TG5 - Computational chemistry and advanced physicochemical characterization - quantitative reconstruction and modeling of BGIs, their properties and interactions

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Introduction

Modelling of biogeochemical interfaces in soil by means of advanced molecular simulation methods is one of the important and new approaches in soil science [1]. Bridging and linking of molecular and higher (e.g. microscopic) scales of complex and heterogeneous BGIs systems investigated by simulations and/or various experimental techniques (e.g. AFM) represent big challenges.

Approach

How to overcome challenges:
• intelligent simplification of complex reality of BGIs in a model preparation
• using of multiscale modeling, combination a broad range of modeling methods and techniques
• application of modern experimental techniques operating on microscales (e.g. STM, AFM, XPS,...)
• linking of modeling and experimental outputs
  → mutual verification between experiments and modeling
  → design of suitable model experiments
  → measure & calculate
• collaboration between experimental and modelling projects

Discussion & conclusions

I. Surface properties of soil minerals

• sorption of PAHs, bentazone and MCPA on soil minerals - Fe(OH), montmorillonite
  - Observed (Eggle et al., J. Colloid Interf. Sci., 2010; Krüger & Totsche, Geoderma, 2010; groups: Gerzabek, Totsche)
• wetting of kaolinite (001) surfaces – CA simulations. Observed hydrophobicity/hydrophilicity of tetrahedral/octahedral surfaces.
  - Observed (Sak et al., Geoderma, 2010; groups: Gerzabek, Schachtner)
• calometric measurements and sorption isotherms
  - Observed (Gibson
• d) AFM characterization of surfaces. Force-distance and force-volume AFM measurements on column materials after reaction with phenanthrene
  - Observed (Stach et al.)

II. Supramolecular associations of SOM

• verification of experimentally predicted bridges of water molecules between SOM segments (Aquino et al., J. Phys. Chem. C, 2009; Schaumann et al., 2010; groups: Gerzabek, Schaumann)
• effects of hydration and cations in soil organic matter
  - Observed (Aquino et al., Chems. Lett., 2010; groups: Gerzabek, Schaumann)

III. Black carbon

• adsorption of alkali cations on pyrene (BC model) (group: Gerzabek)

Challenges

• further development of simulation techniques
• sophisticated planning of experiments
• better linking of modeling and experimental achievements

AIMS & OBJECTIVES

The main objective of the thematic group Computational Chemistry and Advanced Physicochemical Characterization is:

Quantitative reconstruction and modeling of biogeochemical interfaces, their properties and interactions on and from molecular scale to higher spatial and temporal scales.

BGIs will be reconstructed on the basis of:
• original, artificial and model BGIs
• advanced molecular simulation methods
• advanced experimental physicochemical characterization methods

The overall objective is to link processes of BGIs operative at molecular scale to phenomena observed at higher scales in a mechanistic way.

Achievements

I. Surface properties of soil minerals

1. a) sorption of PAHs, bentazone and MCPA on soil minerals - Fe(OH), montmorillonite
2. b) wetting of kaolinite (001) surfaces – CA simulations. Observed hydrophobicity/hydrophilicity of tetrahedral/octahedral surfaces.
3. c) calometric measurements and sorption isotherms
4. d) AFM characterization of surfaces. Force-distance and force-volume AFM measurements on column materials after reaction with phenanthrene

II. Supramolecular associations of SOM

1. a) verification of experimentally predicted bridges of water molecules between SOM segments
2. b) effects of hydration and cations in soil organic matter

III. Black carbon

• Adsorption of alkali cations on pyrene (BC model)

Plans

I. Surface properties of soil components

1. a) interactions of PAHs, Bentazone, MCPA, with soil mineral surfaces (clay minerals, Fe/Al oxyhydroxides), effect of water on the stabilization
2. b) advanced instrumental techniques (e.g. AFM) in characterization of soil mineral surfaces
3. c) evaluation of effective parameters to describe wetting, adsorption and sorption phenomena on BGIs
4. d) measurement, simulation and controlling of hydrophobicity/hydrophilicity of model mineral surfaces

II. Supramolecular association, interactions, and aging of SOM

1. a) water and cation effect on the formation and stability of supramolecular association of SOM
2. b) reconstruct a suitable model polymer to link modeling with experiment
3. c) effect of heating, wetting and drying on the aging of SOM
4. d) model entrapment of organic chemicals in microvolds

III. Black carbon – component of SOM

• characterization of structural defects (e.g. Stone-Wales sites and functional groups (–OH, –COOH)) of BC

IV. Radical sites in model humic acids

• accurate ab initio studies of reaction mechanisms and spectroscopic properties (EPR, NMR, IR)

Active TG5 members and their contributions:

Reference: