Tuesday, November 23th

Session Nano: Health, Environment & Risks

10:50 - 11:20 Keynote

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Abstracts

Keynote Speakers

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Biography

Prof. Dr. Bernd Nowack holds a MSc. (1992) and a PhD (1995) in environmental sciences from ETH Zürich. After research stays at the Johns Hopkins University in Baltimore, USA, Eawag and ETH Zürich, he is leading since 2007 the «Environmental Risk Assessment and Management» group at Empa, the Swiss Federal Laboratories for Materials Science and Technology. He is also adjunct professor in the Department of Environmental Systems Science at ETH Zurich. His current research deals with the environmental risks of engineered nanomaterials, nanobiomaterials and microplastics, comprising a wide spectrum of different approaches, e.g. material flow modeling, environmental risk assessment; experimental studies about release from products. He has published 185 peer-reviewed publications and has an h-factor of 68. He acted as co-advisor of 25 PhD projects, is co-Editor-in-Chief of NanoImpact and Associate Editor of *Environmental Pollution*. He is listed since 2014 each year as "Highly Cited Researcher".

ADVANCES IN ENVIRONMENTAL RISK ASSESSMENT OF ENGINEERED NANOMATERIALS

For a quantification of the environmental risks of engineered nanomaterials (ENM), information on both hazard and exposure needs to be available. Whereas many ecotoxicological studies provide data for hazard assessment, no specific measurements of ENM in environmental systems are available. Modeling has therefore been used since many years to obtain environmental exposure information. Recently several improvements of material flow models have increased our confidence in the results of these models: the inclusion of dynamic aspects and the separation of the flows into different forms of ENM. Dynamic material flow analysis is able to quantify the accumulated ENM amount in environmental sinks and can be used to predict future emission scenarios. Most existing models for assessing the releases of ENMs into the environment are based on the assumption that ENM remain in their pristine forms during their whole life cycle. It is known, however, that this is not always the case as ENMs are often embedded into solid matrices during manufacturing and can undergo physical or chemical transformations during their life cycle, e.g. upon release to wastewater. We therefore developed a method to systematically assess the forms in which ENM exist throughout their life cycle.
The improved material flow models provide a starting point for quantitative environmental risk assessments. A form-specific assessment resulted in predicted environmental concentrations for anatase vs. rutile nano-TiO_2, single-wall vs. multi-wall CNTs and α- vs. γ-nano-Al_2O_3 that varied by a factor of 2 to 13. Additionally, the material-specific predicted no-effect concentrations for the nano-forms were derived.
For nanocellulose, a prospective environmental risk assessment was performed, indicating that by 2025 there is no environmental risk within the surface water compartment, even assuming a compound annual growth rate of 19% for nanocellulose production in upcoming years.
Coupling the form-specific flow assessment with form-specific hazard assessments, a first specific risk assessment for different released forms of nano-Ag, nano-ZnO and nano-TiO_2 could be obtained, i.e. considering pristine, dissolved, transformed, and matrix-embedded forms.

Keywords: engineered nanomaterials; environmental exposure; environmental risk assesment.

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Thematic Session: Nano: health, environment & risks
Keywords: Nanoplastic, Transport, Ice (4-5 keywords are required)

Modeling nanoplastic fate in the Arctic: Mechanisms of transfer from saltwater to ice

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The dissemination of plastic within ecosystems is a proven ecological risk[1]. This type of waste includes nanoplastics, colloids that originate from the unintentional degradation of plastic. The environmental fate of nanoplastics must be characterized in order to quantify organisms' exposure rate and *in fine* describe the ecological and health risks that are specific to this particle[2]. One of the most fragile environmental compartments which reveals the consequences of the Anthropocene is located in the polar regions. In oceans and sediments, plastic debris belonging to all size classes (macro, micro and nanometric) have been quantified. However, in sea ice only microplastics have been studied[3,4]. Thus, this study aims to shed some light on the behavior of nanoplastics at the interface between seawater and sea ice. A bench-scale experiment reproduced the seawater/sea ice interface in order to determine the capacity of sea ice to capture nanoplastics. To describe the thermohaline gradients occurring in this experimental setup, the system was numerically modelled using COMSOL Multiphysics. Three nanoplastic models were used, with varying sizes and shapes, and in the absence and presence of natural organic matter (NOM). The results are unexpected. While microplastics are known to accumulate in sea ice[4], nanoplastics appear to be expelled from sea ice. The nanoplastic models exhibit different behaviors, with shape and size controlling transfer to sea ice. Finally, the presence of NOM does not alter this expulsion mechanism but stabilizes the nanoplastics by avoiding their sedimentation.

