

Emissions of engineered and unintentionally produced nanoparticles to the soil an exposure assessment for Switzerland

Master Thesis

Author(s):

Würth, Barbara

Publication date:

2007

Permanent link:

<https://doi.org/10.3929/ethz-a-005541618>

Rights / license:

[In Copyright - Non-Commercial Use Permitted](#)

Diploma thesis

**Emissions of
engineered and
unintentionally
produced
nanoparticles
to the soil**

**An exposure assessment
for Switzerland**

Author
Barbara Würth

Supervisor
PD Dr Bernd Nowack

ETH Zurich
Department of
Environmental Sciences

EMPA
Materials Science & Technology
Technology and Society Lab

October 2007

ETH

Eidgenössische Technische Hochschule Zürich
Swiss Federal Institute of Technology Zurich



Materials Science & Technology

Contact:

Barbara Würth

barbara.wuerth@hotmail.com

Cover picture:

Nanoparticles clumping up in water

John Fortner of Georgia Tech School of Civil and Environmental Engineering

Source:

DailyTech, http://images.dailytech.com/nimage/3644_large_nanowaste.jpg (October 2007).

Executive summary

Nanoparticles are already unintendedly produced in large amounts since years by e.g. combustion processes. Nowadays engineered nanoparticles are used or planned to be used in numerous technical fields due to their benefits resulting from small particle size. Despite their omnipresence, the application of nanoparticles is not regulated and risks are only insufficiently assessed. Addressing exposure of humans and the environment to engineered and unintentionally produced nanoparticles is important for preventing negative impacts.

In this diploma thesis the exposure of Swiss soils to engineered and unintentionally produced nanoparticles was assessed. Using substance flow analysis, the nanoparticle fluxes from applications and products to the soils were modelled considering the life cycle stages use, recycling and disposal for one year. Two scenarios were drawn, a realistic one with the most convincing values and a worst case scenario resulting in highest releases possible. Further, the current knowledge on nanoparticle behaviour in soils was reviewed.

Applications of engineered nanoparticles generating significant emissions to the soil were found in automotive equipment, coatings and sealing, soil remediation, biocides, and fertilizer. Among them, the amounts of carbon black released by tyres and nanosized silica used in coatings, sealing, tyres, and plant protection products lead to highest concentrations in soils. Free nanoparticles were identified to get emitted by additives for diesel particulate filter regeneration. Deposition of unintendedly produced nanoparticles near traffic lanes and in densely populated area were highest.

This study shows that current exposure of soils to nanoparticles is rather low but as nanotechnological applications are in a developing state in many product fields and nanoparticles are partially accumulated in soils, the potential for raising exposure levels exists. For a thorough exposure assessment further research is needed on nanoparticles behaviour in soils and uptake into plant material and into food chains.

Table of contents

1	Introduction.....	1
2	Methods.....	3
2.1	Literature and web review.....	3
2.2	Personal communications.....	3
2.3	Substance flow analysis	3
2.4	System boundary.....	4
2.5	Statistical analysis	4
3	Behaviour of nanoparticles in soils.....	5
4	Nanoparticles flows between soil and its environment	8
5	Model environment	9
5.1	General model assumptions	9
5.1.1	Emission distribution	9
5.1.2	Waste incineration plant.....	9
5.1.3	Landfill	10
5.2	Traffic model.....	10
5.2.1	Rolling stock	10
5.2.2	Road length and mileage	13
5.2.3	Fuel consumption.....	14
5.3	Coatings	15
6	Products and product categories	19
6.1	Biocides and plant protection products	19
6.1.1	Plant protection products	19
6.2	Fertilizers.....	22
6.3	Soil remediation.....	24
6.3.1	Organic compounds.....	25
6.3.2	Metals	29
6.3.3	Potential application of nanoparticles for soil remediation in Switzerland	29

- 6.4 Automotive equipment30
 - 6.4.1 Catalytic converters30
 - 6.4.2 Coated diesel particulate filters and fuel borne catalysts34
 - 6.4.3 Tyres.....41
 - 6.4.4 Automotive coatings, sealings and paints.....49
 - 6.4.5 Automotive light-weight construction53
- 6.5 Building materials and coatings55
 - 6.5.1 Coatings and sealings.....55
 - 6.5.2 Building materials.....60
- 6.6 Other fields leading to nanoparticles fluxes to the soil.....61
 - 6.6.1 Water and air61
 - 6.6.2 Foodstuff, textiles, cosmetics and sports goods61
 - 6.6.3 Sewage sludge, combustion, electronics, landfills, irrigation62
- 7 Discussion63
- 8 Bibliography.....67
- Annex 1: Derivation of mileage and road length77
- Annex 2: Fertilizer78
- Annex 3: Sealings81

Acknowledgments

I like to thank my supervisor PD Dr Bernd Nowack for his effort in coaching my diploma thesis. He let me a wide scope for choosing my subject in the broad field of nanotechnology exposure and risk assessment and also for finding my own way elaborating it. He always found time to answer my questions and to give helpful comments.

I also want to thank Claudia Som for her helpful inputs.

A diploma thesis in such a new scientific field is not practicable without many people of science, industry and government granting insight in their knowledge on their technological fields. Special thanks go to

R. Blessing, auto-schweiz
Hr. Christinger, Caprol
G. Diriwaechter, Syngenta
L. Fluri, BFS
J. Gottet, BAV
A. Hauser, BAFU
H. Jenk, BAFU

W. Koch, NanoSys GmbH
A. Mayer, TTM
Reifen Verband Schweiz
J. van Leeuwen, AkzoNobel
C. Reusser, BAFU
L. Rocher, Rhodia
A. Ulrich, EMPA

With this diploma thesis a long path of education is coming to an end for me which would not have been possible without encouragement and support of my family and especially of my parents. Therefore I want to thank them specially for all they did for me during this long period of time.

Last but not least I thank Marc Weiss for always having time to listen and discuss when needed.

List of abbreviations

CC	catalytic coating
CH	chlorinated hydrocarbons
CH	Switzerland
conc.	concentration
DPF	diesel particulate filter
FBC	fuel borne catalyst
n	nano-
NP	nanoparticle
nZVI	zero-valent iron nanoparticles
OH	operating hours
PAH	polycyclic aromatic hydrocarbons
PCB	polychlorinated biphenyls
PGE	platinum group element
PM	particulate matter
RS	realistic scenario
STP	sewage treatment plant
WIP	waste incineration plant
WS	worst case scenario
WW	world wide
WWI	Woodrow Wilson International Center for Scholars

Definitions

- Nanoparticles:

In dependence on Meili et al. (2007) nanoparticles are defined as solid particles with at least two dimensions between 1 and 100 nm.

- Engineered nanoparticles:

For engineered nanoparticles the definition of Meili et al. (2007) was adapted. Thus, engineered nanoparticles are purposefully manufactured solid particles with at least two dimensions between 1 and 100 nm (intentionally or unintentionally). Subsequently engineered nanoparticles are also called just nanoparticles.

- Unintentionally produced nanoparticles:

Nanoparticles are defined as unintentionally produced if these are produced in bulk in traditional industries. Subsequently unintentionally produced nanoparticles are also called just nanoparticles.

- Soil:

Soils are the upper layer of earth on land. To the top and the bottom of soils the boundaries are formed by the atmosphere (or vegetation) and solid or loose rock, at the sides they turn into other soils. Soils consist of minerals and of organic matter (definition of Scheffer & Schachtschabel, 2002).

For this thesis soils are defined as the most active upper layer (0.2 m) of soils.

1 Introduction

Great visions go along with the development of nanotechnology: providing potable water, solving the world hunger problem, inhibiting climate change and environmental pollution, medical applications, and environmental cleanup (Tratnyek & Johnson, 2006), to name a few.

