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Report from the Workshop on Nanotechnologies for Environmental Remediation

JRC Ispra 16-17 April 2007

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Executive Summary

This report describes the outcomes from the workshop on "Nanotechnologies for Environmental Remediation" which took place at the Joint Research Centre, Ispra, on the 16th and 17th April 2007. The workshop brought together leading scientists from across the EU to present their latest work in environmental remediation and discuss the following issues:

- 1) Which are the most effective nanotechnologies for prevention or cleanup of pollution?
- 2) How dependable and close to market are remediation techniques based on nanotechnologies?
- 3) What additional research is needed to exploit the full potential of nanotechnology for remediation?
- 4) Which environmental nanotechnologies are the most promising and should be further explored?
- 5) What are the potential risks of using nanotechnologies in remediation applications?
- 6) Is there a need for targeted funding for infrastructure to support nanotechnologies for environmental remediation?
- 7) What opportunities are there for setting up EU collaborative projects on environmental nanotechnologies?

The issues of environmental remediation are quite substantial and poorly addressed by conventional technologies. They include access to clean drinking water, removal of airborne pollutants, and the clean-up of industrially contaminated sites (in particular ex-military sites in the new Member States). Although there have been a number of laboratory demonstrations of nanotechnology applications for environmental cleanup, there remains the issue of translating these into industrial level processes.

The workshop consisted of two principal sessions: "Water Treatment and Purification", and "Air, Water and Soil Decontamination". A total of 15 presentations were given.

At present the solution for ground contamination is largely topsoil removal and burial in landfill. A less-than-ideal situation; it requires a better understanding of the mechanics of natural ground water and soil remediation through the interaction of mineral strata, soil and resident micro-organisms, in order to engineer more efficient systems. For example, nickel that has leached into groundwater from industrial sites or natural pyrites can be absorbed by natural chalk or calcite. Similarly different iron oxide minerals can be used to remove heavy metal and arsenic contaminants from groundwater. A number of studies have taken place that combine modelling with sampling at various points throughout the affected site. This allows a better, more moderated response to pollution. Investigations of the interactions between pollutants and minerals such as calcite and iron oxide have shown that increasing the surface area of each, through nanostructuring; results in a greater take-up of pollutants.

Solar photocatalysis is an active method which harnesses UV energy from the sun to degrade many different pollutants such as nitrous oxides (NO_x) and volatile organic compounds (VOCs). Titanium dioxide nanoparticles have shown significant efficacy in this respect and have already been incorporated in paints and cement for construction products (in controlled tests, such products

demonstrate an 80% reduction in atmospheric NO_x levels). Doping with noble metals can increase their efficiency by harnessing energy from larger numbers of incident photons.

Moreover, they are now being adapted for drinking and groundwater remediation. Titanium dioxide nanoparticles can be immobilised on substrates through a number of processes or be applied as thin films. Systems developed by EU projects such as SODIS Water and PHOTOPURE have been shown to be highly effective against water-borne microbes, including bacterial spores and chlorine resistant organisms. They are also effective at degrading organic pollutants (such as herbicides and pesticides).

Technologies using nanostructured boron-doped diamond coated electrodes have shown efficacy in the oxidation of pollutants in waste water, regardless of water turbidity (some three to five fold faster than conventional chlorine dosing). Such systems also have the advantage of self-cleaning by reversing current polarity.

Membrane technologies utilising nanoscale pores (nanofiltration) bridge the gap between reverse osmosis and ultrafiltration, and allow the removal of many contaminants without the energy costs required by reverse osmosis. However, the fluid dynamics of such membranes still need to be fully elucidated to resolve issues regarding membrane fouling, and dealing with the waste (or concentrate). Nevertheless, such technologies are very near market.

Other interesting work includes the enhancement of natural precipitation of pollutants through the introduction of specific microbial species (e.g. iron precipitating bacteria, which can accelerate the co-precipitation of pollutants and iron oxides some thousand-fold).

Nanostructured metal oxide catalysts such as CoCr₂O₄ have been found to be more effective than currently used catalysts, in terms of soot and NO_x reduction from vehicle exhausts. Titanium dioxide nanoparticles have been doped with boron to harness visible light and therefore be effective remediators of indoor air. EU initiatives in this area include PHONASUM, Self Cleaning Glass and a joint initiative with Japan (EJIPAC).

The potential risks associated with using nanoparticles for environmental remediation is also under investigation, in particular free nanoparticles, such as iron, which can have wider ranging effects on soil ecosystems.

Recommendations from the workshop include:

- need to develop effective monitoring devices to ensure that remediation processes are working as expected;
- implementing life-cycle analysis for assessing the environmental consequences of implementing new technological approaches;
- stronger support for EU level research in environmental technologies; including support for networks, improved facilities (such as pilot test facilities, core facilities with all appropriate equipment accessible to researchers across the EU), the development of an ETP;
- more fundamental research to better understand naturally occurring processes at the nanoscale and their relation to macroscale phenomena;
- harnessing the power of natural systems and augmenting where appropriate with nanotechnologies, rather than independent systems (i.e. the development of hybrid systems).

Introduction

Environmental nanotechnologies have the possibility to contribute to economic growth and innovation while at the same time allowing sustainable development and protecting the environment. In fact, the Environmental Technologies Action Plan for the European Union¹ acknowledges the significant part nanotechnologies could play. Although the EU does not at present have a dedicated research effort on environmental nanotechnologies, some significant pan-European collaborations have already been initiated in this area².

There is considerable commercial potential in environmental technologies because the development of innovative solutions to prevent and remediate pollution is needed to ensure sustainable development. In fact, the projected world market for applications of environmental nanotechnologies by 2010 is approximately \$6 billion³. This market can be sub-divided into four principal sectors: remediation, protection, maintenance, and enhancement, of which remediation represents the fastest growing area, while maintenance and protection constitute the bulk of the remaining applications, and enhancement is the smallest sector.

Various applications of nanotechnologies for environmental remediation have been successfully demonstrated at the laboratory scale but, in the majority of cases, these still require verification of their efficacy and safety in the field. Conventional remediation technologies have so far have shown only limited effectiveness in reducing the levels of pollutants in the air, water, and soil and in responding to the challenges of major cleanup operations. Present day filtration and purification plants used for supplying drinking water generally achieve only partial success because the active materials are of limited efficiency. However, because of their much greater specific surface area, nanoparticles are able to perform significantly more effectively as filtration media than larger particles with the same chemical composition.

This report examines the opportunities that exist for the use of nanotechnologies in environmental remediation, considering the relevant phenomena from the nanoscale to the macroscale level. It is based on the findings of the JRC-Nanoforum Workshop on Nanotechnologies for Environmental Remediation, which was held at the Joint Research Centre, Ispra, Italy from 16-17 April 2006. The workshop was structured around sessions dealing with nanotechnologies for water treatment and purification and decontamination methods for air, water and soil. A number of leading European experts, together with scientists from JRC Institutes working in relevant fields, were invited to present their research results and express their views on future directions in this important area.

¹ Commission of the European Communities, Stimulating Technologies for Sustainable Development: An Environmental Technologies Action Plan for the European Union, Brussels, 28 January COM(2004) 38 final

² D.G. Rickerby and M. Morrison, Nanotechnology and the Environment: A European Perspective, Science and Technology of Advanced Materials 8 (2007) 19–24

³ F. Boehm, Nanotechnology in Environmental Applications, Report NAN039A, BCC Research, Norwalk (2006).

This meeting was a follow-up to a previous Workshop⁴, with a similar format, held in Brussels in March 2006, that already considered the wider issues concerning the safe use of nanotechnologies for the benefit of the environment, including applications in pollution monitoring and resource saving as well as remediation methods.

The following questions were proposed to participants as a basis for discussion:

- 1) Which are the most effective nanotechnologies for prevention or cleanup of pollution?
- 2) How dependable and close to market are remediation techniques based on nanotechnologies?
- 3) What additional research is needed to exploit the full potential of nanotechnology for remediation?
- 4) Which environmental nanotechnologies are the most promising and should be further explored?
- 5) What are the potential risks of using nanotechnologies in remediation applications?
- 6) Is there a need for targeted funding for infrastructure to support nanotechnologies for environmental remediation?
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General Considerations

The analysis of pollution may be focused down from continental to regional and local areas, together with the identification of measures required for action and specific policy issues to be addressed. In response to the Water Framework Directive⁵, for example, the HORIZON 2020 initiative⁶ proposes to decrease water pollution in the Mediterranean area by 80%. Specifically targeted areas are municipal waste, effluent emissions and industrial pollution.

The priority sites for cleanup differ across the EU Member States. The most urgent ones requiring action are probably ex-military sites, particularly those in the new Member States. Topsoil removal at present is the most important single method of choice for land remediation, in up to 90% of cases. However this creates additional problems regarding the disposal of hazardous waste. Currently

⁴ Report on the Nanotechnology and Environment Workshop, Brussels, Nanoforum, 2006
<http://www.nanoforum.org/events/nanoenvironment>

⁵ Directive 2000/60/EC of the European Parliament and of the Council of 23 October 2000 establishing a framework for Community action in the field of water policy

⁶ Communication from the Commission to the Council and the European Parliament establishing an environment strategy for the Mediterranean, SEC(2006)1082

there are no real regulations for the disposal of contaminated soil. The new Soil Directive⁷ is expected to address this problem more closely.

There are several initiatives at European level for abating atmospheric emissions and the relevant EU policy is governed by the Framework Directive on Ambient Air Quality⁸. This Directive covers the revision of previously existing legislation and the introduction of new air quality standards for previously unregulated air pollutants, setting the timetable for the development of daughter directives on a range of pollutants.

From Macroscale to Nanoscale

Full scale field trials have been carried out, as well as laboratory studies and modelling of in-situ environmental engineering methods for the attenuation of pollutants in soil and aquifers. Passive biotechnology is employed, using soils and aquifers as natural bioreactors. Such in situ approaches, such as Monitored Natural Attenuation, rely on naturally occurring processes to reduce environmental risk. These processes include dilution by mixing with clean recharge or groundwater to reduce contamination concentrations, adsorption to retard the transport of soluble contamination and biodegradation to destroy contaminant mass. Quantifying the extent of these processes in situ can demonstrate that more aggressive intervention is not necessary. This avoids excavation or pumping of contamination, which reduces the energy and carbon footprint for remediation, decreases worker exposure to contaminated materials and eliminates the need to otherwise treat contaminated water and to transport soils for disposal as hazardous waste. The estimated market for soil and groundwater remediation is expected to grow to around £16 (€23.6) billion worldwide with the UK and Japan identified as expanding near-term markets and central and eastern Europe as important mid-term markets⁹. Less interventionist approaches to remediation, such as Monitored Natural Attenuation (MNA), are cheaper than other methods, but their effectiveness is uncertain. At best, this requires significant monitoring costs, but more often this results in the selection of far more expensive and aggressive remediation than is actually needed.

Improved predictive capability is therefore required. This can be achieved through acquisition of high quality data, obtained by sampling at various horizontal and vertical points within the polluted zone, in combination with site simulation using reactive transport models. Microbial and geochemical analysis is performed to determine the change in pollutant concentration and the underlying processes. Computer simulations of reactive transport quantify the concentration and mass flux within the in-situ bioreactor and can be used to assess the ability of the reactor to achieve the required remediation outcomes within specific time scales. Current models employ high-speed computing methods with analogous calculation power and precision as models used for global climate change evaluation.

⁷ Proposal for a Directive of the European Parliament and of the Council establishing a framework for the protection of soil, COM(2006) 232 final

⁸ Council Directive 96/62/EC of 27 September 1996 on ambient air quality assessment and management

⁹ Contaminated Land: Applications in Real Environments (CL:AIRE) Newsletter, Winter 1999 (www.claire.co.uk/).

Within these models, the microbiological ecosystem dynamics are coupled with a geochemical reactions and physical transport. Currently, the physical and chemical processes are reasonably well understood but better understanding of the microbial processes is still required. One area of importance is fundamental mechanisms of biodegradation within attached growth communities, and the biodegradation reactions that occur at the cell mineral interface. Such fundamental work includes quantification of rates of biodegradation in biofilms, characterization of physical and community structure during attached growth, identification of functional organisms that degrade pollutants, elucidation of physical chemistry influencing attachment, comparison of the influence of different mineral substrata, and studying how microbes are transported as living particles in the sub-surface.

With an increased understanding of the processes and interactions occurring within these in situ bioreactors, it is possible to intervene and be much more proactive to beneficially influence engineering outcomes. Advances in in-situ engineering could allow much more reliable cleanup of contaminated soil and water and treatment of waste, thus safeguarding aquifers, rivers and coastlines, and saving of water. Other engineering applications include carbon sequestration, and the development of construction materials and structural platforms through in situ microbial processes that strengthen soil. All of these methods would exploit the indigenous microbial community, reduce the carbon footprint and energy requirements of engineering schemes, while increasing knowledge and predictability of complex systems and reducing the level of uncertainty for industry and regulatory acceptance.

By studying solid/fluid chemical reactions at the nanoscale scientists can discover how to exploit nature's own tricks. Suitable techniques for such nanoscale surface studies have only become available during the last 15-30 years. Investigations focus primarily on nanoscale reactions in calcite and iron oxide, minerals that are abundant in nature. An important objective is to reduce contamination of and develop methods of purifying drinking water at the source.

Nickel is released into groundwater from industrial sites, waste leakage, and by oxidation of natural pyrite (FeS_2), where it is present as a trace component. Experiments on natural chalk columns have shown that decreasing pumping rates results in lower nickel concentrations in the water because nickel has time to react with, and be taken up by calcite. The greater the surface area the faster and more extensive is the uptake. The structure of naturally occurring chalk is studied in order to develop an understanding of the fundamental mechanisms of biomineralisation. The eventual aim is to develop calcite nanoparticles for decreasing the nickel content in drinking water.

The mechanism of conversion of green rust, which is rich in Fe(II), to red rust, which contains Fe(III), is of interest for the protection of groundwater from contamination with heavy metals such as, for example, in fly ash. Powdered iron and sand can be used to form a reactive barrier. Nanoparticles of green rust, which form during oxidation of the original metallic iron by water, contain reactive Fe(II) which is effective at removing redox sensitive elements, such as chromium and chlorinated solvents.

The development of methods of CO_2 sequestration (capture, geological storage) requires an understanding of reactions with the host rock. Among proposed methods are using CO_2 to decrease viscosity of oil to enhance oil recovery, but the gas is not removed; it simply returns with the oil. Another scenario is to inject CO_2 into depleted reservoirs but this carries the risk of catastrophic release if the cap rock fails. An alternative method is to react CO_2 with rocks or sand,

and immobilise it by formation of carbonate minerals and clay; so that the CO₂ is stabilised in solid form. One of the most promising methods of fixing CO₂ permanently is by reaction with basalt.

Nanoparticles may be used for: air and water treatment; mesoporous materials for green chemistry and catalytic applications; environmental molecular science; or can be naturally occurring nanoparticles. As particles decrease in size, they acquire interesting and novel physical, chemical and electronic properties. Advantages include unique catalytic properties that can accelerate oxidation or reduction reactions with various pollutants for particle sizes less than 10 nm.

