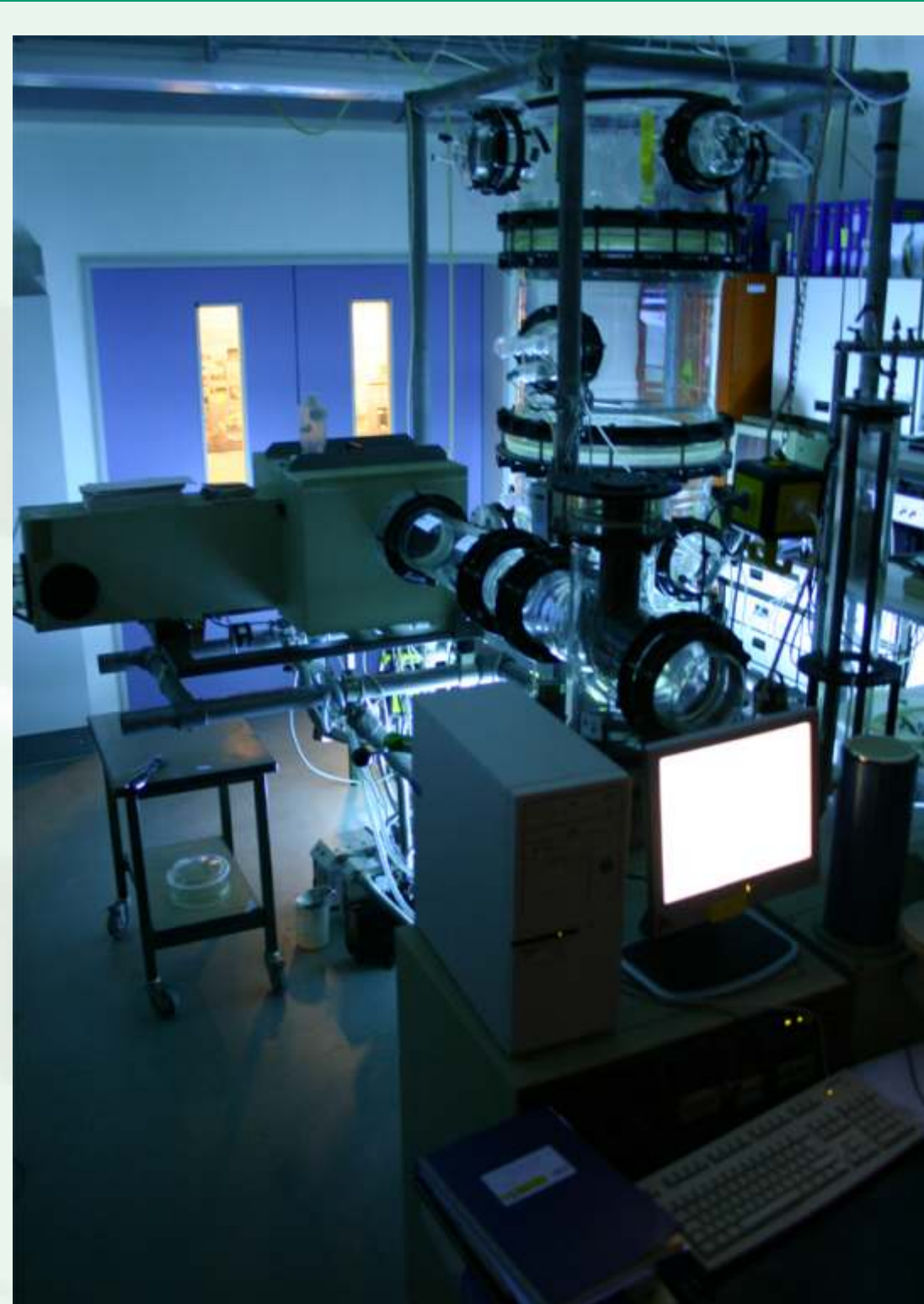
Within the HALOPROC project (Natural Halogenation Processes in the Environment Atmosphere and Soil) the halogenation of SOA and HULIS by seasalt activation is topic of research. Therefore smog-chamber-experiments are carried out, whereas heterogeneous aerosol reactions can be studied.



Samples of secondary organic aerosol are electrostatically deposited on an ZnSe-ATR-crystal and can be analysed using FTIR-spectroscopy.

Analysis of trace gas concentrations is performed with GC-ECD, GC-FID and GC-MS techniques. Longpath-FTIR-spectroscopy enables direct spectroscopic investigations of the aerosol within the smog-chamber.

Out smog-chamber-facilities feature possibilities to do qualitative analysis of homogeneous or heterogeneous reactions of the atmosphere but also to record kinetic data of these reactions.