Nanoparticles are naturally occurring on the whole world. But they can also be engineered and produced in a bottom up or a top down approach where nearly no limits are set to their application (Allianz & OECD). And today indeed, nanoparticles are used in most technical and scientific fields. The unique properties, which distinguish nanoscale from conventional bulk materials, are caused by their small size. A large surface area is the logical consequence providing an active substrate for physical, chemical, and biological reactions (Adams, Lyon & Alvarez, 2006a; Navrotsky, 2000).

Nanoparticles are released – intentionally or not – during manufacturing, use, disposal, recycling or accidents. They can accumulate in the environmental compartments such as soil, water and air, in food webs, and in human beings, too. Because of their small size, uptake of nanoparticles is simplified, and a risk for public health and ecosystems is not excludable (Adams et al., 2006a). The need for regulations of engineered and unintentionally produced nanoparticles before significant releases have occurred is therefore urgent (Gardiner et al., 1996), and extensive investigations of the impacts are needed.

For an accurate risk assessment both exposure and toxicity have to be considered (Lecoanet & Wiesner, 2004). To date research has focused mainly on nanoparticles toxicity (e.g., Borm & Donaldson, 2007; Brunner et al., 2006; Oberdörster et al., 2002) and less on exposure assessment, especially of ecosystems. But as nanoparticles are applied, their leakage is inevitable and first supporting evidence has shown the relevance of nanoparticle ecotoxicity (e.g., Adams et al., 2006a; Hund-Rinke & Simon, 2006; Oberdörster, 2004; Oberdörster, McClellan-Green & Haasch, 2006; Oberdorster et al., 2006). An early addressing of the exposure of the environment to engineered and unintentionally produced nanoparticles is important for protecting ecosystems from negative impacts and subserves even economy because uncertainties on risks may cause setbacks. Exposure assessment includes an analysis of the amount released, of the contact to organisms, mobility and persistency of the material in environmental compartments and organisms (Lecoanet & Wiesner, 2004).

In this thesis the exposure of soil to engineered and unintentionally produced nanoparticles was analysed. Precautionary protection is of outstanding relevance for soils as the central functions of soils often cannot get sustained or restored and accumulation of pollutants is expected to be higher in soils than in other environmental compartments.

The annual releases of engineered and some unintentionally produced nanoparticles during usage, recycling, and disposal of products to the environmental compartment soil were modelled for Switzerland. The study addresses a life cycle perspective view of emissions occurring of products and applications.

The questions answered in this diploma thesis are

(1) from which products relevant amounts of engineered or unintentionally produced nanoparticles are emitted to soils during use or disposal and recycling, respectively,

(2) what the emission pathways are,

(3) what the amount of nanoparticles emitted to soils is, and

(4) what is known on nanoparticles behaviour in soils.

The following working hypotheses are set up:

- Exposure of soil is highest to nanoparticles emitted unhindered to soils or in a free form.
- Most nanoparticles get transported to soils by air.
- Allocation of nanoparticles is mainly in the densely populated regions.
- Behaviour of nanoparticles in soils is mainly affected by their surface properties.

2 Methods

2.1 Literature and web review

Scientific literature was searched through in a broad general way and specifically by theme. The papers were provided by Bernd Nowack or searched on the Web of Knowledge. A few papers were found in the web by Google search. The references of helpful papers were scanned as well as the newer citing literature. Thereby mainly information was generated on current nanotechnological product and particle research and on general particle behaviour. About a thousand papers were considered. Because nanotechnology is a relatively new research field, scientific literature on the theme is rarely older than ten years.

For nanoparticles containing traded products the web was searched by Google. Thereby, product inventory sites were very useful¹. Further sources of information on applications of nanoparticles were reports of governmental and non-governmental organisations.

All interrogations were done between March and October 2007.

2.2 Personal communications

Because the literature and web review did not generate much technical and quantifying information on nanoparticles in products, experts from government, industry, and science were asked directly per e-mail or phone. Nearly hundred experts were contacted. The experts were identified from literature and web review and via recommendations.

It was set value on the circumstance that opinions were obtained from various experts but often none or only one helpful answer was achieved. The questions asked were arranged newly for each interview, depending on the gaps of knowledge.

2.3 Substance flow analysis

A substance flow analysis was made coming from product categories or subcategories. After a first qualitative analysis based on the results of the general literature and web review, the fluxes were quantified by specific data of amounts and percentages if ever possible of the year 2006. The reality was thereby modelled as precise as possible. A qualitative flow diagram was also drawn for the environmental compartment soil integrating all fluxes to and from the soil for Switzerland. Import

¹ A Nanotechnology Consumer Products Inventory, Woodrow Wilson International Center vor Scholars: <http://www.nanotechproject.org/44/consumer-nanotechnology>

Nano in Germany, VDI Technologiezentrum GmbH: <http://www.nanoingermany.com/smr/>

Nanotechnology Product Directory, Nanoshop.com: <http://www.nanoshop.com/>

and export fluxes of nanoparticulate emissions over the geographical system boundary were not considered.

Two scenarios were conducted, a realistic one where the qualitatively most likely values were inserted, and a worst case scenario with the values leading to highest emissions.

Lacking information was completed through analogy of similar materials or products or estimated if no other data were available. Estimations were declared.

For some soil concerning product fields quantitative investigation were not available. Thus, for several product categories it was not possible to calculate the substance flows. In this case an approach was used for flux quantification based on the percentage of nanoparticles containing products found in a web review. Further information on this method and its explanatory power are described in chapter 5.3.

Due to uncertainties in the field of nanotechnology and also in processes and statistical data not concerning nanotechnology the method had to be adapted to the individual case. Differences to the original method and assumptions are listed in the particular subchapter of the results.

2.4 System boundary

Geographically, the system boundary is defined as the border of Switzerland. This is because of the good data availability within Switzerland and the familiarity of the author with the system. Furthermore, a worldwide view of the problem would have implicated a rough estimate of the fluxes because of lack of time and the heterogeneity of the world regions as well as the lacking data.

It was aimed at a life cycle perspective. Therefore fluxes from different stages of product life were considered including use, recycling and disposal of products but without fabrication of nanoparticles, product fabrication and accidents.

The fluxes from the products to the environmental compartment soil were quantified. Direct and indirect pathways were calculated so that the amounts expected in soils were described as precise as possible. Fluxes away from the soil to other environmental compartments were not considered because of lacking data on nanoparticles behaviour in soils. All types of soils were included except sediments.

This work considered engineered and unintentionally produced nanoparticles released from products which were expected to be of major relevance for soil contamination.

2.5 Statistical analysis

No statistical analysis has been done because of the heterogeneity of the available data and the resulting diversity of methods used as well as because too much data were lacking and values had to be assumed.

3 Behaviour of nanoparticles in soils

The investigation of the behaviour of engineered nanoparticles in soils is at the beginning only. Natural colloids, oxides and viruses which have a similar size distribution to engineered nanoparticles have been investigated since many years (see Figure 3.1). Therefore the behaviour of engineered and natural nanoparticles could be compared. This is a rough simplification and not valid for nanoparticles with different surface properties. Because of the broad range of different nanoparticles, a generalization of their environmental behaviour is limited, too. Nanoparticles and colloids were categorised as highly mobile in the environment due to their small size (Lecoanet & Wiesner, 2004).

Unlike in water and air, mobility of particles in soils is limited due to soil structure. Point or linear sources of nanoparticles can therefore lead to point or linear contamination.

In the absence of soil solution, nanoparticles are transported similar to other materials by soil displacement like turbation processes or wind erosion, gravitational mass movement like landslides or soil creep, as well as diffusion in the gas phase.

Movement of particles in water is of greater importance especially for transportation through soil. In soil water colloids move in fractures, macropores between soil aggregates or in micropores through the aggregates. Nanoparticles are mainly transported with the flow stream lines. Rahe (1978, in McGechan & Lewis, 2002) observed a fast and relatively unrestricted transport of colloids in fractures and macropores and Kretzschmar et al. (1994) mentioned the possibility that macropores were the only pathways by which suspended matter can pass through the unsaturated zone, since such particles are efficiently retained by physical filtration processes when moving through the more tortuous soil matrix pores. Nanoparticles move isolated, aggregated, or sorbed onto other mobile particles. Of smaller microorganisms (viruses and bacteria) and chemical contaminants it is known that they are transported mainly by adsorption onto mobile colloidal clay particles or soil organic matter (McGechan, 2002).