The basic principles of photocatalysis are already exploited in some commercial products such as self-cleaning glasses, architectural coatings and building blocks able to remove NO_x from air. Current objectives include development of new catalysts with significantly increased activity. Of particular interest is titanium dioxide modified with gold nanoparticles. At very small particle sizes (2-3 nm diameter) gold loses its metallic properties and becomes a semiconductor. Even at concentrations of less than 1 % the photocatalytic activity of the TiO₂ is doubled. A laboratory scale fixed bed reactor has been constructed to study photocatalytic groundwater remediation and field trials are now underway.

Nitrogen doped titanium dioxide nanoparticles are also being developed for indoor air treatment by visible light catalysis. Catalysts that work under visible light have been produced on the basis of theoretical calculations using novel methods of chemical synthesis. Doping with nitrogen increases light absorption but does not necessarily increase catalytic activity. Experiments confirmed, however, that that doped titania is indeed catalytically active under visible light. Catalytic coatings based on these doped titania nanoparticles are currently under development for environmental and public health applications. The nanoparticle size is in the 1-30 nm range and can be selectively controlled.

Mesoporous and microporous materials are being developed for green chemistry and catalytic applications, including selective catalysis, photocatalysis, membranes and energy applications. These materials are functionalized by depositing catalysts inside their pores. Examples include silica based mesoporous molecular sieves modified with titanium for 4-chlorophenol decomposition, or with manganese for gas-phase oxidation reactions with propene.

Naturally occurring atmospheric nanoparticles in Europe originate mainly from the North African desert, and greatly outnumber those from anthropogenic sources. They have a major impact on production of HONO, which is an important atmospheric contaminant because mineral dust provides a large surface area for catalysis reactions. Work is being carried out to identify and quantify possible photocatalytic sources of HONO on photocatalytic components of mineral dust, starting with TiO₂, which is the most active component and the fourth highest component by mass.

Water Treatment

Photocatalytic treatment of water is an effective method for degradation of pollutants and the destruction of micro-organisms. The research activities in this area include water treatment and purification, electrolysis using solar energy, self-sterilising surfaces, and sensors. Currently more than 5000 publications exist on photocatalytic organic degradation.

A laboratory scale reactor has been developed that uses electrochemically assisted photocatalysis (EAP), to break down organic molecules in water. The photocatalytic destruction of persistent organic pollutants in water such as oestrogen, 17- β -oestradiol, p-nitrophenol (PNP) and atrazine have been investigated. Atrazine is a herbicide widely used to control weeds in agriculture and is now banned in the EU. It is commonly found in surface and groundwater and its persistence in the environment is due to the presence of the s-triazine ring, which limits biodegradation.

TiO₂ nanopowders can be immobilised on substrates by dip coating, spray coating, or electrophoretic coating. Sol-gel routes and plasma processing have also been used to produce TiO₂ films on FTO glass substrates. A photogalvanic system with a TiO₂ photoanode has been constructed to allow photodegradation of organic pollutants and recovery of dissolved metal ions from plating waste via a galvanisation process using a two compartment cell with a copper mesh cathode and a titanium dioxide anode. The current conversion efficiency is about 10%.

The photocatalytic inactivation of bacterial spores (e.g. *cryptosporidium*) has been studied with river water samples and shown to be effective over a period of a few hours. Photocatalytic disinfection of water containing pathogenic microorganisms is an effective method for providing clean drinking water and works also for chlorine resistant organisms such as *Clostridium perfringens*, which are an indicator of faecal pollution. These results could have implications for clean drinking water in developing countries or in emergency situations, where water borne diseases constitute a severe threat. Tests on *E. coli* have shown significantly increased disinfection efficiencies using photocatalysis as compared to UVA irradiation alone.

Two relevant projects in this field are:

- SODIS Water¹⁰ - solar disinfection of drinking water for use in developing countries and emergency situations;
- PHOTOPURE¹¹ - a photocatalytic point-of-use water purification device, using a low power UV light source.

The main barrier to commercialisation is the need for education of potential customers regarding the limitations of conventional treatment systems.

Photocatalysis on both a laboratory and pilot scale has been shown to be an effective method for the treatment of water containing pollutants and microorganisms. Solar photocatalysis will be the main technology breakthrough for water treatment and purification, particularly in developing regions. Further

¹⁰ <http://www.sodis.ch>

¹¹

<http://www.engj.ulst.ac.uk/engineer/resprojects1.php?action=showProject&projectId=864>

research is needed in order to control the treatment to eliminate toxic products. Investigation is also needed of the potential risks of using nanoparticles for the purification of water and air.

An alternative method for the treatment of process and waste water is the use of membrane technologies for nanofiltration. This involves the use of a semi-permeable membrane that transports one component more readily than the other due to differential transport, separating them into a retentate, enriched in less mobile components, and a permeate, enriched in faster components. Applied pressure drives fluid through the membrane. The pressure required is lower than that for reverse osmosis because nanofiltration membranes have larger free volumes in the polymer. Both methods are effective in removal of multivalent ions and small organic molecules.

Among important factors that have to be considered when developing membrane systems are rejection, flux and yield. Membranes have inherent problems associated with concentration (typically 10-20% of material ends up in the concentrate). Membrane pores are of the order of 1 nm diameter and new polymeric structures have been developed that incorporate charged surfaces. The pore size is similar to that of pesticide molecules and other chemicals found in water. Nanofiltration lies between reverse osmosis and ultrafiltration techniques in terms of the size of the molecules removed and there is thus a continuum between these methods. It has potential uses in water softening, removal of natural organic matter (NOM), micropollutants and heavy metals, disinfection, desalination, and ion separation. Applications include safe discharge and reuse of wastewater, high quality drinking water, groundwater treatment, removal of organic and inorganic pollutants from surface water, and the recycling of process water.

There are a number of technical challenges:

- modelling of membrane structures and development of simulation tools to provide a better understanding of transport mechanisms
- membrane-solvent interactions for prevention of fouling, increased flux, and high rejections
- better process design for lower energy consumption and improvement of separation

Nanofiltration membranes consist of a multilayer structure with separation occurring in the top layer, which is ultrathin and mechanically supported by a series of asymmetric layers. The synthesis parameters that determine the structure of the membrane are the wt% of polymer, solvent type, temperature, air humidity and additives. Modification of the structure is possible by grafting a polymeric membrane to obtain a hydrophilic surface to reduce fouling of the membrane and to allow stable operation. Membrane fouling depends on the interaction between solute parameters and membrane parameters. Modelling of rejection can be carried out using transport equations and approximate expressions have been derived assuming a pure filtration process. The more hydrophobic a compound is the lower the retention is, so pore size is not the only factor.

Other membrane types, such as ceramic membranes consisting of a colloidal interlayer with an anatase top layer on an alumina support, are also being studied. New process designs are currently being developed using membrane cascades with recycling of permeate or concentrate for better separation between ions and organic solutes or between different organic solutes. The quality of the

permeate can be "tuned"; this aspect needs much more fundamental studies to be carried out.

Nanofiltration is an effective method for production of high-quality water but there are problems related to further treatment of concentrates, membrane fouling, and the difficulty of obtaining a complete separation, development of suitable membrane structures, improvement of process design. However it is cheaper than reverse osmosis because lower pressures are needed. Membrane life-time may be up to 5 years but this varies. The concentrate or retentate can contain high levels of heavy metals and toxins.

Colloids and surfaces play the principal roles of interaction in nature. Colloidal and interface chemistry study forces between colloids, the charges on them, and particle size and morphology. Interest is focused on the interface between the particles and their surroundings. Colloids are typically 1 nm - 2 μ m in diameter while nanoparticles are 1 nm - 100 nm; both are investigated and characterized at the nanoscale. The materials studied include: aqueous ions, complexes and clusters; colloidal particles such as clay and humic substances; bacteria; exopolymers; enzymes; crystallites; gels and amorphous materials; and soils.

The development of a system utilising iron precipitating bacteria to co-precipitate organic and inorganic pollutants such as arsenic, which affects more than 100 wells in Denmark, is studied using X-ray microscopy. Laboratory models have demonstrated that the inclusion of bacterial exopolymers enhances the precipitation of arsenic. Investigation of the differences between kinetics of chemical catalytic and biological elimination of iron compounds in raw water for drinking water is one of the research objectives. Another is to understand and optimize applications of co-precipitation activity between iron oxides and pollutants in water. The kinetics of biological iron oxidation is about 1000 times faster than for non-catalyzed oxidation and precipitation. Chemically catalysed iron oxidation and precipitation is slower than the biological process. The particle size for biological oxidation and precipitation is larger than that of chemically catalysed oxidation and precipitation. Exopolymers consist principally of carbohydrates that together with iron oxides can co-precipitate arsenic and other pollutants.

A method is being developed for sol-gel synthesis of nanosized TiO₂ particles on polypropylene fibres for the photocatalytic degradation of organic pollutants. The reaction has been studied at room temperature and atmospheric pressure and in supercritical CO₂ at elevated pressure. A processing temperature of 87 to 96 C was required to produce nanoparticles with a crystalline rather than amorphous structure. The primary cluster, which is \sim 1 nm diameter, grows to the secondary particle stage of 4-6 nm diameter by reaction limited aggregation, then to the primary aggregate stage of 20 nm before reaching a final size of 400-500 nm.

Other research involves development of a low temperature process for producing nanocrystalline metal oxides. This allows synthesis of nanosized metal oxides with controllable particle size, crystal phase, and degree of crystallinity with no post-reaction processing needed. The nanocrystallites have an average particle size of approximately 5-10 nm with a narrow size distribution. In addition polyaluminium clusters are being produced as coagulation agents. After filtration the solution can remain stable for several years. Aluminium ions in acidic aqueous solution form clusters of aluminium in which the tridecamer is stable. The structure is unchanged after heating up the system to the temperature of production.

Ultra nanocrystalline diamond (UNCD) coatings have crystallites of 10-30 nm and are normally un-doped and insulating. Nanocrystalline diamond (NCD) coatings have crystallites of 20-100 nm, and may be doped with boron. Submicron crystalline diamond (SMCD) coatings have crystallites 100-800 nm, thickness 0.1-5 μm and may also be doped with boron. Diamond is non-toxic, biocompatible, erosion resistant, corrosion resistant against all chemicals, and is electrically conductive if it contains boron. It has the largest electrochemical window of any material, can be used as an anode as well as cathode, and is resistant to fouling.

A method has been developed to deposit homogeneous polycrystalline 0.1-5 mm thick boron doped diamond (BDD) film on a silicon substrate of up to 0.5m². BDD/Si electrodes allow a very high anodic potential to be used to produce very efficient oxidants for water treatment and disinfection. Disinfecting agents are generated from water and mineral salts and disinfection is achieved without chlorine, independently of water turbidity, and with low by-product potential. This allows wastewater oxidation with no sludge generation, COD, TOC, N-organics and ammonia removal/reduction, and biodegradability. Bipolar electrodes are coated with diamond on both sides, between monopolar electrodes and self-polarized. Parallel and homogeneous water distribution gives better efficiency. A mixture of very strong oxidants is generated that is more efficient than chlorine. No added chemicals are needed.

For viruses and bacteria (*E.Coli*, *Legionella*) inactivation is 3-5 times faster than with conventional chlorine dosing. Destruction of algae, fungi and protozoan is assured. COD/TOC is reduced by the production of hydroxyl radicals for the destruction and increased biodegradability of organic pollutants (pesticides, phenols, solvents, PCBs). Future objectives are to further reduce COD and to find an alternative cathode material to BDD in order to lower costs, reduce energy through the use of a low overpotential cathode, reduce N-organics and NH₄ content, and optimise the efficiency by increasing the process temperature (70°C). The current target is to decrease phenol in wastewater below 100 ppm. Disinfectant production is possible in raw water with low salinity. It permits inactivation of bacteria, virus and algae without any chemical injection while eliminating the disadvantages of chlorine. Self-cleaning can be carried out by regular polarity reversal. Outstanding efficiency can be achieved, offering the potential to solve wastewater problems.

A feasibility study of a lab-on-a-chip device for analysing highly radioactive solutions has been carried out. Reduction of the sample volume for analysis of nuclear waste solutions has the advantages of dose reduction, a faster and simplified analysis procedure with no sample preparation or dilution, smaller uncertainty in the analysis of results and reduced risk of cross contamination. Field analysis is possible because a transportable device is employed and the generation of radioactive waste is reduced. Modelling of the microfluidic laminar flow shows that the small volume helps reduce the decay heating effect; so no cooling element is necessary. The dose reduction is almost proportional to the volume reduction, but a conservative limit should be used. The flow in microchannels differs strongly from classical flow in macrochannels. The surface charge on the walls induces an ion concentration within the microlayer, which causes a significant increase in surface energy.

Flow is characterised by fluid properties (e.g. density and dynamic viscosity) and their variation with concentration are measured at different temperatures. There are no dead zones, laminar flow and integration over the channel width gives representative results. Decay heating of the solution might affect the analysis because temperature influences absorption spectra and could distort the microchannel, which would affect the absorptiometry because the light needs to

transverse the complete channel length. However, the microvolume of radioactive solution generates a maximum of 1.5mW, for which the maximum temperature difference corresponds to less than 0.2°C. Concentration measurements by photospectrometry of light absorption peaks are reproducible. Other potential applications of this device include environmental sampling and detection of clandestine reprocessing activities.

Air Purification

Current European legislation (EURO V) fixes emission levels at < 0.005 g/km for particulate matter. To meet this standard requires the development of catalytic trap technology and advanced systems such as the noble-metal-free wall-flow catalytic trap. These new types of catalysts should be much less expensive than the noble metal supported catalysts (e.g. Pt/ CeO₂-Al₂O₃) currently employed.

Catalyst crystals with a size similar to that of the particulate provide the highest number of contact points. A novel catalyst preparation method called solution combustion synthesis is being used experimentally to produce crystals in the size range 20-50 nm. Catalyst performance was checked in a Time Programmed Reaction (TPR) pilot plant. The CoCr₂O₄ catalyst was compared with the reference catalysts MnCr₂O and CoFe₂O₄ and was found to give the best compromise between soot reduction and NO_x abatement.

A CoCr₂O₄ catalysed trap based on a SiC wall-flow monolith was prepared by in situ combustion synthesis. Results for loading and regeneration runs for the this trap, a commercial catalysed and a non-catalysed trap showed that the commercial catalysed trap performed worse than the CoCr₂O₄ one but better than the non-catalytic SiC monolith. In addition, a LiCrO₂ catalyst has been compared with the reference catalysts LaMnO₃, LaFeO₃ and LaCrO₃. The temperature corresponding to the CO₂ peak is an index of the activity of the catalyst – the lower this is, the more efficient the catalyst.

The regeneration of CoCr₂O₄ and LiCrO₂ catalysed traps is faster than that of the non-catalytic ceramic filter, resulting in a reduction in the regeneration time. Nearly no nanoparticles are released during regeneration by the LiCrO₂ and non-catalytic traps but they are emitted during the fast regeneration required by the CoCr₂O trap. The CoCr₂O₄ catalyst has a higher activity during regeneration and generates a significant quantity of nanoparticles (<30 nm) during fast regeneration. Formation of these secondary particles is probably a result of oxidative fragmentation of soot aggregates, formation of sulphuric acid droplets, or condensation of hydrocarbons during the fast oxidation process.