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3. Obbard, R. W. *et al.* Global warming releases microplastic legacy frozen in Arctic Sea ice. *Earth's Future* **2**, 315–320 (2014).
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Thematic Session: Nano_health_environment_risk
Keywords: Atmosphere - Plasma - Nanostructured films - Nanocristallites - Durability

Origin, properties, environmental/health concern of plasma-formed polymer nanocomposites traced in natural resources and living organisms

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Films, filaments in air, water and living organisms are widely considered as microplastic residues tracing exponential Earth's contamination by petrochemical byproducts. In contrast, we have shown that part of these are plasma-formed nanocomposites from charged nanoparticles tracing aerosol ionization[1, 2]. Here their further characterization is presented to elucidate their environmental-health concern.
The unprecedented COVID-19 outbreak with 90% air pollution reduction has allowed to identify the association in rainfall of cyanophyceae filaments with coiled nano-films. Laboratory plasma using the same rainwater has allowed to synthetize from the biofilaments the atmospheric nanocomposites: translucent films at low power, to coloured, twisted nano-filaments with wrinkled surfaces at high power. The TEM characterization shows increase in the aliphatic matrix of dispersed 2D-nanosheet crystallites formed of native metals and oxides with power increase of the plasma discharge. ^{14}C measurements of the nanocomposite films extracted from present-day air, water and living organisms indicate a formation from slightly aged carbon but not from fossil combustible. In contrast, the sudden decrease in the atmosphere of high energy nanocomposite films with the COVID-19 lockdown suggests that the oxide and native metal nanosheets (i.e. TiO_2) could partly originate from fossil resources. The synthesis by plasma discharge of high energy nanocomposite films using hydrocarbon liquids fully confirms this hypothesis.
The strong bounding of the nanosheets to the aliphatic matrix and the densely-stacked coiled nanofilms seem to explain their remarkable durability. These properties are suggested to induce potential adverse effects on the bioresistance of biosourced carbon and the basic functioning of living organisms.

Références

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[2] A. Hamdan et al., 2017, https://doi.org/10.1007/s11090-017-9816-8

Thematic Session: Nano: health, environment & risks
Keywords: Silver nanoparticles, bronchial epithelium, secretome, protein corona

Investigating protein-nanoparticle interactions in 3D cell culture models for the long-term toxicity study of inhaled silver nanoparticles

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The need for toxicity screening of a large number of nanomaterials has favored the development of *in vitro* cellular models. In airways, the epithelial cells lining the respiratory tract are covered by mucus that forms the first line of defense against inhaled agents. The interaction between nanomaterials and the biological medium leads to the adsorption of proteins, forming a protein corona (1) which determines their biological identity *in vitro* and *in vivo*. To study the long-term toxicity of silver nanoparticles (Ag NPs) (2), two different *in vitro* 3D models of the human bronchial epithelium were used: primary normal human bronchial epithelial cells (NHBE) and the Calu-3 cell line. With Calu-3, a functional epithelium could be maintained for 25 days at the air-liquid interface allowing repeated exposure to Ag NPs at low doses (10 µg/cm²). The composition of the apical secretome of Calu-3 and NHBE cells was analyzed by quantitative mass spectrometry. Calu-3 and NHBE secretomes share 405 proteins, albeit with different abundances. The analysis of the reactome pathways shows that proteins secreted by Calu-3 cells participate in the immune response. The stability of Ag NPs and the evolution of the protein corona following incubation in the secretome were investigated by small angle X-ray scattering (SAXS) and proteomics respectively. The analysis of the protein corona *in situ* is reported. These results support the use of the Calu-3 model to evaluate the chronic toxicity of nanomaterials on the lung following NP inhalation, and their effects on the epithelial cell secretome.

References:
(1) Sanchez-Guzman D. *et al. In Situ* Analysis of Weakly Bound Proteins Reveals Molecular Basis of Soft Corona Formation. *ACS Nano*. 2020;14(7):9073-9088.
(2) Sanchez-Guzman D. *et al*. Silver nanoparticle-adjuvanted vaccine protects against lethal influenza infection through inducing BALT and IgA-mediated mucosal immunity. *Biomaterials*. 2019;217:119308.

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Thematic Session: NanoBioMedicine
Keywords: AFM, Automation, Biomechanic.

Beyond the paradigm of nanomechanical measurements on cells using AFM: an automated methodology to rapidly analyse thousands of cells

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Nanomechanical properties of cells could be considered as cellular biomarkers. The main method used to access the mechanical properties is based on nanoindentations measurements, performed with an operator manipulated Atomic Force Microscope (AFM) which is time-consuming, and expensive. This is one of the reasons preventing the transfer of AFM technology into clinical laboratories. In this presentation we report a methodology[1] which includes an algorithm (transferred to a script, executed on a commercial AFM) able to automatically move the tip onto a single cell and through several cells to record force curves combined with a smart strategy of cell immobilization. Cells are placed into microwells of a microstructured polydimethylsiloxane (PDMS) stamp. Inside a classical 100x100 μm^2 AFM field, 80 to 100 cells are immobilized. In an optimal configuration we were able to measure a population of 900 *Candida albicans* cells both unmodified and caspofungin treated in 4 h, which represents an unprecedented performance[2]. This strategy can be applied to cell arrays, proteins or glycan arrays. The big amount of data generated is compatible with the analysis by machine learning and will most probably generate unexpected understanding of the biological processes.