Transport of microorganisms in soils is influenced by soil type, soil solution content, soil solution flow, intensity and type of rainfall, surface properties of microorganisms and presence of plant roots (Mawdsley et al., 1995). It is expected that similarly nanoparticles are affected. Due to func-

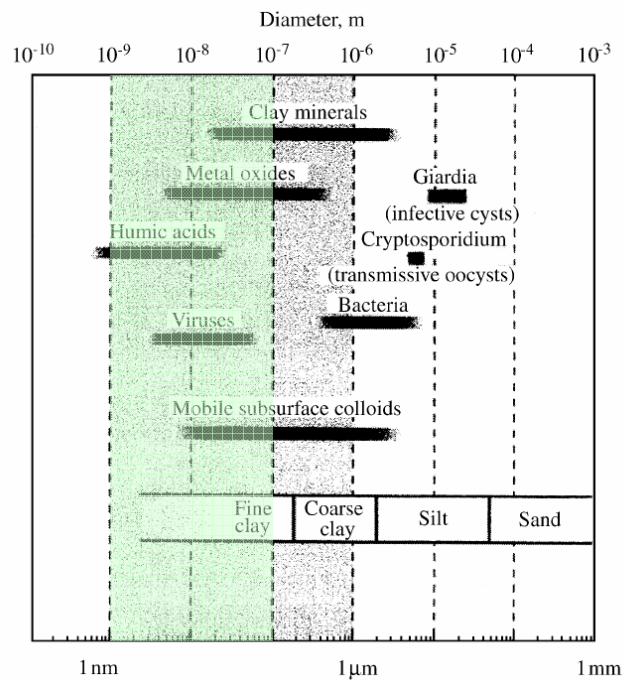


Figure 3.1: Size ranges of colloids and microorganisms. Nanoparticulate size range is coloured. (adapted from Kretzschmar et al., 1999, in McGechan & Lewis, 2002)

tionalization of nanomaterials required for industrial applications, their affinity for the aqueous phase may increase (Lecoanet & Wiesner, 2004) and with it their mobility which is expected to be higher than for bulk sized materials anyway. On the other hand O'Melia (1980) presented that (unmodified) particles of 1 μm are removed from the aqueous phase by minimal efficiency and submicron particles were effectively removed.

Colloids are retained by two main mechanisms which may reduce also the mobility of engineered nanoparticles: filtration and straining. Straining takes place when particles are of a similar size like pores, and thus they get physically trapped (McGechan, 2002). According to an analysis conducted by McGechan (2002), 90% of the water flow at field capacity is through pores $>19.1 \times 10^{-6}$ m in diameter and only small amounts of particles are retained by straining. Even less particles are strained at field capacity exceeding water flow, and only under dry conditions straining is of concern to smaller colloids (McGechan, 2002). It has to be considered that colloids can form aggregates, and thus they are larger.

Filtration takes place when particles are much smaller than soil pores and includes diffusion, interception and sedimentation (Kretzschmar et al., 1997; McGechan, 2002). Interception occurs when particles pass closer to the solid surface than one particle radius and are restrained by electrostatic forces (Lecoanet & Wiesner, 2004; McGechan, 2002). The underlying mechanism is a velocity gradient which leads the particles to the surface (O'Melia, 1980). Sedimentation due to gravitational forces is assumed to be very low for inhibition of nanoparticles movement, since they are of such a small size (Ives, 1975, in McGechan & Lewis, 2002). But vertical transport is depending on buoyant weight of particles (O'Melia, 1980) and particle classes may differ in sedimentation rates.

Of most importance for transporting particles smaller than 100 nm to solid surfaces is the Brownian diffusion, a diffusion caused by bombardment by surrounding water molecules undergoing Brownian motion (thermal reasons) (Lecoanet & Wiesner, 2004; McGechan, 2002; O'Melia, 1980). This movement leads to deposition on pore walls, vertical deposition on particles and collision of solvated particles (O'Melia, 1980). It is assumed that smaller particles are therefore not very mobile (Lecoanet & Wiesner, 2004).

Suspended particles can collide and therefore their movement is affected. Processes leading to collision of suspended particles are Brownian diffusion, fluid shear, and differential settling. Fluid shear emerges, if velocity differences or gradients occur (O'Melia, 1980).

Once transported to a surface, particles can get attached by sorption processes. These are influenced by forces such as the London van der Waals and double-layer forces, steric interactions, and hydration forces (Lecoanet & Wiesner, 2004). But based on an experiment conducted by Lecoanet & Wiesner (2004), not all of contacts of nanoparticles with surfaces cause particle attachment. Differences in the amount of attached particles were due to their functionalisation for the enhancement of their affinity for the aqueous phase (Lecoanet & Wiesner, 2004).

Further of concern for the fate of engineered nanoparticles may be redox transformations because they are very important for the degradation of organic compounds and because they are the basis of various precipitation and dissolution reactions that influence the sequestration and mobility of in-

organic metals (Lecoanet & Wiesner, 2004). By chemical or biological oxidation functionalities associated with mineral nanoparticles may be added, removed, or modified, and the adsorption of natural organic matter may alter their charge and stability in suspension (Lecoanet & Wiesner, 2004).

Not only nanoparticles are influenced by soils but they also may influence other components of soils, for example contaminants or pathogens (Lead & Wilkinson, 2006). As nanoparticles are at the small end of the size range of colloids, they have the highest specific surface area and so they can transport proportionally more pollutants (McGechan, 2002). And as transport by adsorption onto other particles is the most important mechanism for chemical pollutants like phosphorus and some pesticides (McGechan, 2002), a large amount of engineered nanoparticles in the soil could enhance contaminant transport through soil. For copper and zinc Karathanasis (1999) reported enhanced metal transport in soil with colloids and even more when smaller colloids were present.

A potential toxicity of engineered nanoparticles in soils is not sufficiently examined yet as well as uptake of nanoparticles by plants. Tong et al. (2007) examined recently the impact of fullerene (C₆₀) on a soil microbial community and observed little impact on processes and community of microorganisms.

4 Nanoparticles flows between soil and its environment

Nanoparticles come to the soil and leave it through various processes. Out of information on nanoparticles applications found in web and literature studies, a chart of nanoparticles fluxes to and from soil could be drawn (see Figure 4.1). Included are only fluxes within the system boundary.