Indoor as well as outdoor air pollutants must be taken into account. The indoor pollutants are often at ppb levels, whereas outdoor pollutant concentrations are typically in the ppm range. Photocatalysis reactions at near ambient temperature can be used to degrade air pollutants. Titanium dioxide is the most commonly used photocatalyst because it has a high oxidative ability, is chemically stable, and is very abundant and inexpensive. The major areas of research on titanium dioxide photocatalysis concern self cleaning, anti-fogging, water treatment, antibacterial effects, and air cleaning applications. An improved knowledge of the mechanisms of photodegradation and the photocatalytic efficiency of the materials is needed, together with testing at the laboratory scale and the macroscopic real world scale.

Incorporation of titanium dioxide in building materials or surface coatings imparts to them self cleaning and de-polluting properties. When exposed to solar radiation it acts as catalyst for photodecomposition of pollutant molecules adsorbed on its surface and transformation into non toxic compounds. A consistent reduction in levels of NO_x by approximately 80% was observed for paints and cements containing titanium dioxide nanoparticles tested in the Indoortron¹². This facility allows online monitoring of ozone, NO_x, CO, and VOCs inside an environmental chamber with controlled temperature, relative humidity, air quality, air exchange rate.

In canyon street tests, NO_x concentrations were reduced 40 to 80% depending on differences in emission sources, wind direction and orientation of the walls. In the Indoortron, pollutants are consumed by the sink effect on the walls of the chamber, absorption on the sample surface, photolysis by UV, photocatalysis by TiO₂ and UV. Measurements can give information on the TiO₂ activity provided these effects are taken into account. The photocatalytic conversion of NO and toluene increases with decreasing relative humidity and toluene degradation is enhanced by the presence of NO. An inhibition effect on NO conversion occurs only at high concentrations.

Nitrates are the transformation products for photocatalysis of NO and the level of nitrates increases with the photocatalytic activity of the material. Aldehydes are the main transformation products for photocatalysis of organic pollutants. Carbonyls (formaldehyde, acetaldehyde, propanal) were detected in photocatalytic tests with the TiO₂ containing paints. The amount depends on environmental conditions and photocatalytic efficiency of the materials.

The next steps will be to investigate, in dynamic mode, the efficiency of pollutant conversion and release of by-products, the influence of light intensity, and the effect of multicomponent mixtures (benzene, acetaldehyde, formaldehyde, CO and NO₂, xylenes, naphthalene, styrene, toluene, α -pinene, d-limonene).

In air purification typically only 0.01 % of the incident photons are actually used for photocatalysis (e.g. by self cleaning glass) but 10% might ultimately be achievable. Photocatalytic activity can be enhanced by using noble metal (Pt, Au, Ag) nano-contacts, SnO₂/TiO₂ composite materials, or by doping with Fe(III). Nanoparticles of TiO₂ in colloidal suspensions form chain-like structures, which can act as antennae to enable transport of electron-hole pairs. This mechanism explains the high quantum yields of formaldehyde formation during the CH₃OH-Oxidation at TiO₂/Fe(III) colloids.

A double skin sheet reactor (DSSR) for water purification was designed in PMMA, a material that is transparent to UV radiation. A pilot plant was constructed but the pressure drop was found to be too high. In order to solve this problem an aerated cascade photoreactor (ACP) was developed. Tests showed that the TOC levels in industrial wastewater could be reduced to levels equivalent to drinking water quality. Titanium dioxide coatings on glass can be produced by a sol-gel dipping process. The coating thickness depends on the pulling speed of the glass from the solution. The photocatalytic activity is determined by the removal rate of methylstearate adsorbed on the TiO₂ film surface.

For gas phase reactions for air purification, standardised test methods are being developed by ISO and JIS using a continuous flow type testing system. For liquid

¹² The Indoortron laboratory is a unique, 30m³ volume walk-in environmental chamber featuring controlled temperature, relative humidity, air quality, and air exchange rate. http://ihcp.jrc.ec.eu.int/Scientific_Labs/indoortron.htm

phase reactions test methods are being developed by DIN and ISO based on the measurement of methylenblue degradation. Photocatalytic activity tests based on dichloroacetate (DCA) degradation can be carried out using a thin film fixed bed reactor (TFFBR).

The COST Action PHONASUM¹³, deals with the development of novel highly reactive photocatalytic materials sensitive to visible light and coating systems for commonly used substrates (polymers, glass, metals), characterization of the properties of photocatalytic materials and the design of standard test methods, and industrially relevant applications of new photocatalytic materials. The European STREP Project on Self Cleaning Glass¹⁴ develops modelling methods and laboratory tests for thin film coatings in support of a European standard for self cleaning glass. The European-Japanese Initiative on Photocatalytic Applications and Commercialisation (EJIPAC)¹⁵ aims at establishing collaboration between Japanese and European companies and institutions in the field of self cleaning surface coatings and air and water purification methods.

Potential Risks

One of the potential dangers of environmental remediation is that the products might be more toxic than the original pollutants. Other risks are represented by entry of toxic by-products into the foodchain, plant pathology and soil degradation. The most urgent problems for remediation are old and abandoned contaminated industrial and military sites. Some of the contaminants of particular interest are TCE, TNT, Cr(VI), As(III).

The application of nanoparticles for soil remediation is currently under investigation. Materials under consideration are zerovalent iron and iron oxides, catalysed by noble metals such as Pd. Permeable barriers with iron filings are already used to remediate groundwater. Iron nanoparticles could represent a more cost effective solution as they have a much higher reactivity per unit mass but further studies are needed of agglomeration/aggregation. There are however serious concerns regarding the effect of nanoparticle release on soil ecosystems. This is a major research challenge as there are relatively few data available.

Among fundamental requirements are physico-chemical equilibrium and kinetic data, information on effects on living organisms and development of modelling methods on a case by case basis. Alternative techniques to nanoparticle remediation involve the use of micro-organisms and phytoremediation methods. The complexity of systems involved means that there are many unknowns. It is therefore necessary to establish a system of defining acceptable and unacceptable risks.

¹³ <http://www.cost540.com>

¹⁴ <http://www.self-cleaning-glass.com>

¹⁵ <http://www.ejipac.de>

Points from Discussions

- Nanotechnology offers the possibility for development of new materials for process intensification.
- Gas phase remediation of sulphur dioxide and nitrogen dioxide is the area with the most potential applications.
- The technical challenges are greater for water purification than for air purification, for which there are already effective systems on the market.
- Commercial systems are already available employing photocatalytic methods for water purification.
- Photocatalysis uses sunlight, which is free of charge, so that running costs are low.
- There is a need to develop monitoring devices that can determine whether a remediation process has worked correctly or not.
- It is necessary to find more effective methods to deal with the problem of transport of pollutants - molecules could be immobilized in situ by chemical binding.
- The existing knowledge within the chemical industry could contribute to prevention and remediation of pollution.
- Nanosized titanium dioxide is already being produced by at least three companies in Europe on a commercial scale.
- Additional research is needed on methods to demonstrate the effectiveness of products.
- Life cycle analysis is an essential tool for assessing the environmental consequences of implementing new technological approaches.
- What can be learned from the US experience in setting up field tests?
- Support for European level research networks in environmental (nano) technologies and field sites to establish proof of concept is needed.
- The development of a European Technology Platform for Environmental Technologies, (including but not limited to nanoscale technologies) would act to stimulate progress by encouraging interaction between scientists and technologists from relevant fields.
- The development of new tools to obtain a better understanding of fundamental processes at the nanoscale and their relation to macroscale phenomena is essential.
- The most effective new methods for environmental remediation are likely to consist of a combination of more than one technology in hybrid systems.
- Some technologies, such as nanofiltration, are already quite close to market but additional research and development are needed to improve their efficiency.
- The application of modelling and simulation methods will allow a deeper understanding of the fundamental principles involved and ways to overcome problems and improve performance.
- A proper evaluation of the risks is required, particularly with respect to the release of nanoparticles and their fate in the environment.

Responses to Questions

1) Which are the most effective nanotechnologies for prevention or cleanup of pollution?

Discovering nature's secrets and applying them to make improvements is important, because there is very little work done in that area, globally. Thus, there is a great potential for making some important discoveries but unfortunately, there is very little funding for it. Application of nanotechniques (instruments) to natural materials and processes is a topic that falls between the boxes – it does not fit in nanotechnology programs because it is "environmental", while nearly all environmental research funding goes for monitoring and large-scale (field scale) studies.

Risk assessment is important but really belongs in the realm of those who develop new materials, *before* a product comes to the marketplace. Developing microsensors for environmental monitoring is useful, but in many cases, sensors developed for medicine and food applications can be applied (directly or with small modifications) in nature and sensor development is already funded through nanotechnology incentives.

The most effective nanotechnology is probably a combination of more than one technology in a hybrid system – membrane technologies are well placed to play a role in this.

The answer very much depends on the timescale. Regarding prevention, in the long-term, sophisticated new manufacturing practices and designs, including nanofabrication, reconfigurable artefacts and perhaps even desktop manufacturing should greatly reduce the need for transport, which is one of the major current sources of pollution.

The following 6 areas of technology were presented at the meeting:

- 1) TiO₂ photocatalysis for control of indoor pollution
- 2) " for process/effluent water streams
- 3) " for urban air quality improvement
- 4) " for cleanup of groundwater
- 5) Nanotechnologies in Permeable Reactive Barriers to treat groundwater
- 6) Nanotechnologies using in situ release of reactive materials to assist natural processes to achieve specific outcomes such as to degrade pollutants

2) How dependable and close to market are remediation techniques based on nanotechnologies?

If we consider new knowledge as the commodity and the market is the public literature, then we are very far from market. Fundamental research is critical for driving innovation 10 to 20 years down the road. Some new knowledge acquired using nanotechniques has already been disseminated but a great deal more information about the basic processes of nature remain to be discovered. This new knowledge is critical to environmental protection and clean-up as well as to general scientific and technological development in the future.

Several new products resulting from the application of new knowledge have already gone to market – such as nanoparticles of calcite for making paper white

without bleach, and techniques for filtering groundwater through reduced iron "reactive barriers" which effectively remove toxic elements such as chromium and chlorinated solvents. Many other products remain to be developed. Some of the necessary fundamental knowledge for these developments is in place. However, a host of other very useful and effective (sustainable) products await the results of fundamental research. Basically, the instruments developed as a result of the nanotechnological revolution have opened up four orders of magnitude in dimension scale for our exploration. We can now see at the Ångström level (10^{-10} m) whereas in the past, the limits were the micrometer scale (10^{-6} m). Whole new worlds of nature are now accessible for discovery.

Nanofiltration is already quite close to market but some additional modifications might significantly improve the efficiency of the process.

There seems to be a definite dearth of proper objective assessments. Probably a publicly-funded body should take on this work. Without adequate data it is very difficult to say.

TiO₂ photocatalysis for the control of indoor pollution and process/effluent water streams are close – needs to be made user friendly and "off-the-shelf". TiO₂ photocatalysis for urban air quality improvement is feasible by scoping calculations. For TiO₂ photocatalysis for cleanup of groundwater; field trials for Proof-of-Concept are scheduled with UK at a Canadian site. Nanotechnologies in Permeable Reactive Barriers to treat groundwater- UK field trials are proposed. Nanotechnologies using in situ release of reactive materials to assist natural processes to achieve specific outcomes such as to degrade pollutants- can proceed at bench scale for screening and Proof-of-Concept.

3) What additional research is needed to exploit the full potential of nanotechnology for remediation?

Fundamental investigations that will reveal the secrets of nature, that can then be applied to improve the natural ability of soil, sediments and dust (natural nano-) particles to remove or attenuate contaminants. New materials which will apply the tricks of nature to make more efficient and sustainable filters for immobilising contamination and eventually "mining" it from selective sequestration methods – that can only be developed if fundamental research is promoted.

The use of nanofiltration in hybrid configurations, modelling and simulation studies and developing a better understanding membrane fouling.

Research is definitely needed to better understand possibly deleterious effects of nanoparticle release on ecosystems, including aquatic and soil.

TiO₂ photocatalysis for the control of indoor pollution and process/effluent water streams need further development only. TiO₂ photocatalysis for urban air quality improvement needs Proof-of-Concept and pilot trials. For TiO₂ photocatalysis for cleanup of groundwater; pilot trials in the field are needed. Bench and pilot scale testing methods and better fundamental understanding of transport, reaction and fate in situ are needed for nanotechnologies in Permeable Reactive Barriers to treat groundwater. Nanotechnologies using in situ release of reactive materials to assist natural processes to achieve specific outcomes need bench-scale testing methods and better reaction and transport understanding.

4) Which environmental nanotechnologies are the most promising and should be further explored?

Applying nanotechniques to “see” at the nanometer scale to understand the fundamental physical/chemical processes at work in nature – to discover nature’s secrets.

New materials developed by adopting those secrets, for improving quality of air, water, soil, etc.

The importance of membrane technology should not be overlooked even though the workshop was more focused on nanoparticles.

This question does overlap with that part of 1) dealing with cleanup. The same time the criticism of answer 2) applies: there is a dearth of data at present.

TiO₂ photocatalysis for the control of indoor pollution and process/effluent water streams should get development funding to commercialise. TiO₂ photocatalysis for urban air quality improvement and for cleanup of groundwater should proceed as field trials. Nanotechnologies in Permeable Reactive Barriers to treat groundwater and using in situ release of reactive materials to assist natural processes should have theoretical, bench modelling studies combined to better understand nanomaterials: as sorbents in the environment, oxidation and reduction properties, to help monitor the environment, to deliver nutrients and other substances to help remediation processes.

5) What are the potential risks of using nanotechnologies in remediation applications?

Before a product is applied or comes to market, it must be tested for safety. That is the rule for all products - drugs, chemicals, materials, etc. It is no different for nano-products and processes. So if a product is properly and thoroughly tested, the potential risks will have been identified.

None when membranes are used. Some of the issues with nanoparticles have been described at the meeting.

See answer 3).

Several:

- Long-term performance not as good as promised (remediation goals not being met).
- Incorrect transport and reaction behaviour predicted (reliability not correctly understood).
- Perception as a contaminant if nanomaterials are used in situ (analogous to GM plants seen as contaminants rather than beneficial in crops).
- Unknown side effects arising from moving to field applications too soon.

6) Is there a need for targeted funding for infrastructure to support nanotechnologies for environmental remediation?

Yes. Traditionally, environmental scientists have had no training in nanotechniques so usually, they do not have the expertise required to apply the instrumentation. Also traditionally, nanoscientists have focussed on producing materials for industry and they do not have much background in the natural sciences: Earth science, soil science, geochemistry, geology – so the lack of overlap in scientific communities has led to slow adoption of nano-scale sensitive

instruments or the information that they can offer. Targeted funding would help this.

Yes. In all fields but depending on the scale of the research.

Many laboratories are working on nanotechnology, but it seems no one laboratory has all the instruments it needs. This particularly applies to the environmental analysis field. It would certainly be useful to have a joint European laboratory with such broad capability. The question would then be whether it would pursue its own research programme, or be accessible to others.

The following should be funded:

- Large-scale application of TiO₂ for urban air quality improvement is very interesting and should be funded as a matter of priority
- Because of regulatory concerns, in situ pilot testing of remediation technologies such as zero-valent Fe nanoparticles for groundwater remediation is very difficult. Funding to develop pilot test facilities for transport and reaction behaviour of nanoparticles in soils and groundwater would be very useful to demonstrate predictability for regulators
- Funding for fundamental research on nanoparticle reactions in aqueous systems is important to build confidence in reaction behaviour expected in the environment.
- Funding for fundamental research on nanoparticle transport in porous media and in water streams would help provide the necessary framework to predict environmental behaviour
- Funding for numerical modelling of particle transport and reaction in the environment is critical to bridge between theory and data, and to screen behaviour for the most promising technologies and most worrying threats.