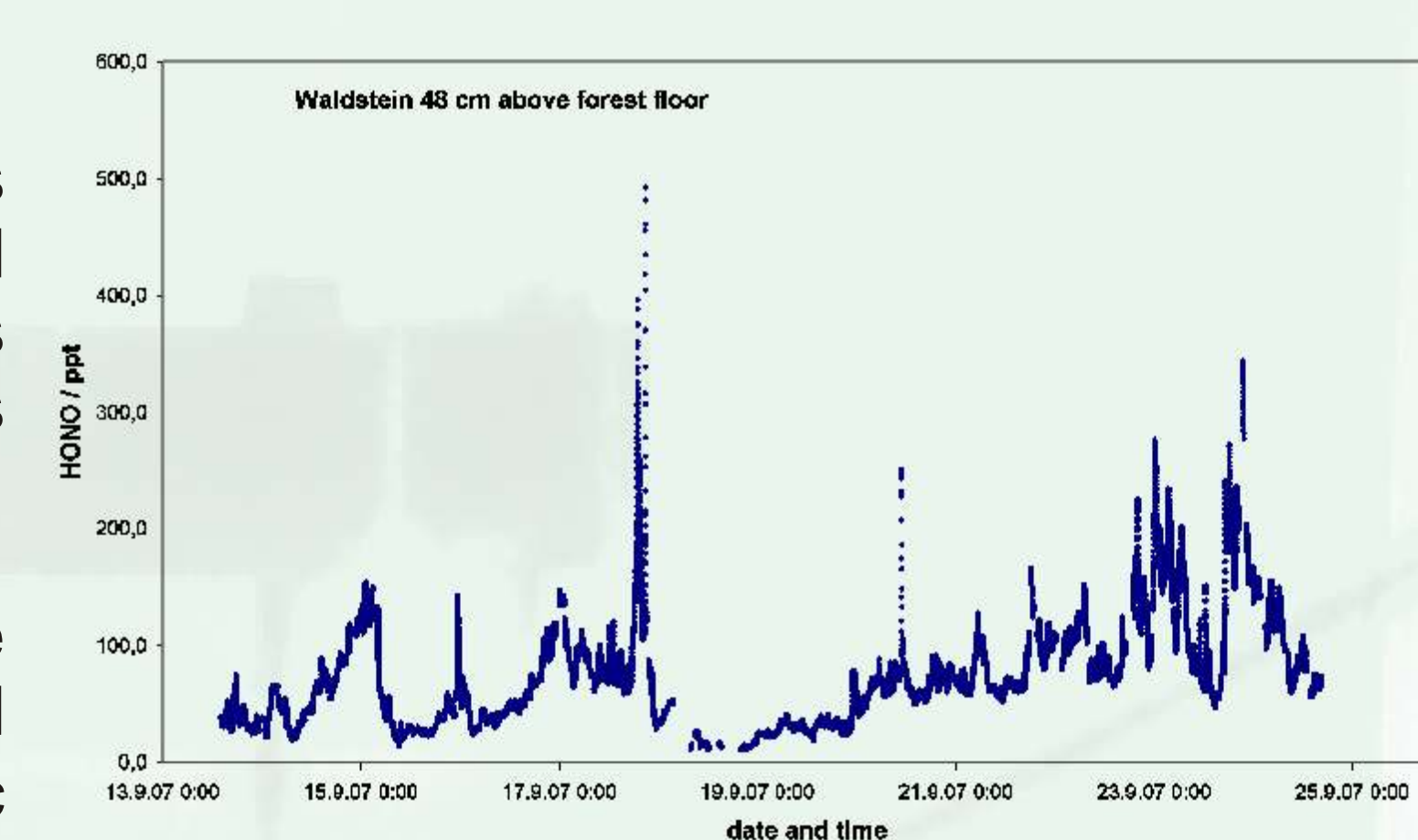


700 L - smog chamber equipped with FTIR longpath White-cell

## HONO-Formation

As part of the EGER project (Exchange processes in mountainous Regions), aiming to investigate trace gas exchange between atmosphere and ecosystems, formation of nitrous acid is investigated in laboratory experiments and measured in the atmosphere.

A heterogeneous flow reactor (see picture) is used to study NO<sub>2</sub> uptake and HONO formation on irradiated organic films, like humic acids. Gas phase HONO is measured with a highly sensitive (low ppt range) Long Path Adsorption Photometer (LOPAP®) which converts nitrite (NO<sub>2</sub><sup>-</sup>) into a strongly absorbing azo dye. This instrument is also used for atmospheric HONO measurements during intensive operating periods of the EGER project at the Waldstein in the Fichtelgebirge mountains.



Atmospheric HONO-measurements at the Waldstein (Fichtelgebirge)



Heterogeneous flow-reactor illuminated by UV-lamps

## Conclusions

Laboratory experiments are a useful tool to identify reaction pathways leading to products, which may be found in the atmosphere or due to deposition in other compartments like water and soil. Our smog chambers provide residence times for aerosol particles, sufficient to simulate atmospheric conditions under aging of the particles. In heterogeneous flow reactors, various surface films can be exposed to reactive trace gases. Kinetic and mechanistic studies are carried out by varying temperature, moisture, light intensity, contact time and trace gas concentrations.

N-deposition is mainly caused by the water soluble acids HONO/HNO<sub>3</sub> or aerosol nitrate, nitrite and ammonium. It is linked to fertilization of ecosystems and therefore indirectly to biodiversity. So understanding and quantifying the atmospheric nitrogen cycle is essential to estimate the impacts of NOx emissions caused by human activities. For future studies, pieces of soil may be investigated in smog chambers to assess their potential for HONO formation.

Halogenated secondary organic aerosols deposit on soil and sea. They form a source of natural halogenated matter which may interact with chemistry and biology of the ground. Even organic gaseous emissions from the ground, plants and trees are responsible for the formation of secondary organic aerosols (SOA) and HULIS. Therefore the interaction and transfer of matter between the abiotic compartments is important for studying one single component of the complex system 'Earth'.