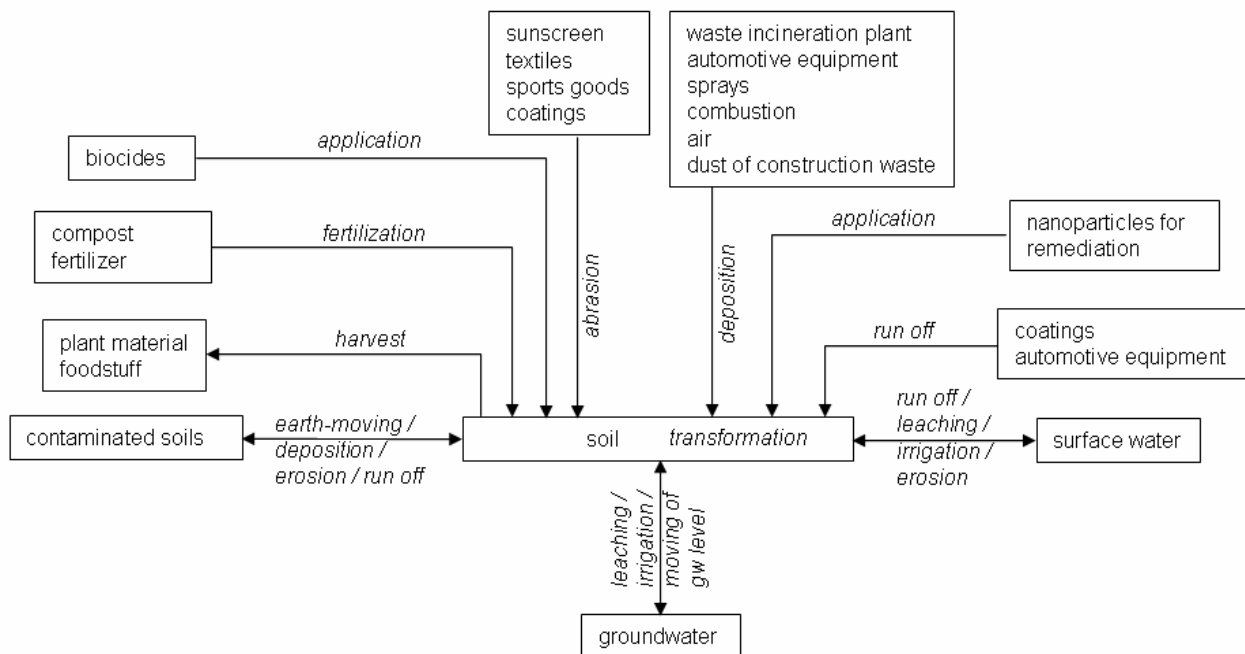


Figure 4.1: Ways of nanoparticles flow to and from the soil. gw = ground water

Nanoparticles released from products and applications can get directly or indirectly to the soil. To a direct soil contamination lead purposefully applied products like biocides, compost, fertilizer, and nanoparticles for remediation, and products which contaminate soil unintentionally like abraded material, some coating materials, contaminated soils, and water for irrigation. Product ingredients reaching soils indirectly on the other hand are released to other environmental compartments, e.g. air, water, or groundwater. Between the environmental compartments nanoparticles get exchanged.

Of major relevance for soil contamination are the directly applied products and nanoparticle applications with indirect flows to the soil, either because of mass production or high concentrations of nanoparticles in the products. These are especially automotive equipments, biocides, fertilizers, soil remediation, irrigation, coatings, and air deposition. Because the nanoparticulate flows to water and air are not yet investigated, it is not possible to model fluxes of these compartments to the soil, and irrigation and deposition are therefore only briefly discussed in chapter 6.6. Thus, the remaining application fields, biocides, fertilizers, remediation, coatings, and automotive equipment, are modelled in this thesis (chapter 6). Complexity and incomplete data basis asked for a simplified model environment which is derived in chapter 5.

5 Model environment

5.1 General model assumptions

5.1.1 Emission distribution

For the case that even distribution of emitted nanoparticles in Switzerland is supposed, calculations are based on Swiss area statistics (BFS, 2007g) (see Table 5.1). The relevant depth of land is 0.2 m, the uppermost soil layer. It is assumed that all particles released to the air are deposited on land or water surface.

Bulk particulate matter originating from traffic or point sources was assumed to be distributed near the sources. An even distribution was modelled within 50 m distance from the emitting object and to a soil depth of 0.2 m. The resulting area, soil volume, and soil mass for traffic lanes are shown in Table 5.2. Distribution of bulk particulate matter from point sources is shown in the concerning chapter.

For Swiss soils an average density of 1.3 kg/L was taken for conversion of mass per volume to mass per mass concentrations (Nowack, personal communication, 2007).

Table 5.1: Area, volume and fraction of Swiss water and land (BFS, 2007g).

	area	volume	mass	fraction
	[km ²]	[km ³]	[kg]	[%]
Switzerland	41,285	8.257		100
water	1,740	0.348		4.20
land	39,545	7.909	1.03*10 ¹³	95.80

Table 5.2: Area in which bulk particulate matter is distributed near roads.

	area [m ²]	volume [m ³]	mass [kg]
national roads	175,820,000	35,164,000	4.57*10 ¹⁰
cantonal roads	1,803,964,200	360,792,840	4.69*10 ¹¹
municipal roads	5,149,635,600	1,029,927,120	1.34*10 ¹²
total	7,129,419,800	1,425,883,960	1.85*10 ¹²

5.1.2 Waste incineration plant

In Switzerland waste is combusted in 28 waste incineration plants (WIP) (VB SA, 2007). Emissions are supposed to be less than 1% for nanoparticles (Müller, 2007, and citations). Thus, an even distribution on the Swiss area is assumed for the 1% of nanoparticles leaving WIPs.

Temperatures in WIPs are minimal 850 °C (Köhler et al., 2007), and therefore carbon black particles are expected to be completely incinerated in presence of oxygen.

5.1.3 Landfill

The slag of WIPs is landfilled and it is assumed that no emissions occur from landfills. This seems acceptable as landfills are sealed and the amounts of nanoparticles incinerated of the investigated product categories are small at present.

5.2 Traffic model

For modelling automotive nanoparticulate emissions, Swiss statistical data on traffic were taken as basis (BFE, 2006; BFS, 2006a; BFS, 2006b; BFS, 2007a; BFS, 2007c; BFS, 2007d; BFS, 2007e; BFS, 2007f) and completed with other written sources, personal communications or estimations.

5.2.1 Rolling stock

Swiss statistical data on vehicles were provided of stock, kind of fuel and diesel particulate filter (original equipment) for all onroad vehicles and of catalytic converters for passenger cars (BFS, 2007c; BFS, 2007d; BFS, 2007f). Other data on catalytic converters and diesel particulate filters are derived as described below. Data are shown in Table 5.3.

Catalytic converters

- The category transport vehicles consists of heavy duty transport vehicles and delivery vans. According to estimations of Blessing (2007, personal communication) over 99% of all heavy duty transport vehicles are operating with diesel fuel and it is therefore assumed that all of them are operating with diesel fuel. Delivery vans (number: 260,642 (BFS, 2007d)) were assembled of remaining diesel, petrol and other vehicles. The situation of delivery vans concerning catalytic converters is comparable to passenger cars (Blessing, 2007, personal communication), so 100% is assumed. Equipment of diesel vehicles with catalytic converters is assumed to have the same fraction as passenger cars.
- All passenger transportation vehicles with diesel particulate filter or operating with petrol fuel are expected to be equipped with catalytic converters. Diesel vehicles with catalytic converters are assumed to have the same fraction than passenger cars.
- Agricultural vehicles are not equipped with catalytic converters (Frehner, 2007, personal communication).
- Industrial vehicles are not equipped with catalytic converters (Blessing, 2007, personal communication).
- Motorcycles are equipped with catalytic converters since about two years, BMW motorcycles since 1998 (Lovato, 2007, personal communication). It is assumed that all other vehicles are without catalytic converters.
- No catalytic converters are installed in offroad vehicles (assumption).

Diesel particulate filters (DPF)

- Passenger cars are not expected to be retrofitted, because there is no guideline regulating DPFs.
- For passenger transportation vehicles it is assumed, according to Jenk (2007, personal communication), that two-thirds of all busses will be equipped with diesel particulate filters until the end of the year 2007.
- Similar to passenger cars, there is no guideline for heavy duty onroad vehicles regulating diesel particulate filter equipment. It is assumed that transportation vehicles are using Denox-catalysts for meeting the emission guidelines and no retrofitting with diesel particulate filters is done.
- According to Frehner (2007, personal communication), less than 1% of agricultural vehicles get retrofitted. 1% is assumed for modelling.
- For industrial vehicles 1% retrofitting is assumed.
- Retrofitting is not possible for motorcycles (Lovato, 2007, personal communication).
- About 10% of passenger ships are originally equipped or retrofitted with diesel particulate filters, transport ships are bound by guidelines to diesel particulate filter equipment and private boats are mostly not equipped (Gottet, 2007, personal communication). For latter 1% retrofitting is assumed.
- According to Suva (2006), 5,500 construction machines were retrofitted at the end of 2006.
- 10% of the military vehicles are assumed to be equipped with diesel particulate filters as new vehicles have to be equipped and the renewal rate is about 10% (Mayer, 2007).
- For forest vehicles 1% retrofitting and no original equipment is supposed, similar to agricultural vehicles.
- Power generation: 10% retrofitting is assumed.