7) What opportunities are there for setting up EU collaborative projects on environmental nanotechnologies?

Development of nano-devices – excellent opportunities for setting up EU collaborative projects; EU frameworks already insure funding for development of nano sensors and there are many centers of research focused on this sort of work. Money boxes and a good pool of European experts already exist.

Defining risk of nano-materials – this has become a very hot topic very quickly. There is incentive in industry to guarantee the safety of its products and keep public confidence and funding opportunities exist in nanotechnology subdivisions as well as health, medicine and safety of the workplace. National funding, industrial funding and EU funding are all available and there are plenty of experts.

Use of nanotechniques to understand nature's secrets – there is very little research. There are not many researchers in the EU with expertise in the chemistry and physics of natural systems as well as expertise in the techniques and approaches of nano-technology and nano-science. There are perhaps 10 active research groups in the world but a number of these, more than half, are in the EU. Likewise, funding is nearly impossible to find. The research field falls between environmental and nanotechnology packages and industry involvement, which is a limiting factor for most EU applications, is not easy to encourage, because of the fundamental nature (i.e. long-time-to-market) of the research tasks. The EU has the potential to jump ahead of US and Asian competition in a big way, if it would support this direction now.

Development of nanomaterials for natural application – there is very little research. Again, there are very few researchers with the necessary expertise and

the topic does not fit into the EU environmental package (which is focussed on monitoring) or the nanotechnology package (which focusses on the classic nanotechnology areas: thin films, super-materials, semi-conductors and nano-devices). However, with some directed funding, the potential in this topic for EU dominance is very, very good.

Significant opportunities exist for bringing together people from very different areas and backgrounds in interdisciplinary collaborations.

The EU has some world-leading groups that work on nanosciences applied to environmental and geological systems. They would be able to contribute significantly to R&D on potential applications of in situ nanotechnology for remediation. Cross-disciplinary calls that require materials scientists, physical scientists and environmental scientists and engineers to work together would be very useful to create a new generation of experts to take this area forward.

Appendix 1 – programme

Monday 16 April

Introductory Session (Chair: D. Rickerby)

09:45 D. Rickerby, IES JRC Ispra
Potential Application of Nanotechnologies for Environmental Improvement

10:00 G. Bidoglio, IES JRC Ispra
Chemical Pollutants in Terrestrial and Aquatic Ecosystems

10:35 A. Skouloudis, IES JRC Ispra
Environment and Health Effects of Pollution in Heavily Populated Areas

11:10 Coffee

Water Treatment and Purification (Chair: M. Morrison)

11:40 S. Banwart, Sheffield University
Nanometre-Scale Observation of Biodegradation

12:15 A. Orlov, University of Cambridge
*Nanotechnology for cleaning up contaminated air and water:
The environmental impact of atmospheric nanoparticles*

13:00 Lunch

14:30 J.A. Byrne, P.S.M. Dunlop, T.A. McMurray, J.W.J. Hamilton, D. Alrousan, G. Dale, University of Ulster
Photocatalytic Water Treatment and Purification

15:05 B. Van der Bruggen, Catholic University Leuven
Application of nanofiltration for treatment of process and waste water

15:40 Coffee

16:10 E.G. Søgaard, Aalborg University
Environmental Nanotechnology

16:45 W. Haenni, Ch. Provent, L. Pupunat, Ph. Rychen, Adamant Technologies
Water Purification with Nano-Crystalline Diamond as an Environmental Friendly Process

17:20 Discussion

18:00 End of First Day

Tuesday 17 April

Air, Water and Soil Decontamination (Chair: A. Skouloudis)

09:15 D. Fino, Politecnico di Torino

Escape of Nanoparticles during Diesel Particulate Trap Regeneration

09:50 P. Leva, T. Maggos, J. Barrero, J. Bartzis, D. Kotzias, IHCP JRC Ispra

Studies on photocatalysis of priority indoor pollutants with titanium dioxide based building materials

10:25 D. Bahnemann, Leibniz University Hannover

Nanoparticles for Photocatalysis: Cleaning Polluted Water, Air and Surfaces with Sunlight

11:00 Coffee

11:30 G. Janssens-Maenhout, P. Richir, S. Nucifora, IPSC JRC Ispra

Analysis of Radioactive Solutions by a Microsystem

12:05 S. Stipp, University of Copenhagen

Nano Methods for CO₂ Sequestration and Groundwater Treatment

13:00 Lunch

14:30 J. Ramsden, Cranfield University

Complexity and Risk in Environmental Remediation using Nanoparticles

15:05 **Discussion**

15:40 Coffee

16:10 **Conclusions**

16:30 End of the Workshop

Appendix 2 - abstracts of presentations

Potential Application of Nanotechnologies for Environmental Improvement

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Environmental nanotechnologies can assist in reconciling the Lisbon objectives (growth, innovation) and the Gothenburg priorities (sustainable development, environment). The Environmental Technologies Action Plan for the European Union [1] acknowledges the important role that nanotechnologies could play. Potential applications include integrated clean technologies, environmental monitoring and environmental management systems as well as end-of-pipe technologies and remediation methods. A European Commission - Nanoforum Workshop [2] has explored ways in which nanotechnology could be used for the benefit of the environment, while remaining aware of the potential risks. Applications of nanotechnologies in monitoring, remediation and resource saving were considered and conclusions drawn regarding the research priorities needed to ensure safe and responsible technological development. While the EU does not at present have a specific research initiative on environmental nanotechnologies, some significant European projects in this area are already being carried out [3].

Nanotechnologies can contribute to improving the environment by providing effective monitoring, pollution prevention and remediation methods. Detection and measurement of pollution is a necessary step towards initiating remedial action and nanotechnology is an essential component in the development of improved systems for monitoring and cleanup. Advances in sensor and biochip technology, for example, are being applied to provide more sensitive detection techniques for air and water quality monitoring. New synthesis methods for efficient metal oxide nanocatalysts will help reduce pollution due to industrial and transport sources. The photocatalytic properties of titanium dioxide nanoparticles are being exploited to manufacture “self-cleaning” architectural coatings that are able to degrade volatile organic compounds (VOCs), nitrogen oxides and other pollutants into less toxic species.

Conventional environmental remediation techniques have proved relatively ineffective in reducing the levels of pollutants in air, water, and soil and, as a consequence, only limited results have been achieved in responding to the challenges presented by major cleanup operations. Filtration and purification plants used to supply drinking water are generally only partly successful due to the relative inefficiency of the active materials. Because of their greater specific surface area, nanoparticles are significantly more effective filtration media than larger particles of the same material. Activity is dependent on the crystal and surface structures as well as the constituent elements, so precise control at the nanoscale during synthesis is a key factor in improving performance.

There is considerable commercial interest in environmental nanotechnology because the development of innovative solutions to fight pollution is essential to ensure sustainable development. By 2010 the total world market for applications based on environmental nanotechnologies has been estimated to be \$6.1 billion [4]. This can be divided into four sectors: remediation, protection, maintenance, and enhancement, of which remediation is the fastest growing, maintenance and protection applications constitute the bulk of the remainder, while environmental enhancement represents the smallest sector (Fig. 1). Numerous applications of remedial nanotechnologies are already close to market and, once performance and safety have been verified in field trials, these have potential for very rapid growth.

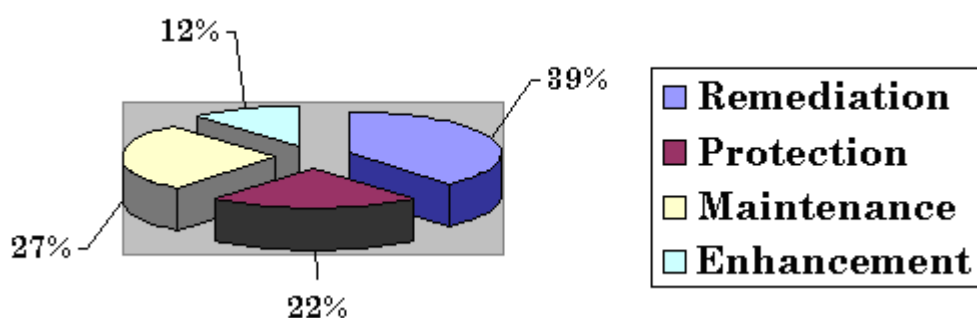


Fig. 1. Forecast for Nanotechnologies in Environmental Applications by 2010.
(Source: BCC Research)

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3. D.G. Rickerby and M. Morrison, Nanotechnology and the Environment: A European Perspective, Science and Technology of Advanced Materials 8 (2007) 19–24.
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FATE of Pollutants in Terrestrial and Aquatic Ecosystems in Europe

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<http://ies.jrc.cec.eu.int/rwer.html>; <http://ies.jrc.ec.europa.eu/ateam.html>;
<http://ies.jrc.cec.eu.int/ensure.html>; <http://ies.jrc.cec.eu.int/agrienv.html>

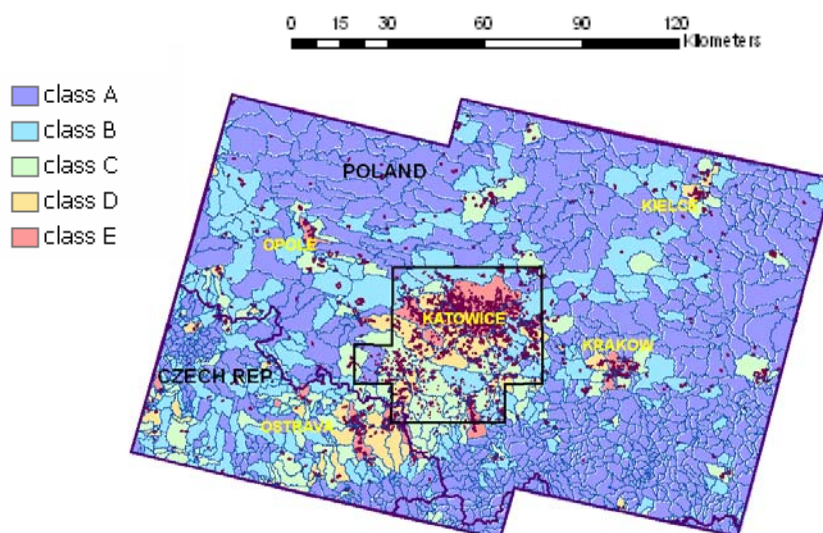
Human activities are undeniably related to the uncontrolled or accidental release of pollutants into the environment. Contaminants spread across different environmental media through atmospheric deposition, leaching from soil to groundwater, accumulation in rivers and lakes, and discharge into the sea. The understanding of the fate and impact of pollutants on the functioning of the terrestrial/aquatic interface is a scientific challenge that requires a combination of several disciplines, tools and datasets. The JRC has taken up this challenge by launching the FATE project, aiming to answer policy questions arising from a number of environmental Directives, EU Thematic Strategies and International Conventions. The adopted tiered approach links modelling and monitoring for a multi-scale impact assessment in a risk-based framework.

The FATE project addresses the fate and impacts of pollutants across a range of temporal and spatial scales depending on the policy question and making best use of available data. The outcomes are pollution risk and vulnerability maps, which are very useful to assess the impact of EU policies, raise public awareness and facilitate planning of management scenarios. At the scale of continental Europe the focus is on identifying “hot-spots”, spatial trends and general pathways of pollutants; at the catchment/coastal zone scale the interest is more on the apportionment of mass inventories and aggregated in and out fluxes; at the local scale attention is eventually paid to the prediction of concentrations in different compartments, generating input information for exposure assessments of ecosystems to potential pollutant risks, which is the information requested by decision-makers for implementing environmental management strategies.

In the multi-scale FATE mapping of environmental pollution risks in Europe, a network of case study regions and coastal sites provide a snapshot of impacts of decisions taken at sub-national and national levels, and act as testing ground of methodologies for the identification of priority risk sources and most vulnerable endpoints. Examples of pilot-targeted activities include a network of Southern European lagoon-estuarine systems exhibiting a range of pollutant pressures (agriculture, industry and tourism), where analyses of ecosystem effects of lagoon fluid-dynamics, river runoff influence, nutrients cycles, shellfish farming, macro-algal blooms, as well as the economical implications of different scenario analysis have been conducted.

Another example of pilot-targeted activities is the Upper Silesia region in Poland, an acknowledged “hot-spot area” in the context of environmental impacts from multi-source environmental contaminants from strongly interrelated industrial and mining activities. The spatial decision support system under development here will be the

basis for the determination of the extent of the problem at regional scale in terms of comparison among different sources of pollution, the management of degraded land including methods for the identification of potentially contaminated sites, and ranking of impacted receptors (sensitive terrestrial ecosystems, ground- and surface water resources) for prioritization of remedial actions. The outcomes of the pilot project will be useful also for the classification of mining sites and will provide a reference for pan-European assessment exercises and potential use by Member States in the context of the implementation of, *inter alia*, the Mining Waste Directive, the Soil Thematic Strategy, the Groundwater Directive.



Map of source anomaly index for 1st order catchments as junction of surface geochemical remote sensing anomalies associated to mining and contaminated sites in South-Poland and the North-Czech Republic of Upper Silesia (Sommer et al.)

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Environment and Health Effects of Atmospheric Pollution in Densely Populated Areas

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The complexity of processes associated with atmospheric pollution through chemical reactions, transformation from vapor to particulate and dispersing under complex global circulation mechanisms makes prohibitive the distinction of environmental effects on human health. Taking into consideration the recent efforts of the European Commission for implementing an action plan (COM-2004-416 final) for “reducing the disease burden caused by environmental factors in the EU and for identifying and prevent new health threats caused by environmental factors”.