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Beyond the paradigm of nanomechanical measurements on cells using AFM: an automated methodology to rapidly analyze thousands of cells.
Nanoscale Horizons, DOI : 10.1039/c9nh00438f

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Thematic Session: Nano-Gold by young researchers
Keywords: Indoor air quality, nitrogen oxides, photocatalysis, decorated nanomaterials

Nano-gold decorated TiO_2, ZnO and WO_3 for NO degradation: new photocatalytic materials for the improvement of the in Indoor Air quality.

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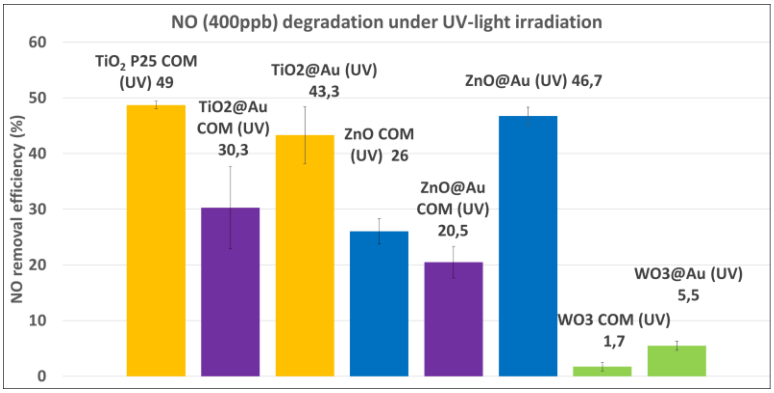
Advanced oxidation processes (AOPs) like photocatalysis are environmentally friendly techniques, acting at standard pressure and temperature conditions for the removal of pollutants in water or in the air. Applying this photocatalytic processes, new building materials with air pollutants removal, self-cleaning ability and anti-bacterial properties can be achieved[1,2]. For while, TiO_2 P25 Degussa® has been used to improve the global indoor air quality thanks to its ability to degrade gaseous toxic pollutants under UV and light irradiation [1]. Nevertheless, many efforts have been made to increase its photocatalytic efficiency under visible light for examples, TiO_2 surface modification by dye molecules or graphitic carbon nitrides, doping, or mixing with other semi-conductors including ZnO & WO_3 have been reported [2-3]. One innovative approach is to use the localized surface plasmon resonance effect (LSPR) of metallic nanoparticles (MNPs) such as Au and Ag grafted at the surface of the metal oxide semi-conductor. This work presents a rational study on the photocatalytic degradation of NO under UV-A and visible light of commercial TiO_2, ZnO, and WO_3 as well as Au MNPs supported on commercial TiO_2 and ZnO. The latter are prepared by photodeposition of a molecular gold precursor or salt and tested under NO gaseous pollutant. Correlation between the physical-chemical properties of these materials and their photocatalytic response for NO degradation is studied. Preliminary results presented in Figure 1 show that, as expected, the performances of the commercial TiO_2 P25 are higher compared to the other commercial oxides even when decorated with Au MNPs. Remarkably, we show that Au MNPs decorated ZnO material prepared with our procedure exhibits strong efficiency improvement compared to the commercial ZnO material and the commercial Au@ZnO catalyst. The overall performance under UV and visible light of our AuMNPs@ZnO material competes well with the removal yield of TiO_2 P25. This Au MNP decoration of ZnO offers an interesting alternative to TiO_2 material which is more and more regulated, in the field of pollutant removal *via* photocatalysis reactions.



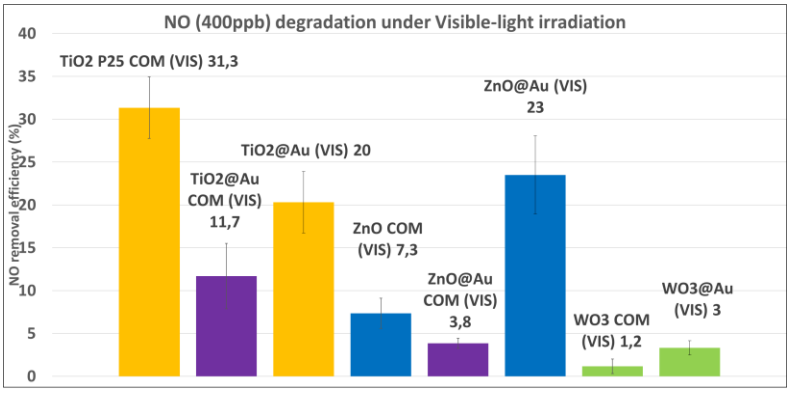


Fig. 1. NO (400 ppb) photocatalytic degradation yield (%) of TiO_2, ZnO, WO_3, TiO_2@Au (Au 1%wt) & ZnO@Au (Au 1%wt) commercial Au catalysts (in purple) and Au (1%wt) decorated commercial TiO_2, ZnO, WO_3 under visible light (6W, 20 minutes) and UV (1W, 20 minutes). The experimental setup is described in [4]. The materials were deposited on mortar surfaces (3-4 $g.m^{-2}$) by spray deposition.

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