The resulting amounts of utility vehicles agree with information received by Mayer (2007, personal communication) that 14,000 utility vehicles are originally equipped or retrofitted with diesel particulate filters in Switzerland.

Table 5.3: Swiss rolling stock. No information was received, when fields are blank.

	fuel				catalytic converter		diesel particulate filter (DPF)			
	stock	petrol	diesel	other	with catalytic converter	without cat. converter	originally with DPF	DPF retrofit	without DPF	thereof with DPF and catalytic converter
passenger cars	3,899,917	3,442,224	450,973	6,720	3,538,031	361,886	35,713	0	3,864,204	35,713
passenger transportation vehicles	46,445	13,601	32,634	210	18,635	27,810	685	2,300	43,460	685
transport vehicles	314,020	109,598	203,489	933	138,690	175,330	1,976	0	312,044	1,976
agricultural vehicles	185,450	20,590	164,041	819	0	185,450	3	1,640	183,807	0
industrial vehicles	53,437	7,843	43,174	2,420	0	53,437	12	432	52,993	12
motorcycles	608,648	605,177	1,274	2,197	98,832	509,816	0	0	608,648	0
offroad										
ships	99,166	0	60,007	39,159	0	0	796		98,370	
rail										
construction machines			35,000					5,500		0
military vehicles	3,000							300	2,700	0
forestry vehicles	14,000							140	13,860	0
power generation	3,000							300	2,700	0

5.2.2 Road length and mileage

Data on mileage of public transport, private traffic and goods traffic for the years 1990 to 2004/2005 and on road length for the years 1990 to 2005 were provided by Swiss statistics (BFS, 2006a; BFS, 2006b; BFS, 2007a). Mileage and road length were linearly extrapolated to the year 2006 (see annex 1). The total mileage was averaged to vehicles operating with petrol or diesel fuel, catalytic converters or diesel particulate filters if needed. An average utilisation was assumed for all roads. The mileage driven on national roads was calculated with equations 5-1 and 5-2.

$$\text{mileage}_{\text{national roads}} = \text{length}_{\text{national roads}} \cdot \text{vehicles}_{2005}/\text{d} / \text{measuring points}_{2005} \cdot \text{rate}_{2004-2005} \cdot 365\text{d/y} \tag{5-1}$$

where

$\text{mileage}_{\text{national roads}}$ is the total mileage driven on Swiss national roads [vehicles km/y];

$\text{length}_{\text{national roads}}$ describes the total road length of national roads [km];

$\text{vehicles}_{2005}/\text{d}$ means the average number of vehicles counted per day at the measuring points [d^{-1}];

$\text{measuring points}_{2005}$ is the number of measuring points in 2005 on Swiss national roads [];

$\text{rate}_{2004-2005}$ describes the rate of change of vehicles counted per day at the measuring points []

$$\text{fraction}_{\text{mileage national roads}} = 100 / \text{mileage}_{\text{tot}} \cdot \text{mileage}_{\text{national roads}} \tag{5-2}$$

where

$\text{fraction}_{\text{mileage national roads}}$ means the part of the total mileage driven on national roads [%];

$\text{mileage}_{\text{tot}}$ is the total mileage driven on Swiss roads [km];

$\text{mileage}_{\text{national roads}}$ is the total mileage driven on Swiss national roads [vehicles km]

Thereby 255 measuring points were supported in 2005 and from 2004 to 2005 vehicles counted per day were increased by 1.4% (ASTRA, 2006), which is adopted as rate of change from 2005 to 2006. In 2005 on average 6,452,000 vehicles were counted per day at the measuring points (ASTRA, 2006). Data on mileage and road length are shown in Table 5.4. Remaining mileage was assumed on other roads. All data are shown in Table 5.4, Table 5.5 and Table 5.6.

Table 5.4: Length and mileage of Swiss national, cantonal, and municipal roads for the year 2006.

	length [km]	mileage [%]	mileage [km]
national roads	1,758	26	16,444,077,288
cantonal roads	18,040	19	12,011,073,838
municipal roads	51,496	55	34,287,073,674
total	71,294	100	62,742,224,800

Table 5.5: Mileage for public transport, private traffic, and goods traffic for the year 2006.

	mileage 2006 [km]
public transport ^a	290,270,800
private traffic	56,980,900,000
goods traffic ^a	5,471,054,000
total	62,742,224,800

^a public transport and goods traffic are together heavy duty onroad

Table 5.6: Mileage for passenger cars with coated DPF and for vehicles with catalytic coating for the year 2006.

	mileage 2006 [km]
passenger car with CC	78,269,315
catalytic coating	46,605,251,436

5.2.3 Fuel consumption

Data on fuel consumption in Switzerland (Table 5.7) were received also by BFE (2006). The specific diesel consumptions for vehicle type and vehicles with DPF shown in Table 5.8 were calculated by using the total diesel fuel consumption in Switzerland, mileage, and vehicles stock. Because for offroad vehicles the definite number of vehicles was not known, fuel consumption for offroad vehicles was derived from fuel consumption of passenger cars and heavy duty onroad vehicles. For diesel fuel a density of 0.83 kg/L was reported (TCS & BFE, 2007).

An average diesel consumption of 6.86 L/100 km was used for cars, calculated from the annual average diesel fuel consumption of cars from 1996 to 2004 weighted by the number of diesel vehicles sold in each year. Data on average diesel fuel consumption and number of diesel vehicles sold are derived by Blessing & Burgener (2004). This approximation seemed acceptable because more than 95% of all vehicles put in circulation since 1996 have been in use, yet, except accidental vehicles. Calculations are shown in equations 5-3 and 5-4.

Table 5.7: Swiss fuel consumption 2006 (BFE, 2006).

	fuel consumption 2006 [t]
petrol	3,484,000
diesel	1,852,000

Table 5.8: Diesel consumption of heavy duty onroad/offroad, passenger cars, DPF and coated DPF

	fuel consumption 2006 [kg]
heavy duty offroad	415,532,534
heavy duty onroad	1,061,144,935
passenger car	375,322,530
DPF heavy duty onroad	16,869,992
DPF heavy duty offroad	105,540,000
DPF passenger car	29,722,164

$$\text{diesel consumption}_{\text{average}} = \Sigma(\text{diesel consumption}_{\text{average year } x} * \text{rate}_{\text{new diesel vehicles year } x}) \quad 5-3$$

where

$$\text{rate}_{\text{new diesel vehicles year } x} = 1 / \Sigma(\text{new diesel vehicles}_{\text{year 1996 to 2004}}) * \text{new diesel vehicles}_{\text{year } x} \quad 5-4$$

where

$\text{diesel consumption}_{\text{average}}$ is the amount of diesel consumed per vehicle on average on 100 km in the year 2006 [L/100 km];

$\text{diesel consumption}_{\text{average year } x}$ describes the amount of diesel consumed per vehicle on average on 100 km in the year $x = 1996 \dots 2004$ [L/100 km];

$\text{rate}_{\text{new diesel vehicles year } x}$ is the rate of diesel vehicles introduced in the year x of all diesel vehicles introduced between 1996 and 2004 [];

$\Sigma(\text{new diesel vehicles}_{\text{year 1996 to 2004}})$ means the total amount of diesel vehicles introduced between the years 1996 and 2004 [];

$\text{new diesel vehicles}_{\text{year } x}$ is the amount of diesel vehicles introduced in the year x [];

For heavy duty onroad vehicles 30 L/100 km diesel consumption was assumed based on specifications found in the web and for offroad vehicles 15 kg/OH were assumed with 1,000 operating hours (OH) per year.

Emissions per fuel unit are assumed to be equal for all vehicle types.