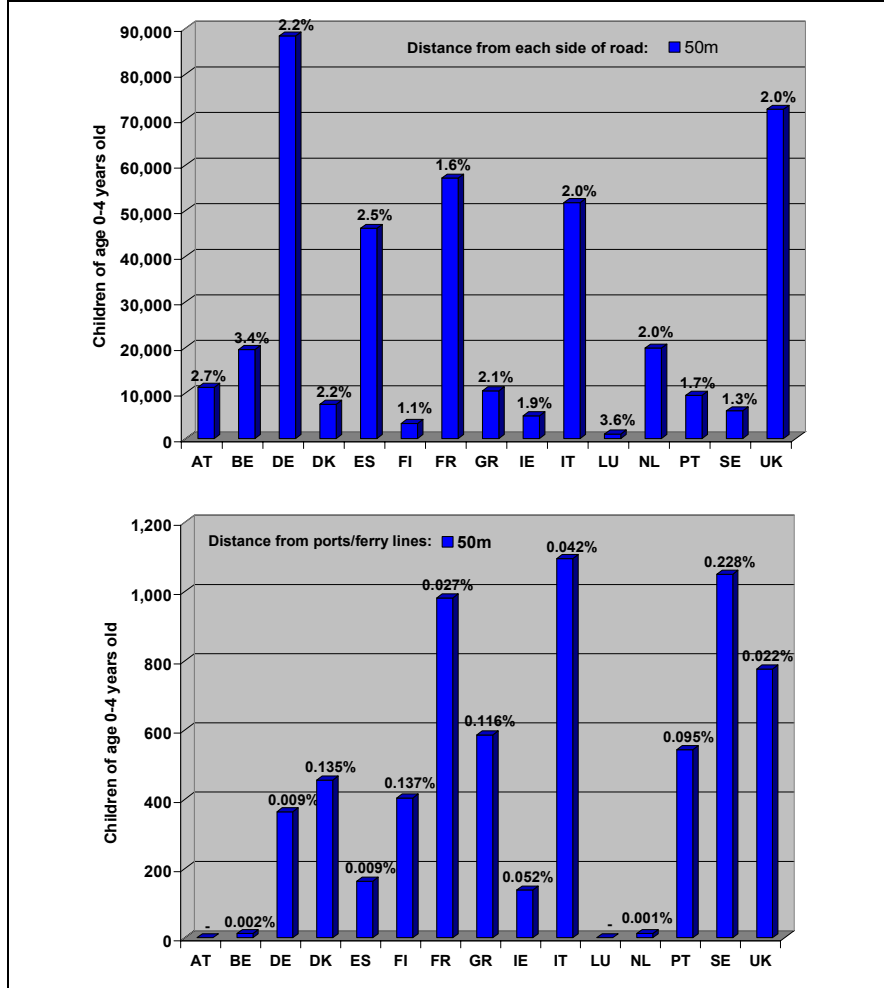
Directives	Year	Main Provisions
90/313	1990	Established requirements for the public’s freedom of access to environmental information.
91/441	1991	Extended small-car standards of 89/458 to all size classes.
91/542	1991	Tightened heavy-duty diesel vehicle CO, HC, NOx standards. Established heavy duty diesel PM standards
92/72	1992	Requires O ₃ monitoring. Sets health and vegetation-based O ₃ concentration standards.
94/12	1994	Introduces more stringent limit values for all ambient pollutant concentrations. Reflects Auto/Oil study recommendations to evaluate all transportation-related policies according to cost/effectiveness guidelines.
96/61	1996	Integrated Pollution Prevention and Control Directive created multi-media permitting system.
96/62	1996	Air-Quality Framework Directive. Defines and sets objectives for ambient air quality. Requires assessment of ambient air quality and the availability of this data to the public, including alert notices when threshold values are exceeded. Requires maintenance of good air quality.
96/63	1996	Controls VOC emissions from petrol storage and distribution.

There are several efforts for abating atmospheric emissions and relevant EU legislation regarding to emissions and air-quality are shown at the aforementioned table as well as at http://europa.eu.int/comm/environment/legis_en.htm. From this table it is also shown an initial emphasis on mobile-source regulation, other than heating and stationary source regulations. Then an “optional harmonization” process was introduced which was then followed by examination of the ozone-forming VOCs and NOx. These were thought to be primarily mobile-source problems whereas acidifying sulphur dioxide emissions were thought to be primarily stationary-source problems.

Regarding health effects, the current understanding of the situation at densely populated areas should be increased, before commitments are taken for decreases in total emissions as well as for assessing the effects of reduced trans-boundary fluxes. As target group are taken children of up to 5 year’s old living at three different distances from heavily trafficked roads (50m at each side of the road) are identified.

Similarly the children exposed at the vicinity of ports and major ferry line areas are also identified.

Fig 1: Country comparison of children within the proximity of from heavily trafficked roads, ports & ferry lines



By examining areas of high population density, it is now possible to demonstrate “dose-response” relationships with population numbers which are outside the error margins of statistical analysis as was frequent the case with most epidemiological studies until now. The add-value of this work is also the direct comparisons of atmospheric emission and combined with country health statistics (hence, identifying hot-spots where the Environmental Burden of Diseases is higher).

By comparing the data in EU15, it is shown that in general 2% of children between 0 and 4 years old seem to be exposed to risks due to the vicinity of main roads at a distance up to 50m from each side of the road. Countries with more population are appearing to have more children exposed to this indicator. Countries with dense network of roads are affecting more children at the specific age group examined. Countries (LU, BE, ES) with average high population density appear to have higher percentage of children exposed to traffic sources. Countries with long coasts and islands (SE, FI, DK and GR) appear to expose a higher percentage of children between 0 and 4 years old due to port and ferry activities.

In Situ Engineering at the Cell-Mineral Interface in Soils and Groundwater

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Background

Soils and groundwater provide tremendous biological potential for purification of groundwater and treatment of waste. An important example is the legacy of industrial contamination to aquifers and the capacity of the groundwater system to reduce the resulting environmental risk through in situ reactive transport processes. Current approaches to risk management quantify the in situ processes that reduce contaminant mass or flux (biodegradation), transport rate (sorption) or concentration (dilution by dispersive mixing). Of particular importance is the role of indigenous microbial populations to biodegrade organic pollutants.

The principles of engineering biotechnology are applied to the in situ system. Although the processes being studied are carried out in natural bioreactors, bench-scale testing is carried out with microcosm reactors constructed with site-specific groundwater, sediments and inocula. Likewise, field investigations at contaminated sites provide pilot-scale information about the ongoing in situ processes. Even though the in situ reactor system is not constructed by humans, engineering performance assessment is carried out in order to support engineering design decisions. Of priority is an assessment on whether to rely solely on the naturally-occurring processes to reach specific engineering outcomes. These outcomes may include maintaining water quality above a specific standard or ensuring the spatial extent of contamination will not reach a drinking water well. Engineering performance is determined within a risk assessment framework that considers the source-pathway-target linkages at a location, and the likelihood that engineering performance measures (such as maintaining water quality) will be met at the target.

More pro-active approaches include biostimulation where dissolved nutrients or other transportable substances are delivered to the sub-surface, bioaugmentation where active microbial populations are injected, or construction of permeable reactive zones. Future applications will become more pro-active to achieve a larger range of desired engineering outcomes. These may include biogenesis of carbonate minerals to sequester carbon and to strengthen soil as a construction material, in situ production of both hard (oxide minerals) and soft (biological polymers) nanomaterials to influence specific soil properties such as cohesion or water retention or to better monitor and control in situ microbial activity and function.

To illustrate current state of knowledge for in situ bioengineering, outcomes from two projects are described below. The first describes advanced numerical modelling of reactive transport at field scale¹⁶. This is used to interpret large data sets from field studies in order to better identify biodegradation processes and quantify rate parameters for contaminant biodegradation within an aquifer. The second is new

¹⁶ Watson I.A., Oswald S.E., Banwart S.A., Crouch R.S. and Thornton S.F. (2005). Modelling the dynamics of fermentation and respiratory processes in a groundwater plume of phenolic contaminants interpreted from laboratory- to field-scale. Environ. Sci. Technol., Vol. 39, No. 22, 8829-8839.

bench-scale model systems to obtain better understanding of particle transport behaviour in soil and groundwater systems¹⁷.

In Situ Bioreactors for Pollutant Degradation

When applying the principles of hydrochemistry to contaminant plumes, biodegradation processes are represented as stoichiometric electron-transfer reactions. The organic pollutants which act as energy sources for microbiological activity, and the terminal electron acceptors or “TEAs” ($O_2(aq)$, NO_3^- , $MnO_2(s)$, $FeOOH(s)$, SO_4^{2-} , HCO_3^-) associated with microbial respiration, are treated respectively as reductants and oxidants which react to produce biodegradation products such as inorganic carbon species. This approach allows translation of the conceptual model of the in situ bioreactor into a mathematical framework for engineering performance assessment. This is done by formulating mass and electron balances for the system, using the individual biodegradation processes. Through proven multi-level sampling techniques at field sites, it is possible to obtain large sets of high quality data yielding good spatial resolution of groundwater head, permeability, water composition, mineralogy of drillcores, and measures of microbial activity.

These data sets are utilized with the mass and electron balances in order to help parameterise numerical process models for flow and reactive transport. Current models include process descriptions of aqueous geochemical speciation, phase equilibrium, mineral dissolution and precipitation kinetics, abiotic reaction kinetics and microbial population dynamics and biodegradation kinetics¹⁶. These processes are embedded within a groundwater flow and transport model based on a spatially-variable permeability of the aquifer. It is possible to manage this level of complexity using advanced computational techniques such as parallel processing. Process models for these complex in situ bioreactors are thus limited primarily by the budget available to obtain good site data and, more importantly, conceptual understanding of the in situ system. A particular limitation and current research focus internationally, is the unknown microbial genotypes, their physiologies and interactions, and their potential function for mass transformation within the indigenous microbial ecosystem.

Reactive Transport of Particles in Soils and Aquifers

Because microbial processes in soils and aquifers are dominated by attached growth communities, particular research attention is given to interactions of cells and minerals. One important consequence of these interactions is the transport of microbes within the porous medium flow field. In order to obtain well-constrained data sets to quantify transport behaviour, novel bench-scale physical modelling techniques are used. This approach emphasises fluorescence imaging in order to measure both the spatial structure of the porous medium flow field and its chemical state; i.e. the spatial distribution of solute or particle mass. These systems are designed as scale-model soil and aquifer systems. Fluorescent molecular probe molecules are used to track particular processes or chemical compounds and particles. Quantitative digital imaging of the specific emission wavelengths under UV-excitation allows exceptionally good signal-to-noise ratio when measured in a darkroom. Results demonstrates that these techniques quantify, non-destructively and

¹⁷ Bridge J.W., Banwart S.A. and Heathwaite A.L. (2006). Non-invasive quantitative measurement of colloid transport in meso-scale porous media using time-lapse fluorescent imaging. *Environ. Sci. Technol.*, *40*, 5930-5936.

in real time, both transport and deposition parameters for micron-sized and smaller particles. One current application is the study of pathogen transport in soil. However, these model systems offer a potentially powerful technique to obtain far better empirical data sets, and to extend current theoretical concepts, for aqueous nanoparticle transport and reaction in natural porous media. As a first step, these systems can provide bench-scale models to test in situ engineering application of reactive nanomaterials.

Nanotechnology for cleaning up contaminated air and water. The environmental impact of atmospheric nanoparticles.

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Nanotechnology is an emerging area of environmental remediation. It has several promising areas of applications, including: (a) contaminated air and water treatment, (b) energy applications; (c) novel functionalized adsorbents for environmental and industrial applications; (c) self-cleaning materials, and (d) materials for sustainable energy production. There are also naturally occurring nanomaterials, which can profoundly influence the quality of the environment. Various issues related to characterization and detection of nanoparticles and observing the processes on nanoscale are also of significant importance. This presentation will address some of the topics outlined above.

Nanoparticles for water treatment: Modification of TiO₂ with noble metals has shown significant promise in increasing the activity of titania for a variety of catalytic processes. Even so, relatively few studies have been carried out on Au-modified TiO₂ where metal particle sizes < 5 nm give rise to unique physical and chemical properties. In particular, the effect of Au nanoparticle size on photodegradation of organics in solution is largely unknown. Our study has explored the effects of nanoparticles on the efficiency of decomposition of various organic pollutants. We found that very small loadings of nanomaterials (sub-atomic %) can have a dramatic effect on their catalytic properties. By using electron microscopy we confirmed the narrow metal particle size distribution, with average particle size varying from 3.6 to 5.5 nm, depending on the metal loading. Finally, we have explored practical applications of photocatalysis. Both engineering and chemistry departments have designed a large scale chemical reactor and used it to clean up contaminated groundwater at an air force base in Canada. [1,2,3]

Nanoparticles for indoor air treatment: Combining solar light with photocatalysts can destroy a variety of dangerous pollutants in air. It has the potential to address the sick building syndrome, affecting millions of people worldwide. However, there are still many challenges concerning the efficiency and reliability of this approach. We have investigated the fundamental and applied aspects of visible-light absorbing materials based on N-doped TiO₂. The advantage of visible light active materials compared to UV light active materials is higher efficiency of energy utilization, as the solar spectrum contains only a small UV component. These materials can also utilize artificial illumination, commonly in use inside the buildings. In this project we have developed various novel nanoscale materials extremely active under visible light. Based on theoretical calculations and model system studies we have also addressed the issues of reproducibility and activity of such materials. [4,5]

Mesoporous materials for green chemistry and catalytic applications: Mesoporous materials are those with pores in the range 2-50 nm diameter. They have very high surface areas providing numerous sites for adsorption and reactions. Such materials are used in catalysis, separation, energy applications and various other fields. We have developed various functionalized mesoporous molecular sieves for

decomposition of organic pollutants in both air and water. The surfaces of silica based sieves (SBA-15) were modified with manganese and titanium, characterized using various spectroscopic techniques and applied in gas/liquid phase reactors. We found that such materials exhibit a significant activity for oxidation of organic pollutants.[6]

Naturally occurring nanoparticles: 'Mineral dust' broadly describes fine particles of crustal origin advected from arid regions and consisting primarily of silica and silicate minerals. In this project we have studied sub-micron particles to explore their impact of various heterogeneous surfaces on various atmospheric reactions. We looked at several pathways for the formation and destruction of HONO, which is an important atmospheric contaminant affecting atmospheric processes and public health). We have discovered a novel source of HONO under conditions pertinent to the daytime troposphere.[7]

Challenges ahead: Nanomaterials offer a great potential to revolutionize various areas of environmental and industrial chemistry. There are, however, significant uncertainties about the biological effects of such materials. Additionally, such issues as long-term fate of nanoparticles in the environment, the detection of nanoparticles in various environmental media, safe disposal, the life-cycle analysis and many others need to be addressed.

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Photocatalytic Water Treatment and Purification

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Semiconductor photocatalysis is a possible alternative to conventional water treatment technologies and, titanium dioxide (TiO_2), is the most widely employed semiconductor material for aqueous applications. When TiO_2 is illuminated with light of $\lambda < 400$ nm, an electron is promoted from the valence band to the conduction band of the semiconducting oxide to give an electron/hole pair. In electrochemical terms, the valence band potential is positive enough to generate hydroxyl radicals at the surface and the conduction band potential is negative enough to reduce molecular O_2 . The hydroxyl radical is a powerful oxidising agent and attacks organic pollutants present at or near the surface of the TiO_2 resulting in their complete oxidation to CO_2 , if allowed to proceed to completion.

In this work, nanoparticle TiO_2 was immobilized onto supporting substrates i.e. glass, ITO glass and titanium metal, using dip coating or, in the case of electrically conducting supports, an electrophoretic coating procedure. Immobilised catalyst films were then tested for their efficiency in the photocatalytic degradation of organic chemical contaminants and for the disinfection of water containing microbiological pathogens. Organic chemical pollutants investigated included 17 β -oestradiol, atrazine, and formic acid as a model pollutant. Microorganisms investigated included *E.coli*, *Clostridium perfringens*, and *Cryptosporidium parvum*. More recent work on disinfection has compared UVA and UVA-photocatalytic efficiency in real water taken from a catchment in Northern Ireland.

Where the supporting substrate was electrically conducting the samples were used in photoelectrolytic cells where the application of an external electrical bias was employed to increase the rate of the degradation. Furthermore, these photoanode materials were employed in a two compartment photogalvanic cell for the simultaneous degradation of organic contaminants and the recovery of dissolved metal ions. A number of different photoreactor configurations were employed in this work.

Experiments had shown that photocatalysis was effective for the destruction of the parent compounds i.e. 17- β -oestradiol, oestriol and oesterone. However, perhaps more important, is the removal of the oestrogenic activity. To this end experiment were undertaken to determine the "oestrogenic activity", following photocatalytic treatment, using a yeast screen bioassay. In this work the TiO_2 (*Degussa P25*) was immobilized onto Ti-alloy using an electrophoretic coating method (Byrne et al. 1998). Photocatalysis was effective for the removal of the oestrogenic activity of 17- β -oestradiol under UVA illumination. Further work also demonstrated the effective destruction of the oestrogenic activity of oestrone and 17- α -ethinyl oestradiol (Coleman et al, 2004). These experiments clearly demonstrate that TiO_2 photocatalysis is a promising technology for the treatment of water contaminated with endocrine disrupting chemicals.

Work was also undertaken to monitor the genotoxicity of intermediate breakdown products of p-nitrophenol during photocatalytic degradation. A commercial toxicity bioassay (Vitotox test kit) was used to determine toxicity. The parent PNP was analysed by HPLC and it was shown that the degradation of the parent PNP was faster than the reduction in genotoxicity during photocatalytic degradation, as a result of the formation of genotoxic intermediates (Sekler et al, 2004).

Experiments were undertaken in a customised stirred tank photoreactor to investigate the use of electrochemically assisted photocatalysis (EAP) using formic acid as a model pollutant under either UVA or UVB irradiation. It was found that EAP did not increase the rate of oxidation of formic acid where the dissolved O₂ concentration was greater than 20% under conditions of good mass transfer. The use of a UVB source as compared to a UVA source resulted in a significant increase in the rate of oxidation and increased apparent quantum yields (McMurray et al, 2005). The photocatalytic degradation of the herbicide atrazine was also compared under UVA and UVB irradiation. The maximum apparent quantum yield for the photocatalytic degradation was higher under UVB (0.59%) compared to UVA (0.34%) (McMurray et al, 2006).

Photoanodes were incorporated into a two compartment photoelectrochemical cell for the simultaneous photocatalytic oxidation of formic acid in the anode compartment and the electrochemical reduction of Cu²⁺ on a copper mesh counter electrode in the cathode compartment (Byrne et al, 2002). The anode and cathode compartments were separated by an anion exchange membrane. The difference between the conduction band potential and the reduction potential of the Cu²⁺ ions is the driving source for this “photogalvanic” cell. Cu metal was recovered with a high faradaic efficiency (95.5%) and formic acid was degraded. The initial incident photon to current conversion efficiency (IPCE) of the system (using two 9 W blacklight lamps) was 9.5%. This type of system could be used for the remediation and recovery of metals from plating waste streams under solar illumination.

More recent work has concentrated on the photocatalytic disinfection of microorganisms in real water using UVA illumination. This work is aimed at the development of photocatalytic systems for water disinfection in developing regions where access to clean drinking water is limited. Results show that the rate of UVA and UVA - photocatalytic disinfection of *E.coli* is reduced in real or natural water as compared to distilled water, however, the rate of photocatalytic disinfection is greater than that found with UVA alone in both cases. Work is ongoing to determine the salient parameters in real water which affect the rate of photocatalytic disinfection under UVA illumination and to design an optimal reactor for solar water disinfection, taking into account the synergistic effects of UV, heat and UV-photocatalysis.

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Application of nanofiltration for treatment of process and waste water

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Introduction

Being one of the most prominent new separation tools, membrane processes are finding their way in various applications for water treatment ranging from particle removal to desalination. Nanofiltration is one of the most recently developed processes, aiming at a compromise between a high product quality and a low energy consumption. Originally intended as ‘low pressure reverse osmosis’, it soon became clear that nanofiltration has a much larger potential as a separation or purification tool. The nanoscale of the ‘pores’ of the membrane is in the same order of magnitude than many relevant organic contaminants found in water: natural organic matter, pesticides, natural and synthetic hormones, pharmaceuticals, chemicals. Using nanofiltration – a filtration on nanoscale – these compounds can be removed [1]. In addition, multivalent ions can be efficiently removed due to interactions with charged functional groups on the membrane.

Research Challenges & Results

Insight in nanoscaled structures

The structure of nanofiltration membranes, and its relation with transport properties within the membrane, are not yet understood. This is due to the fact that nanofiltration membranes are on the interface between dense and microporous materials; depending on the specific membrane type, transport phenomena may be similar to either diffusion in a dense matrix or sieving on nanoscale. This allows using (some) nanofiltration membranes in other separation processes as ‘universal’ membranes [2]. An example of such a structure is shown in Figure 1 for a PDMS membrane. From this figure it can be understood that ‘pores’ should be seen as free volume inside a polymeric structure, rather than well-defined, visible holes.

However, description, modelling and simulation of transport through nanoscale pores is still missing, which necessitates a trial-and-error approach for application of nanofiltration even in aqueous applications. Ongoing research in modelling and simulation will be presented.

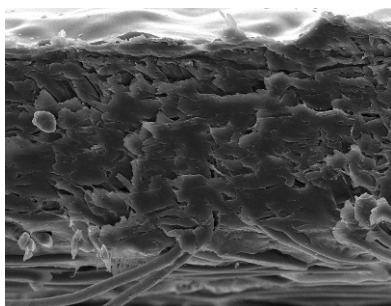


Figure 1: Top layer of a PDMS membrane with nanopores designed for separation of organic solutes

Membrane fouling and energy requirements

Further improvements are to be expected when membrane fouling can be avoided by the use of hydrophilic, low-fouling membranes. This requires the development of improved membrane materials with a better resistance against fouling, by the addition of hydrophilic functional groups into polymeric membrane structures, or the control of membrane charge. This might possibly even allow operating in less energy demanding conditions (dead-end filtration) when fluxes are sufficiently high and stable.

Results will be shown for a modification method based on grafting; further possibilities will be discussed in relation to fouling modelling and control.

Improved separation

A limitation of membrane technology is that they allow to separate a solute from water, but a separation between solutes A and B is (usually) impossible because either the recovery of A or B is too low, or the product purity is too low. In water treatment, the separation challenge is generally to remove the organic fraction – including micropollutants – completely and leave the ionic composition unchanged (apart from softening). In this case, using a conventional membrane setup, either the removal of organics is not complete, or the ions are removed as well.

It will be shown how a good separation can be carried out on nanoscale by applying a membrane design based on a cascade approach, where several separation stages are used with recycle of the permeate or retentate fraction to, e.g., the previous stage [3].

Conclusions

The nanoscale is highly challenging for pressure driven membrane processes because this is the target range for impurities in water. Nanofiltration membranes, operating in this range, are being further developed in terms of structure and fouling resistance. Membrane cascades allow a good separation of solutes from one another.

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Environmental Nanotechnology (CIChem)

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Since 1995 CIChem research Group has performed project in the field of project organized problem based learning and research governed by participants.

The system is organized so that teaching by staff, learning of students, fundamental research and cooperation with companies are an integrated unit.

A project area is determined by head of research group. Students and companies participate if they have a particular interest in the project area in question. After having performed a couple of semester projects in environmental chemistry for a bachelor degree some of the students continue and study to obtain a master degree in chemical engineering with the special profile "Environmental Nanotechnology". General curriculum in chemical engineering is assured by courses and semester bindings with progression and fundamental ideas and coherences in the projects.

An important part of subjects studied belong to a series of advanced oxidative and reductive processes for water remediation and purification. Some of these processes involve oxides either as catalysts or as a product of the purification process. The detailed study of these compounds is based on colloid and interface chemistry. The clusters and particles involved have sizes in the range of nm.

The analytical tools for the investigations involve instrumental chemical and physical analysis and the physics behind them. As a part of the investigations storage ring facilities are involved.

Cases:

1. Iron precipitating bacteria for purification of ground water into drinking water

Investigations involve models of the iron precipitating bacteria and their metabolism. However, the study of co-precipitation of organic and inorganic pollutants by help of iron precipitating bacteria is a very important subject for a lot of purification problems. Microscopy methods and among these X-ray microscopy (XRM) have been used to elucidate the activity of iron precipitating bacteria.

2. The production and identity of aluminium polymers for precipitating of pollutants in waste water treatment and the production of drinking water.

Investigation of the production process of aluminium polymers involved several methods from simple electrochemical methods to advanced ESI- MS and NMR methods before a total model could be described. A simple but concentrated aluminium chloride solution was prepared by increased temperature and pressure. However, a small amount of oligomers was produced as well. By dilution and therefore increasing of pH real polyaluminium chloride compounds showed up. Probably the oligomers acted as precursors for the discovered Al-13 compound.

3. Permeable reactive barriers for ground water remediation processes.

Micro sized grains of iron particles were used to reduce chlorinated ethenes in a polluted groundwater. In big laboratory reactors and a pilot plant in the field mixtures

of iron and other metallic compounds within a sand matrix were investigated for the purpose. Also plant materials and sludge from paper production were involved. Pure iron-sand matrices clogged and became almost impenetrable after some time. Amorphous iron oxides were produced and glued particles together. Plant materials partly decreased pH and partly kept the system penetrable.

4. Photocatalytic degradation of pollutants in water and air.

Methods to produce photo catalysts of semiconductor material, principally TiO₂ were investigated. Primary particle size, aggregates particle size distribution, crystallinity and crystalline phase were the parameters in focus. The reaction conditions were partly 100-200 bar, 100 °C super critical carbondioxide. Identification of clusters in sol-gel processes was involved. Finally, produced powders were compared with commercial powders for photocatalytic activity. Coating and the production of self cleaning surfaces has our present focus.

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Water Purification with Nano-Crystalline Diamond as an Environmental Friendly Process

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Diamond is up to about 570°C chemically the most stable material known today. Diamond is also the best thermal conductor whereas ordinary it is also one of the best electrical insulator. Hence, if diamond contains boron it gets an electrical conductor where the conductivity is directly related to the boron content. The idea of using diamond as an electrode material in electrochemistry has been reported for the first time by (Pleskov, 1987). Since then an increasing number of electrochemists have invested diamond electrodes e.g. Comninellis (2000) reported that Boron Doped Diamond (BDD) has outstanding production capacity of very strong chemical oxidizing agents such as hydroxyl radicals. BDD has the largest electrochemical window of all known electrode materials and are considered today as a really new and very versatile electrode material. Diamond-electrodes can be used as anode as cathode as well as bipolar electrodes as reported in Europe-Patent (2000).

BDD can be grown artificially by Chemical Vapor Deposition (CVD) methods with in-situ boron doping on silicon. Hence, it is impossible to grow dense and compact diamond-films without a model on substrates others than diamond. The C-C bond length in the sp^3 - carbon structure is only 1.54 Å, so there is no other material with a higher molar density than diamond. Therefore, silicon substrates must be seeded before diamond growing by CVD-methods. The most common and known seeding method is scratching or polishing of convenient surfaces like silicon with diamond powder. The finer the diamond powder the higher is the resulting seeding density. Relatively low densities of up to 10^7 seeds/cm² can be reached. This method is also strongly limits to flat geometrical forms. A more convenient and today standard method for seeding is the ultrasonic surface treatment in nano-crystalline diamond slurries of either aqueous or alcoholic colloidal solutions. The nano-diamond crystal shape in these solutions is in the order of 2 to 10 nm. The nano-diamond crystallites can be obtained either by the explosion method (mostly) or by milling processes of diamond powders of bigger shapes. The seeding density by this method can reach 10^9 to 10^{12} seeds/cm². This is near to the theoretical density of about 10^{14} seeds/cm². Due to the so diamond seeded silicon substrate the resulting diamond or BDD coating is typically polycrystalline.

The CVD method allows today production of BDD-electrodes of up to half square meters in one batch. Depending the desired final electrochemical application the BDD coating thickness is between 1 to 5 µm. The crystal-size of the BDD coatings depends of different factors. Essential are the seeding density and the coating thickness but also the growing parameters. Normally diamond growth in a columnar structure, therefore the crystal-size is increasing with growing time or coating thickness. By choosing specific growth conditions the crystal-size of diamond coatings can be managed in a wide range. There are the so-called ultra-nano-crystalline diamond (UNCD) with a crystal-size of 5 to 10 nm, the nano-crystalline diamond (NCD) with a crystal-size typically less then 100 nm and the sub-micron crystalline coatings with a crystal-size of 100 to 800 nm. Finally, more ordered diamond crystal coating reaches crystal-sizes of up to several tenth of µm. Polycrystalline BDD coatings are self-

limiting in crystal-size in the order of 1 μm due to the presence of boron. Boron content relates to secondary nucleation and twinning. The electrical conducting of non-boron doped NCD coatings is related to a certain amount of graphitic sp^2 -carbon. Their uses as electrodes in electrochemical applications are strongly limited due to severe corrosion.

Due to the limited dimension of electrode surface specific well adapted and modular electrochemical cell system have been developed so called DiaCell[®]. The DiaCell[®]-Systems are today installed for water disinfection and conservation e.g. in spas and swimming pools as well as for electro-oxidation of industrial wastewater, hazardous effluents and landfill leachates. It is effectively possible to incinerate electrochemically all dissolved even very refractory aromatics, aliphatics and heteroorganics, like phosphonates, sulfonates, pesticides, EDTA, as well as some inorganic components, like cyanides, ammonia etc.

Only very few articles were published on disinfection and COD reduction (reaching biodegradability) of water as main application of BDD/Si-electrodes. For disinfection purpose, mainly for typical water qualities (pool, ballast, irrigation (gray-) and potable water) were compared with the traditional sodium hypochlorite (NaOCl) dosage containing various spiked microbiological populations (i.e. Legionella, Bacteria H40, Adenovirus, E. coli, Vibrio fischerii, Pyrocystis fusiformis protozoan etc.). The activity of the microorganisms was analyzed by counting the colony forming units and by bioluminescence measurements in case of *Vibrio fischerii* bacteria and *Pyrocystis fusiformis* protozoan.

It could be shown that for organics containing i.e. Benzene sulfonate, typical bactericide, it is important to achieve electrochemical COD reduction in the range of 10 to 15%, at an optimum peak of biological degradation. The actual efficiencies are in the range of 95 to 100% depending on COD concentration. Due to the electrochemical pretreatment step with a DiaCell[®] at an electrical charge of approx. 10Ah/L the biodegradability could be improved under laboratory conditions at 25°C from 0 (untreated solution) up to 4 g $\text{CO}_2/\text{d L}$ of waste water with electrochemical pretreatment. Biodegradability was determined by measuring the CO_2 content of the solution produced by multiple populations of bacteria.

In an industrial wastewater with a very high concentration of 50'000ppm COD biodegradability has been reached by selectively electrochemical incineration of the phenol content from up to 1000ppm to almost 0ppm.

Biodegradability could also be improved for tannery waste water with 16'000ppm COD and 4'000ppm of ammonia and N-containing organics with an energy requirement of approx. 0.35 kWh/L at 50 Ah/L of charge. All ammonia and N-containing organics are transformed by 1/3 to nitrate and 2/3 direct to N_2 -gas.

The electrochemical incineration of refractory and biocide organics with diamond electrodes is a highly efficient electrochemical advanced oxidation process (AOP) working without any addition of chemicals with no residues as well as independent of colors and/or turbidity.