5.3 Coatings

Because of market form and the given time frame, a proper data collection on mass of products used containing nanoparticles was not possible for the thematic fields of (automotive) coatings. Thus an approximation was made. A web search was performed with the keyword *farb* on Swiss web pages and with the keyword *paint* on world-wide websites each with using the search engines Google and AltaVista.

The outputs were looked through and the first twenty of them - or if less than twenty were achieved, all - describing a concrete product of the category were divided into the three categories "containing nanoparticles", "perhaps nanoparticles containing" and "without nanoparticles". This allocation is therefore based on a qualitative assessment of the product and corresponding information. Only products for exterior use which are available on the market were considered because it is expected that fluxes of products used indoors are to the waste water. If several products were shown on the host, all were assessed and calculated as one product. As it is shown in Figure 5.1 only small differences were found between AltaVista and Google search and between Swiss web pages and world-wide websites and because of the results of the two sample u-test, the possibility is not excluded that the two samples are of the same pool (see Table 5.7). The formula for the u-test is shown with equations 5-5 and 5-6 and at a level of significance of $\alpha = 0.05$ the null hypothesis, $p_1 = p_2$, is discarded if $|u| > u_{1-\alpha/2} = 2.241$.

$$u = (k_1 / n_1 - k_2 / n_2) / \sqrt{(p * (1 - p) * (1 / n_1 + 1 / n_2))} \quad 5-5$$

where

$$p = (k_1 + k_2) / (n_1 + n_2) \quad 5-6$$

Where

u is the result of the u-test

p is the probability for event E

n is the number of independent replications

k is the number of event E occurring at n replications

Table 5.7: u-test for the web search with the keywords *farb* and *paint*. NP = nanoparticles; CH = Switzerland; WW = world wide; u is the result of the u-test, p is the probability for event E, n is the number of independent replications, k is the number of event E occurring at n replications.

google CH-WW	containing NP	containing and perhaps containing NP	CH Google-AltaVista	containing NP	containing and perhaps containing NP
k (Google CH)	3	8	k (Google CH)	3	8
n (Google CH)	18	18	n (Google CH)	18	18
k (Google WW)	1	11	k (AltaVista CH)	0	3
n (Google WW)	20	20	n (AltaVista CH)	7	7
p	0.105	0.500	p	0.120	0.440
u	1.170	-0.650	u	1.151	0.072
AltaVista CH-WW	containing NP	containing and perhaps containing NP	WW Google-AltaVista	containing NP	containing and perhaps containing NP
k (AltaVista CH)	0	3	k (Google WW)	1	11
n (AltaVista CH)	7	7	n (Google WW)	20	20
k (AltaVista WW)	1	10	k (AltaVista WW)	1	10
n (AltaVista WW)	20	20	n (AltaVista WW)	20	20
p	0.037	0.481	p	0.050	0.525
u	-0.603	-0.326	u	0.000	0.317

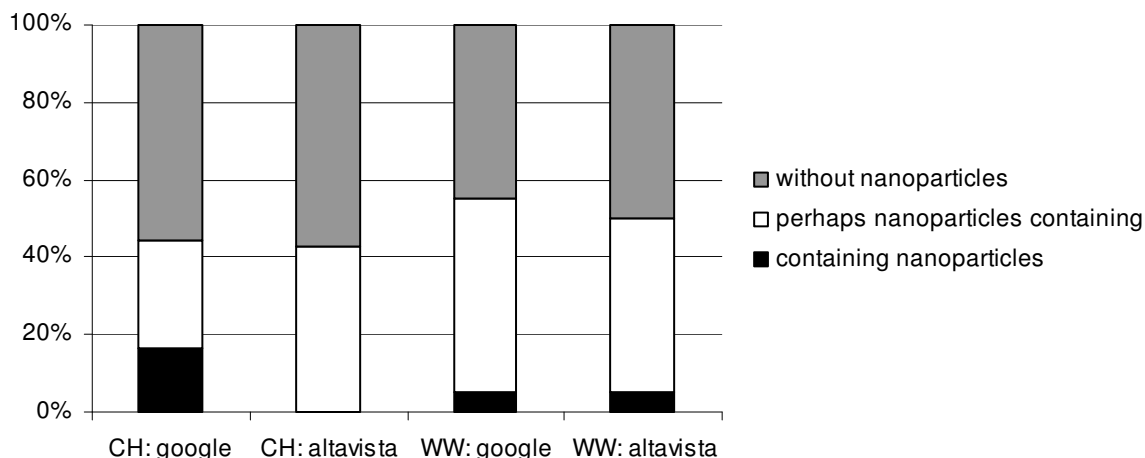


Figure 5.1: Outputs of the web search for the keyword *farb* and *paint* with Google and AltaVista on Swiss and world-wide web pages. CH = Switzerland, WW = world-wide

The search was repeated for a second thematic field, automotive coatings, using the keywords *versiegelung* (egl. sealing, coating). There was no large difference either, as can be seen in Figure 5.2. A search should also be conducted on world-wide websites, but for both keywords *sealing* and *coating*, the resulting product field was much broader and less comparable with the results for Swiss websites and the search was therefore stopped. Reasons for this inequality may be the lacking of an accurate translation and/or an unequal product assortment on Swiss and worldwide market places. The second reason is supported by the fact that products of the Swiss websites originate to a great part from Germany, a leading country in the automotive nanotechnology field.

Table 5.8: u-test for the web search with the keyword *versiegelung*. CH = Switzerland; NP = nanoparticles. u is the result of the u-test, p is the probability for event E, n is the number of independent replications, k is the number of event E occurring at n replications.

	containing NP	containing and perhaps containing NP
k (Google CH)	8	2
n (Google CH)	20	20
k (AltaVista CH)	12	2
n (AltaVista CH)	20	20
p	0.500	0.100
u	-1.265	0.000

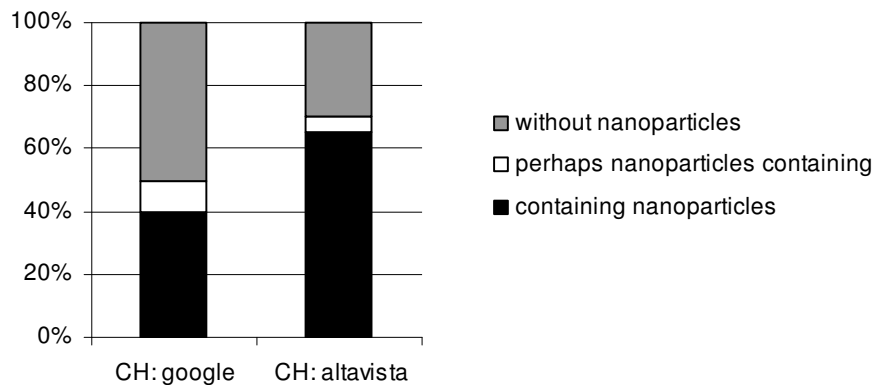


Figure 5.2: Outputs of the web search for the keyword *versiegelung* with Google and AltaVista. CH = Switzerland

The model achieved by the method shown reproduces the internet market and not stringently reality. Possibly the amounts of products sold in the internet are of another size than amounts sold in shops and addressed are people using internet and internet sales platforms. And it is not always obviously if products are for private or commercial use. The web pages shown first are better linked and the keywords are displayed more frequently than on pages shown later. But it can be concluded that the attitude whether products get sold on internet or not is similar for Switzerland and the world-wide market and also differences between search engines are small.

6 Products and product categories

6.1 Biocides and plant protection products

According to the Swiss law biocides are divided into the four major categories disinfectants / general biocide products, preservatives, pesticides and other biocide products (VBP, annex 10).

Products in the categories disinfectants and other biocide products are mostly for interior or water application and are therefore not considered here. Preservatives, containing several sorts of coating additives, are included in chapter 6.5.

Among the biocides in the category pesticides, several types are applied on organisms with direct contact to soil. This category and plant protection products, which are considered here, too, overlap to a certain part, namely rodenticides, molluscicides, insecticides, and acaricides. These are considered in the following section, plant protection products. Avicides, a further product type in the pesticide category with potential soil contamination, are forbidden in Switzerland.