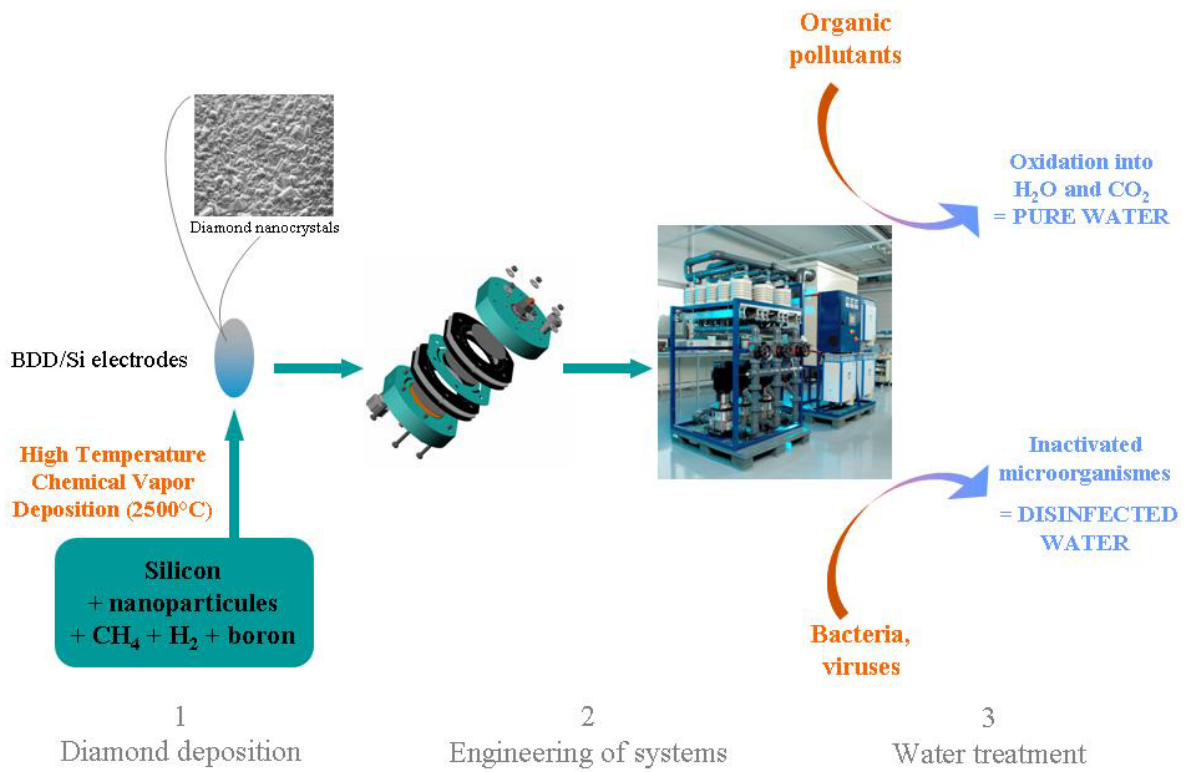
There is still a deficiency of the state of the art water treatment technologies on the market where the diamond (BDD) water electrolysis could provide new and therefore environmental friendly solutions.

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DiaCell® in steps
 From nanocrystalline diamond films to complete water treatment systems



ESCAPE OF NANOPARTICLES DURING DIESEL PARTICULATE TRAP REGENERATION

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There is increasing concern about health effects of particulate matter, PM, emitted from Diesel engines for automotive applications. PM is suspected of causing detrimental acute and chronic damage to the pulmonary and the cardiovascular system. Based on scientific proofs, air pollution legislations of several countries classifies Diesel soot as carcinogenic.

Moreover, several health effects are associated with the ultra-fine particles with diameters below 100 nm [1]. Recent research shows that these particles can penetrate the cell membranes, enter the blood and even reach the brain [2]. Besides, some investigations indicate that particles can induce inheritable mutations [3].

The most promising particulate abatement technology is based on wall-flow catalytic traps, periodically regenerated by a peculiar use of last generation Common-Rail Diesel engines (i.e. post injection of HCs burned out by a specific catalytic converter so as to heat up the downstream trap up to ignition of the trapped soot). The role of the catalyst is to enhance the combustion rate of the soot collected on the filter by reducing its ignition temperature [4].

The particle trap efficiency is very high also with the ultra-fine particles and does not significantly vary with particle size. However, during the regeneration phase itself secondary particulate emissions were clearly noticed at our labs (Fig. 1). This paper aims at elucidating this unexpected phenomenon. For this purpose, a trap based on a novel catalyst, CoCr_2O_4 , synthesised and deposited on a wall-flow monolith via *in situ combustion synthesis*, underwent the phases of a typical bench test performance analysis described in [4].

The distribution of the ultra-fine particles has been measured via a Scanning Mobility Particle Sizer (SMPS by TSI Inc.). This analyser can measure a wide range of diameters (3 nm – 1000 nm). Specific tests for both a catalytic and non catalytic wall-flow trap gave us the evidence of ultra-fine particles formation only during the regeneration of the catalytic trap. Particularly, in Fig.1 a bi-modal distribution of the particles downstream the catalytic trap during the regeneration can be noticed. Several

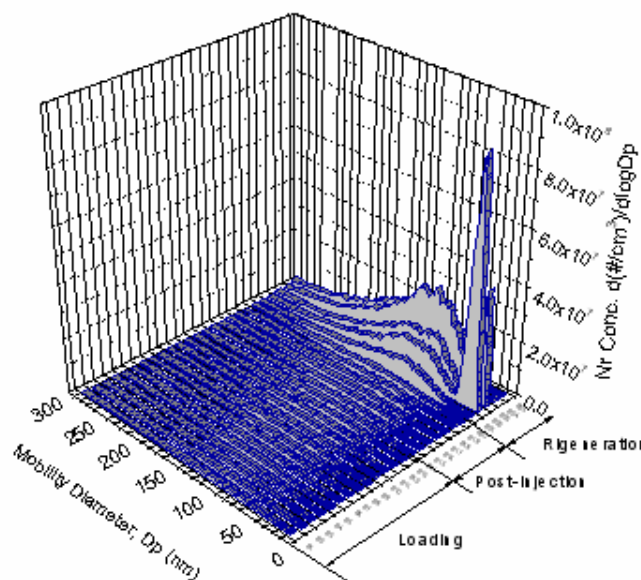


Fig. 1. Concentration downstream a SiC wall-flow trap catalyzed with CoCr_2O_4 .

evidences of the chemical and physical nature of the nanoparticles emitted were derived by X-ray and surface area analysis. The SMPS capability of extracting from a heterogeneous stream a narrow range of particles was extremely useful to study the phenomena in depth. There are suggestions in the open literature about the non-carbonaceous nature of the ultra fine particles emitted by the diesel engine [5]. The most narrow particles were indeed found to be characterised by significant levels of sulphates, as a likely consequence of the oxidative properties of the soot oxidation catalysts. As for the larger secondary particles emitted they seem to be mostly composed of soot particles. Their escape seems to be primarily caused by the comparatively faster regeneration kinetics enabled by the catalyst as opposed to the non-catalytic case. In the former case, the fast release of heat and gases, as a consequence of the catalysed soot combustion process, brings about the disintegration of some soot agglomerates into smaller particles that can eventually find their way throughout the filter. This secondary particle emissions partly counterbalances the positive effect of the presence of a soot combustion catalyst in terms of regeneration effectiveness and time reduction.

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Studies on photocatalysis of priority indoor pollutants with titanium dioxide based building materials (paints)

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Heterogeneous photocatalysis, also known as photocatalytic oxidation or PCO, is an emerging advanced oxidizing technology that uses solar energy (UV light) for reduction of environmental pollutants. Traditionally, photocatalytic studies have dealt with catalysts preparation and the understanding of the photodegradation mechanism using for that purpose high concentration of pollutants that rarely are found in the real environment. The ability of Titanium dioxide (TiO₂) containing materials to degrade air pollutants, especially Nitrogen Oxide (NO), by a photocatalytic mechanism has been already demonstrated both at laboratory and at real scale. Preliminary evidence from experiments carried out in the frame of PICADA¹ (an industry based European research project) indicated, that TiO₂ containing construction materials and paints efficiently destroy the ozone precursors NO and NO₂ up to 80% and 30%, respectively². These materials when used as outer layer on buildings located in highly traffic roads have shown the efficiency to degrade pollutants originated from the traffic exhausts³. This fact has focused the attention of current research on the determination of the efficiency of photocatalytic materials to degrade pollutants in real world settings of temperature, humidity, illumination and pollutant concentration level.

An interesting field of research is to address the potential contribution of the photocatalytic technology application by the construction industry to indoor air quality challenges. In this context, the use of innovative building materials and paints (containing nanosized TiO₂ particles) and the development of visible light catalyst are two fields of research very active.

The scope of the present study is to assess the photocatalytic efficiency of nanoparticles TiO₂ based building materials for reducing inorganic and organic compounds frequently accumulated in indoor environments. In particular to determine the efficiency in atmospheres containing NO and toluene individually or in mixtures at levels found in indoor environments. The materials (ca 4m²) were tested in a high volume environmental chamber (30 m³) under real world setting conditions of temperature humidity, and illumination.

Samples of painted glass panels (4m²) were used in the experiments. Samples were conditioned inside the chamber for 24h under ventilation at 23°C and 50% of relative humidity (RH). Depolluting properties of the TiO₂ containing paint were evaluated by performing experiments, with a known concentration of pollutant, at different environmental conditions of temperature, RH (50%, 20%) and UV intensity (1.25 W/m², 0.588 W/m², 0.296 W/m²).

Atmospheres containing NO at 220 ppb and toluene 120 ppb were created separately in the Indoortron to study the breakdown of the individual compounds. Atmospheres

with simultaneous presence of NO and toluene were created for studies of degradation of the compounds when present in mixtures.

Titanium dioxide based paints demonstrate a good depolluting efficiency both for NO and toluene with maximum pollutant removal of 95% and 32% respectively for the individual compounds. Degradation of NO was slightly influenced by variation of environmental parameters while the efficiency to degrade toluene photocatalytically was more sensitive to environmental conditions, especially to humidity levels (toluene removal increased from 3% at 50% RH to 32% at 20% RH).

The photocatalytic efficiency of the TiO₂ containing paints for the individual compounds was also evaluated in atmospheres containing pollutant mixtures. The photocatalytic degradation of NO was invariable while higher efficiency on toluene degradation was observed when present simultaneously with NO.

As conclusion of the results described here, it can be stated that nanosized TiO₂ based materials have shown their efficiency to reduce the level of pollutants by photocatalysis. The degradation of NO accounts for 98% while the efficiency concerning organic compounds is lower (ca 30% for toluene at 20% RH). It has been observed an enhancement of toluene degradation (up to 65%) when the test was performed in an atmosphere containing a mixture of both pollutants. More studies addressing the efficiency of photocatalytic materials on the degradation of chemical mixtures simulating real environments including determination of by-products are needed in order to clarify the applicability of the technology indoors.

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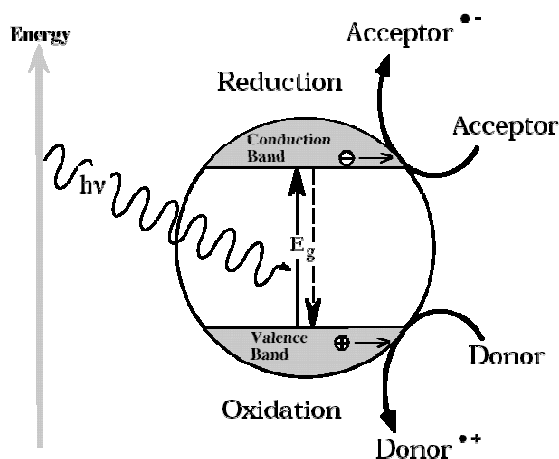
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NANOPARTICLES FOR PHOTOCATALYSIS: CLEANING POLLUTED WATER, AIR AND SURFACES WITH SUNLIGHT

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Photocatalysis using semiconductor nanoparticles (see figure below) has found increasing interest to solve global pollution problems. Compared to other semiconductor photocatalysts, TiO₂ has so far been shown to be the most promising material used for both fundamental research and practical applications because it is highly photoreactive, cheap, non-toxic, chemically and biologically inert, and photostable. The artificial generation of photons required for the detoxification of polluted water is the most important source of costs during the operation of photocatalytic water or air treatment plants. This suggests using the sun as an economically and ecologically sensible light source. Thus Solar Photocatalysis has become an important issue of research and development during the past 20 years. With a typical UV-flux near the surface of the earth of 20 to 30 Wm⁻² the sun puts 0.2 to 0.3 mol photons m⁻²h⁻¹ in the 300 to 400 nm range at the process disposal. Principally, these photons are suitable for destroying pollutants present in water, air, or on photocatalytically coated surfaces. The present lecture will present an overview of the authors' laboratory activities in Solar Photocatalysis.

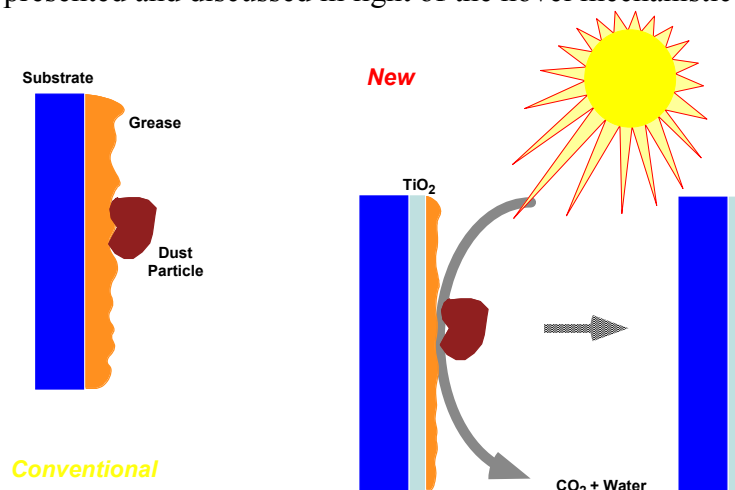


The properties and requirements for efficient photocatalyst materials will be discussed. A few representative model compounds have been selected to illustrate the major reaction pathways in photocatalytic degradation processes. Crucial reaction parameters such as pH, temperature, solute concentration and light intensity, are given together with current theoretical models to explain their effects on the overall process efficiency.

In recent years several reactors for the solar photocatalytic water treatment have been developed and tested. The four most frequently used reactor concepts are presented

and several examples for the treatment of real wastewater are shown together with some initial economic considerations. In particular, the Thin Film Fixed Bed Reactor (TFFBR), the Double Skin Sheet Reactor (DSSR), the Compound Parabolic Concentrating Reactor (CPCR), and the Aerated Cascade Photoreactor (ACP) will be described in detail. Pilot Plants employing these reactor concepts have meanwhile been built and tested by various research teams, hence, a brief overview concerning the first experiences with these installations will be given.

Clear and adherent films of titania are being used in optical coatings, therefore, it is possible to use photocatalytically active films as self-cleaning windows and automotive windshields (see figure below). Attempts to improve the performance of TiO_2 as a photocatalyst under UV illumination and to extend its light absorption and conversion capacity towards the visible portion of the solar spectrum have primarily involved the effect of metal ion doping which aimed mainly to increase the lifetime of charge carriers. Therefore, the optical properties of Fe^{3+} -doped TiO_2 films were investigated and their photocatalytic activities were determined. On the other hand, doping TiO_2 with metal ions with radii larger than Ti^{4+} should primarily result in modifications of its surface properties. Therefore, the effect of Y^{3+} (0.93\AA) doping on the photocatalytic reactivity of these thin films was also studied. Results of these studies will be presented and discussed in light of the novel mechanistic models.