6.1.1 Plant protection products

Plant protection products consist among others of herbicides, insecticides, fungicides, plant growth regulators, and seed treatment products (see BLW, 2007). They are directly applied on plants and soil for use in agriculture, forestry and gardening, or indirectly on infrastructure elements like rails or partially paved places.

Only one plant protection product was found that contains nanoparticles¹. It is a nano silver containing spray for indoor and outdoor use on plant leaves (NanoSys GmbH, 2005) with low sales volume (Gubser, 2007, in Müller, 2007). Further, evidence was found that research is ongoing for new formulations of plant protection products with quantitatively high application potential. In a press release of BASF it says that nanotechnology is applied in long-run research for plant protection (Butstraen, cited in Lick, 2007). More precise information by BASF is not available at the time but a communiqué shall be published, probably at the end of October of this year (Kranz, 2007, personal communication). Formulations of Syngenta do not contain nanosized particles as a typical particle size is in about 20 µm for spray powder and the smallest microcapsules have a diameter of 2.5 µm (Diriwaechter, 2007, personal communication). According to Diriwaechter (2007, personal communication) it can not be excluded that small amounts of microcapsules have a diameter below 100 nm, but this is not specifically analysed except for one singular case where the amount of microcapsules <600 nm is less than 10% and the total amount of microcapsules of the product volume less than 0.1%. The microcapsules break open immediately after application (Diriwaechter, 2007, personal communication). From DuPont the short statement was received that no products containing nanoparticles are sold in Switzerland (Ostermeyer, 2007, personal communication). In a Nanoforum Report it is written that many companies have products with nanoparticular ingredients

¹ Nano-Argentum 10, NanoSys GmbH: <http://www.nanosys.ch/>

within a size range of 100 to 250 nm and that other companies suspend herbicidal or pesticidal nanoparticles of 200 to 400 nm size in oil or water (Joseph & Morrison, 2006), but products were not mentioned.

No information on the research focus or on the state of product development was received by agrochemical companies. Based on recent scientific papers the current research focus lays on the following topics:

- Encapsulation

Oils were proposed as substitute for conventional pesticides because of their better biocompatibility (Lai et al., 2006). Lai et al. (2006) formulated a new delivery system for ecological pesticides by the incorporation of *Artemisia arborescens* L. essential oil into solid lipid nanoparticles. The particles had a mean particle size of 199 to 294 nm depending on the surfactant used and whether the particles were loaded with oil or not. Until now solid lipid nanoparticles were not applied in agriculture, but in pharmaceuticals and cosmetics (Lai et al., 2006).

Liu et al. (2006), Li et al. (2007; 2006), and Wen et al. (2005) developed porous hollow silica nanoparticles for controlled delivery of water-soluble pesticides. The hollow space allows high loadings of pesticides and the porous shell controls the release (Wen et al., 2005). Because of the shell, the active agents inside are protected against destruction by UV light (Li et al., 2007; 2006). Conventional pesticides are decomposed or lost by 90% (Li et al., 2006). The properties of the porous hollow silica nanoparticles are listed in Table 6.1.

Table 6.1: Properties of porous hollow silica nanoparticles for potential use as plant protection products.

source	inner size [nm]	outer size [nm]	shell thickness [nm]	pore diameter [nm]	surface area [m ² /g]	encapsulation capacity	goal of experiment
Liu et al. (2006)	~80		~15				controlled delivery, depending on pH and temperature
Li et al. (2007)			~15	~4-5	~588	625 g/kg avermectin	sustained release, UV-shielding
Li et al. (2006)	100-130	140-180	5-45	4-5			controlled release, UV-shielding
Wen et al. (2005)	70	100		4-5		58.3% w/w avermectin	controlled release depending on pH

- Organo-clays

Organic cations were adsorbed on clay minerals to reduce leaching (slow release of the active agent) and photo degradation of herbicides (El-Nahhal et al., 2001). As clay minerals are negatively charged and hydrophilic, their modification is required for the sorption of hydrophobic herbicides (El-Nahhal et al., 2001).

- Improved storage

Vandergheynst (2007) applied silica nanoparticles (particle size of 7 to 14 nm) in a biological mosquito control product. A watermold parasitizing larvae was stored and delivered better in water-in-oil emulsions than in water. To reduce clumping and settling during storage and therefore improving efficacy of the formulations, silica nanoparticles were added (0 to 0.5 wt%) for oil thickening (Vandergheynst et al., 2007). In the experiment of Vandergheynst (2007) the hydrophobicity of the silica particles was varied. As the silica nanoparticles are inert in biological systems (Vandergheynst et al., 2007), they will persist in soil, water, sediment and air.

The nanoparticulate parts of biocides are usually not the active agent itself but auxiliary materials and only one source mentioned modified active ingredients (ETC Group, 2004).

Because an application of nanoparticles in plant protection products is currently not on the market, only a qualitative and potential model was drawn (see Figure 6.1). A reappraisal will be required in a few years.

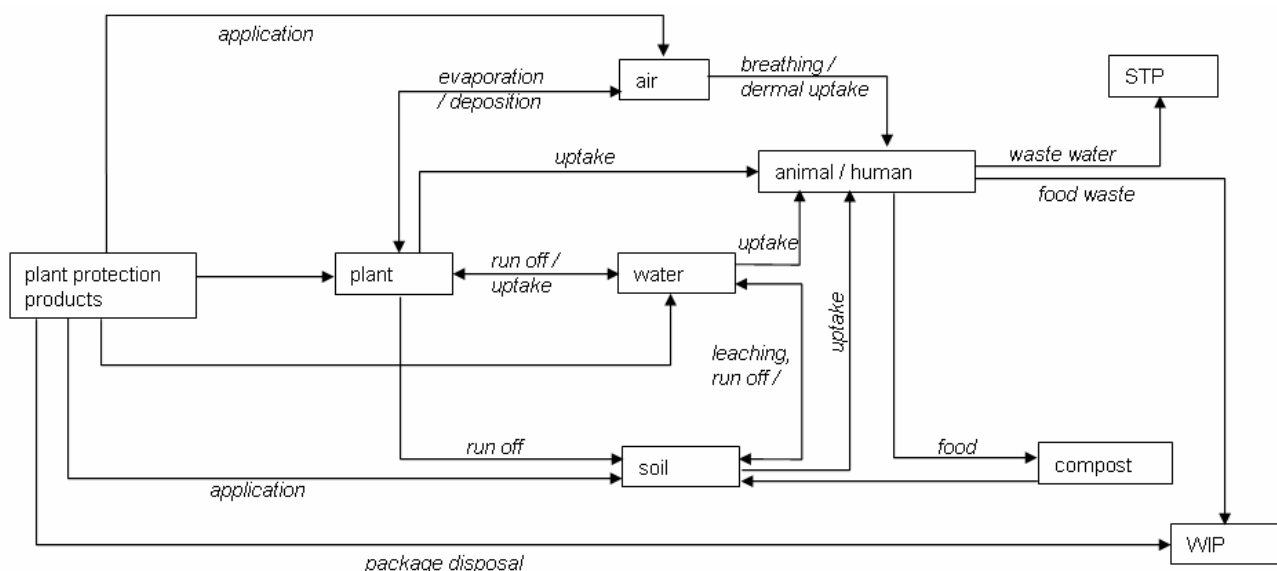


Figure 6.1: Potential flow chart of applied plant protection products.