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Analysis of Radioactive Solutions by a Microsystem

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The challenges in nuclear safeguards have significantly changed over the last decades. In the early days after implementation of safeguards agreements measurements of nuclear material were the backbone of the verification measures. These measurements included also sample analyses under destructive assay (DA). Originally electrochemical or physico-chemical measurement techniques such as titration, coulometry or mass spectrometry were the work horses for sample analysis.

On the one side the measurement techniques have evolved and on the other side also the safeguards requirements have changed. Initially DA methods were applied because their uncertainties were far superior to those associated with radiometric techniques. However, chemical methods require sample preparation and pre-treatment which is very time-consuming and generating waste. Over time, the waste costs have grown exponentially, while on the other side the performance of the radiometric techniques has steadily increased, leaving less room for DA of samples.

The increasing number of samples subjected to accountancy and verification measurements led to a balanced use of chemical, physico-chemical and radiometric methods in today's analytical laboratories. The introduction of strengthened safeguards, the implementation of the additional protocol and the nuclear material intercepted from illicit trafficking led to a more investigative character of analytical measurements. Consequently, new sample types that can more easily be applied also in the field for environmental sampling or for nuclear forensics, are under consideration.

One example is the miniaturization of the sample for analyzing the radioactive solution of a reprocessing plant, which is needed for the characterization and quantification of the nuclear material in the process. Even with on-site laboratories, some delay for the sample analysis is unavoidable mainly due to extensive sample preparation. A dilution factor of up to 20000 has to be applied to enable treatment for analysis in a glove box.

This paper presents the feasibility study of a “lab on a microchip” to analyse such highly radioactive solutions. The application of a micro-electro-mechanical system (MEMS) to analyse microquantities of a radioactive solution would lead to a much more direct and therefore faster and simpler treatment because of the reduced radiation. The analytical analysis would become less complex with possible transportable devices and the quantity of radioactive would decrease.

A specific MEMS for analyzing radioactive solutions of an input solution (with concentrations varying from 20 till 250 g/l) has been designed with three microchannels of 300 μm diameter and 18mm length, as shown in Fig. 1. One channel contains the reference solution with Neodymium, the channel in the centre is the blank and the third channel contains the sample. The concentration of the solution is

determined by the photospectra of the light transmitted along the channel axis and absorbed at nuclide-specific wavelengths.

The dose reduction by volume size reduction has been determined by Monte Carlo simulations. If the volume of a typical input solution sample is reduced with a factor 6300 (for the proposed MEMS design) a dose-reduction of 6000 is achieved. The dose reduction is almost proportional with the size reduction for the different types of fuel (UO₂ and MOX) and for a burn-up varying from 36000 MWd/t to 64800 MWd/t, which confirms that the change in self-shielding for the low energy γ -rays is very small.

High-density polyethylene has been selected for the substrate and cover of the MEMS. In the cover electrode pairs are embedded for imposing an alternating potential. With a total external field of 356V/18mm electrophoresis will suck the ionic solution in a peristaltic way into the microchannel, as demonstrated with electrohydrodynamic simulations.

Further micro-fluidic simulations have shown that the flow is after 150 μ m fully developed and no death zones could be indicated, which justifies the assumption that the average over the cross-section is representative for the entire solution. The laminar flow has a typical Poiseuille profile that is shifted down because of slip conditions, which model the electric double layer.

Finally thermo-fluiddynamic evaluation of the MEMS with the decay heat source of lower than 1mW indicated that the temperature variation over the microchannel is below 0.5°C. Therefore no significant thermal stresses and deformation are present, so that no Peltier cooling element is necessary.

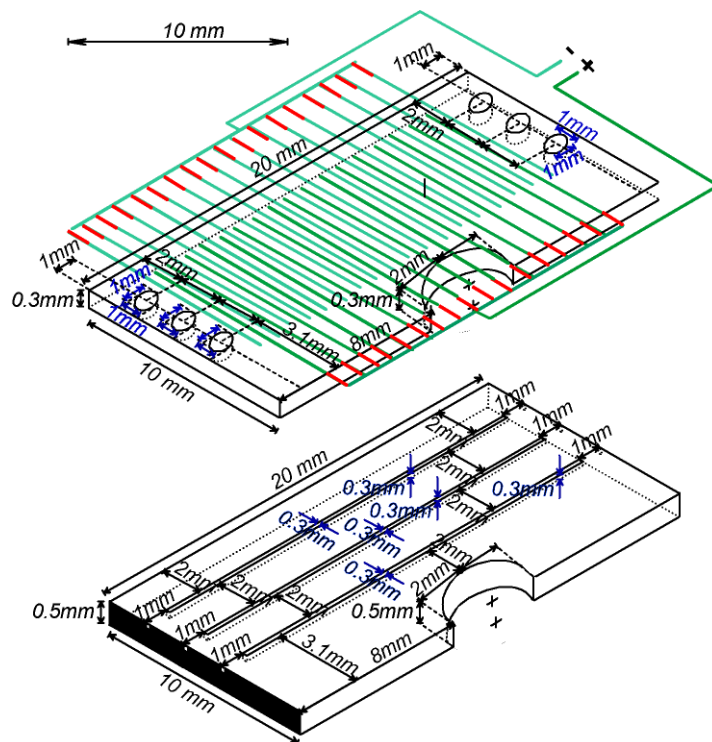


Fig. 1: MEMS design with 3 microchannels for densitometric and spectrophotometric analysis of radioactive solutions. The green grid represents the pairs of electrodes (composed of one left and the closest subsequent electrode right), through which a voltage over each pair is imposed in alternating mode by subsequent activation of one left and one right red connection.

Nanotechnology and the Environment: Cleaner water and CO₂ sequestration

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Sustainable development, both in Europe and for emerging industrial nations, requires better ways to insure safe drinking water, effective waste disposal and efficient CO₂ removal. The development of instruments that “see” directly at the nanometer scale has sparked a techno-logical revolution that makes it possible to measure, monitor and control trace concentrations of substances. These new sensors are what most people think of when “nanotechnology” and “environment” appear in the same sentence and thanks to them, toxic substances can now be detected at much lower levels. But there are two other important environmental applications for nanotechnology. First, nanoscale resolution instruments can also be used to study natural materials, i.e. soil and sediment particles, to define their fundamental properties. Second, this new knowledge can be used to develop nanoparticles and thin coatings on other minerals for use in improving water and air quality. This talk focuses on these two applications of nanotechnology. Once we understand the secrets of solid/fluid reactivity, we can use nature’s own tricks to trap unwanted compounds, thus protecting the environment.

The best way to protect groundwater aquifers and to minimise leakage from waste, is to promote reactions that incorporate contaminants into bulk phases, immobilising them. Long-term removal of CO₂ requires that it react to form a stable solid phase. Pumping CO₂ into depleted hydrocarbon reservoirs, or using it to decrease oil viscosity for enhancing recovery, are not secure, long-term sinks. Recovered oil gives back its CO₂; gas in reservoirs is released if the cap rock fractures. In the NanoGeoScience group, we are working on ways to fix contaminants in or on minerals such as carbonates and Fe-oxides. We focus on these because they are common in nature, they form nanoparticles with high surface area, they precipitate rapidly and their atomic structures can accommodate a spectrum of trace components. We apply nano-techniques because they allow us to see small changes in morphology, composition and structure in minutes or hours, which with traditional methods would be visible only after a few to millions of years. We have many ongoing projects; here are three examples:

Nickel contamination in drinking water

Nickel enters ground water from industrial sites, leakage of waste and sometimes naturally, such as when trace quantities are released from weathering pyrite (FeS₂). Even at 10’s of ppb levels, Ni causes painful skin allergies, so contaminated wells must be treated or shut down. This project’s goal is to optimise water production to minimise nickel concentration. Calcite (CaCO₃) is known to accommodate considerable divalent substitution in its crystal structure. Macroscopic studies show that Ni is rapidly adsorbed from solution by calcite and growth experiments demonstrate that Ni is incorporated as calcite precipitates. Nano-scale observations complement these results, showing that Ni ions substitute for Ca, and that even under conditions where calcite is dissolving, Ni is adsorbed. On dry samples, surface Ni is incorporated into the bulk by solid-state diffusion, proving that in solution, supersaturation is not required for Ni to move into the solid from surface sites. These results prompted us to recommend new water pumping strategies for municipal

supplies in Roskilde Amt (county) in Denmark. We advised slower pumping so Ni-bearing water could be drawn through small pores in chalk aquifers, increasing contact with natural, calcite nanoparticles, removing Ni.

Iron oxide as a sponge for contaminants

Phases containing both reduced- and oxidized iron react and hold a broad spectrum of contaminants. Green rust is an Fe(II),Fe(III) hydroxide that forms at pH>7 where oxidising species are rare and Fe(II) concentration is high. It is layered and forms in hexagonal platelets, ranging in diameter from a few 10's of nanometers to micrometers and in thickness, from a few molecular layers to 10's of nanometers. In the interlayer are anions, cations and water. Because of its redox active iron and high surface area, green rust is very reactive, transforming to an Fe(III)-phase such as goethite (α -FeOOH), lepidocrocite (γ -FeOOH) or magnetite (Fe(II),Fe(III)₂O₄). Cr(VI) is one of many heavy metals in fly ash formed in incinerator chimneys. It is easily leached by rain to groundwater. It is soluble and causes cancer, genetic mutation and deformation of fetuses but Cr(III) is not soluble and is an essential trace element in the body. Ultra high resolution investigations show that chromate (Cr(VI)O₄²⁻) replaces SO₄²⁻ in green rust interlayers, and as Fe(II) contributes electrons, it becomes Fe(III), Cr(VI) converts to Cr(III) and the green rust structure shifts slightly and goethite results. A very favourable aspect is that the Cr(III) is incorporated within the goethite structure, producing a Cr-bearing phase that is even less soluble than goethite alone. Thus nanoparticles of green rust could help decrease the risk of toxic element release from fly ash. There are a number of other projects currently underway in our Fe-oxide research group.

“Mineralisation” of CO₂

CO₂ sequestration research has moved very rapidly to the field-test stage, but little is known about what happens to particle surfaces and pore spaces of the host formation following contact with carbonic acid (H₂CO₃, formed from CO₂ and H₂O). We are working on ways to fix CO₂ by using carbonic acid to weather rocks and form carbonate-bearing minerals. A new project based in Iceland is linking three groups with complementary approaches. The expertise of Siggi Gislason and his group lies in field scale geochemistry and huge (~10 m) column experiments containing basalt sand and carbonic acid leaching. Eric Oelkers and his group from Toulouse are experts in determining kinetic and thermodynamic properties in flow-through reactors. Their focus is on coupled-reactions for dissolution of the basalt and the precipitation of calcium-, magnesium- and iron carbonates. The NanoGeo group will characterise host rock surfaces and define the best parameters for enhancing reaction while maintaining the ever-important pore space connection. Some of our current sub-projects are developing non-destructive methods for examining pore structure, in situ. High resolution X-ray tomography produces 3-d images inside a sample and shows how pores are modified as a function of time and type of treatment. Other experiments are investigating the molecular scale effects when calcite crystallises in the presence of other ions and organic components.

About the NanoGeoScience group

We are ~35 researchers and students. Our funding comes from Danish funding agencies, the European Commission, the Carlsberg Foundation and industry in Denmark and Sweden, chiefly Mærsk Olie og Gas AS and SKB (Svensk Kärnbränslehantering AB). Our instrument park is equipped with traditional bulk

solid and liquid analytical methods (X-ray diffraction, XRD; inductively-coupled plasma atomic emission spectroscopy, ICP-AES; atomic absorption spectroscopy, AAS, ion chromatography; surface area, tension, charge, etc. and others) as well as state-of-the-art facilities for characterisation of nanoparticles and surfaces (scanning probe microscopy, SPM; transmission electron microscopy TEM; X-ray, ultra-violet and Auger spectroscopies, XPS, UPS, AES; low energy electron diffraction, LEED; and others. In addition to studies on water and waste, other NanoGeoScience projects are investigating biomineralisation, to determine how organisms produce bones, teeth and shells and are searching for an environmentally friendly method to recover more oil from chalk reservoirs.

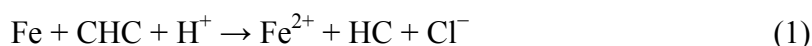
Complexity and risk in environmental remediation using nanoparticles

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This contribution is mostly about nanoparticles introduced into the soil. As discussed elsewhere (e.g. Banwart, this Workshop), the problem being tackled is one or more toxicants (xenobiotics, typically heavy metal ions, M^{n+} , or chlorinated hydrocarbons, CHC) released from some kind of industrial site, either abandoned or still in use; equally problematical are the organic nitro-compounds (e.g. TNT) released from military sites (e.g. Khatishashvili et al., 2004). The release constitutes a 'plume', a zone of elevated concentration of the toxicant below ground, that typically slowly migrates away from the source, potentially contaminating potable water sources.

Iron nanoparticles are able to react with CHC, decomposing them into relatively harmless substances, according to the (non-stoichiometrically written) reaction scheme (after Zhang, 2003)



where HC denotes a hydrocarbon. The strategy for heavy metals is to disperse into the plume iron oxide nanoparticles, on the surface of which the metal ions are strongly adsorbed. The nanoparticles can then be collected using a magnetic field, and thereby eliminated from the vulnerable ecosystem. These methods are as yet untested on a large-scale.

Current remediation practice based on reactive iron has been to sink a relatively shallow barrier into the soil in the presumed path of the plume, and filled the barrier with iron scrap. After the toxic plume has passed through the barrier, it can be removed from the vulnerable ecosystem. Iron filings offer a much higher surface area per unit mass than that of iron, but not only are they expensive, but also they are much harder to confine than scrap iron. Nanoparticle iron has an even higher surface area, and there is evidence that the particles are more reactive per unit area (due to their high curvature), and moreover they can be injected in suspension directly into the plume, where they should react with the toxicant according to equation 1.

The technology is rather new, and it has been difficult to find data with which the effectiveness of the remediation can be assessed. Nevertheless, one should note the following: the expense and environmental burden of preparing the nanoparticles; the fact that the iron can be oxidized by oxygen and/or water before it has had a chance to react with the CHC; that the nanoparticles may in practice be agglomerated or aggregated, vitiating the advantage of their small size.

When assessing the acceptability of nanoparticle remediation, it should be compared with rival technologies, of which bioremediation, using introduced microbial or natural technologies, is the main one. Monitoring remediation sites is already recognized as one of the key requirements for assessing the success or otherwise of bioremediation (Asakawa et al., 2006; Banwart, this Workshop), and monitoring is obviously required for nanoparticle remediation as well.

Like any technology, nanoparticle-based remediation strategies are potentially risky, because even though iron is already abundant in many soils, iron nanoparticles may share some of the potential toxicities that are beginning to be found for many other kinds of nanoparticles (Revell, 2006). Very little is known at present about the longer-

term effects of nanoparticles on the soil ecosystem, including such aspects as its diversity, and this needs more investigation.

These risks must be set against the human life extension that is presumably the ultimate object of any nano remediation work. An appropriate way to quantify the acceptability or otherwise of the risks of any remediation strategy to calculate the Thomas J-value, defined as the annual cost of remediation divided by the maximum amount that may be spent before the life quality index falls (Thomas et al., 2006). At present, further research is required in order to reliably determine the data required to calculate the J-values.

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