6.2 Fertilizers

Fertilizers, especially artificial fertilizers, have a major potential to pollute soil, water and air. Therefore efforts were done to minimize these problems by agricultural practices and the design of the fertilizers. Nanotechnology can be used in this field for slow release mechanisms such as entrapment, encapsulating or dispersing the active agents in a matrix of biodegradable or inert material. Until today, no indications of real applications were found in the scientific literature, in the web and from feedback from experts of associations. But the research is going on and several patents were found in the Derwent Innovations Index available on ISI Web of Knowledge¹. These patents are shown in Table 6.2, arranged by fertilizer type and nanoparticle function, and listed in annex 2. This overview shows that the main research focus for the application of nanoparticles in fertilizers is placed on slow and controlled release of fertilizers. In that group various polymers and clays are mentioned repeatedly. For clays the benefit of nanoparticulate size is not clear as in most cases the interlayer distance matters and in fact several patents were found using clay particles or platelets of larger size. Plants take up nutrients mainly by roots or via leaves and slow and controlled release is advantageous for nutrient supply on both routes. Foliar fertilizers are often used to satisfy short-term nutrient supply where a nanoparticulate nutrient may be better for an efficient nutrient uptake. Future applications of nanoparticulate fertilizers in agriculture will be limited to special issues. Maybe in gardening nanoparticles in fertilizers will be applied more often but that may be a temporary fashion.

Table 6.2: Fertilizer type, nanoparticles' form and function of fertilizers found in Derwent Innovations Index. Patents are listed in annex 2.

fertilizer type	nanoparticles' form	nanoparticles' function
slow/controlled release fertilizer	<ul style="list-style-type: none"> ▪ inorganic filler (particle size <1micron) (Ying et al., 2006); ▪ nanometer-submicron level polyvinylalcohol (PVA) mixed polymer solution (Zhang et al., 2005); ▪ nanometer-scale olefin/starch mixed polymer (Zhang et al., 2004); ▪ nanoclay (Li et al., 2002); ▪ polymer-based nanocomposite (an inorganic anionic clay and a cyclic monomer) (Schomaker & De Vos, 2006); ▪ nano-submicron level pond residues-coal gangue compound hybrid polymer (Zhang et al., 2005) 	coating/covering agent
	<ul style="list-style-type: none"> ▪ nanomicron-submicron foamed plastic organic compound sticker mixed polymer (Zhang et al., 2005); ▪ nanometer-submicron level polyvinylalcohol (PVA) mixed polymer solution (Zhang et al., 2005); ▪ nano-class clay-polyester mixed polymer (Zhang et al., 2003) 	cementing agent (sometimes used as coating agents)
	<ul style="list-style-type: none"> ▪ nanocrystalline divalent metal ion phosphate (MacPhee & Wright, 2007); ▪ nanotubes (Dennis et al., 2004) 	encapsulation

¹ ISI Web of Knowledge: http://portal.isiknowledge.com/portal.cgi?DestApp=XS_PROD&Func=Frame

ff Table 6.2: Fertilizer type, nanoparticles' form and function of fertilizers found in Derwent Innovations Index.

mixed fertilizer	<ul style="list-style-type: none"> ▪ nano-class clay-polyester mixed polymer (Zhang et al., 2003); ▪ nanometer-level sulfonated lignin mixture water solution (Zhang et al., 2003) 	cementing agent
liquid fertilizer	<ul style="list-style-type: none"> ▪ nano silver (Kim, 2005) ▪ titanium dioxide (Lee & Choi, 2006) 	antibacterial effects colloid incorporating a surfactant or a biocidal agent
active organic fertilizer	<ul style="list-style-type: none"> ▪ nano-class fermented active organic fertilizer prepared from ammonium humate organonitrogen, ammonium polyphosphate, ammonium phosphate, calcium potassium pyrophosphate, organopotassium, additive and water (Wu, 2004) 	active agent
biological fertilizer	<ul style="list-style-type: none"> ▪ ? (Min et al., 2003; Min et al., 2003) 	active agent
fertilizer	<ul style="list-style-type: none"> ▪ drug nanoparticles (average diameter of 100nm) (Nagare & Senna, 2004) ▪ free nano-sized particle of an active agent (<500, <200, <100 nm) (Watanabe et al., 2002) ▪ nanoparticles (<1000 nm) (Kerkhof & Ong, 2001) 	active agent
release of active agents	<ul style="list-style-type: none"> ▪ nanoparticulate inorganic core (particle size <1000nm) (Bosch et al., 2003) 	core of a fertilizer
plant growth medium	<ul style="list-style-type: none"> ▪ nano diatomite and zeolite ceramic crystal powder (Yu, 2005) 	maintaining soil moisture level
foliage spray	<ul style="list-style-type: none"> ▪ nano rare earth (Wang et al., 2005); ▪ hydroxide of nano rare earth (Wang et al., 2005) 	?
soil repairing agent	<ul style="list-style-type: none"> ▪ nano scale soil repairing agent containing silicate, zeolite, and mineral salts (Wei & Ji, 2003) 	active agent

6.3 Soil remediation

Nanotechnology is expected to contribute to pollution prevention (source reduction), pollution sensing and detecting, and pollution treatment (Masciangioli & Zhang, 2003). The use of nanotechnology for pollution reduction (e.g., environmental benign materials and products, treatment of waste material) is discussed in separate chapters if emissions occur during use or disposal and recycling, respectively.

For the sector of remediation of environmental contaminants Trantnyek & Johnson (2006) stated that “the range of nanotechnology applications mirrors the spectrum of “non-nano” strategies for contaminant remediation”.

Until today, no evidence could be found that nanoparticles were applied for soil remediation, only laboratory testing is ongoing. In the case of groundwater pilot-scale demonstrations in the field were done (Elliott & Zhang, 2001; Zhang, 2003) and a few companies in the United States offer site remediation by nano zero valent iron (nZVI) application¹. Nevertheless nanoparticles were expected leading to effective treatment of soil and groundwater pollutants because of their large overall surface area, greater density of reactive sites on the particles surfaces, and/or higher intrinsic reactivity of the reactive surface sites (Tratnyek & Johnson, 2006).

Although matter migrates between soil and groundwater and therefore solutions for site remediation should be adequate for both (Schrick et al., 2004), aquifers are not discussed further because they were not inside the system boundary (for definition see chapter 2.4).

Nanoparticles could potentially be applied in situ and ex situ (Tratnyek & Johnson, 2006). Ex situ treatment is often carried out in slurry reactors and/or by elevated temperatures, and therefore the soil functions are destroyed whereas in situ is less damaging to soils.

Pollutants in soils are not dispersed homogeneously and neither are the treatment agents due to sorption processes. And other than in water, contaminants are often sorbed strongly onto the soil colloids and diffusion of them from the soil surface to the surface of the active ingredient is difficult.

Particles for contaminant treatment should be mobile in soil for a good mixing of agent and soil particles and therefore the sticking probability must be very low (He et al., 2007; Lin et al., 2005; Schrick et al., 2004). The particles should also not agglomerate so that they are able to retain their surface activity (He et al., 2007). The dispersion of colloids in soils is affected by particle size, pH, ionic strength, composition of the suspending water, the soil matrix, and flow velocity (Nyer & Vance, 2001). Efforts to enhance mobility and suppress agglomeration include various techniques. Schrick et al. (2004) tested zero-valent iron nanoparticles supported with anionic, hydrophilic carbon (Fe/C) and poly(acrylic acid) (Fe/PAA) and stated a better transport of the particles through soil columns. He et al. (2007) stabilized palladized iron (Fe-Pd) with sodium carboxymethyl cellu-

¹ e.g., Golder Associates: <http://www.golder.com/default.asp?PID=1&LID=1>

lose with the effect that the stabilized particles displayed markedly improved stability against aggregation, chemical reactivity, and soil transport.

A further request to treatment materials is their benign behaviour in the environment, their specific interaction with the aimed substance, and their cost effectiveness (He et al., 2007).

For contaminant treatment two main approaches were discussed, absorptive treatment by removing contaminants by sequestration and reactive treatment by degradation (Tratnyek & Johnson, 2006).

The reactions of nanosized active agents for soil remediation are depending on several environmental factors such as temperature (Varanasi, Fullana & Sidhu, 2007), moisture (mostly water-supported, rarely gas-supported transport), oxic/anoxic conditions (Varanasi et al., 2007), soil composition (especially particle size, clay content, organic matter) (Li et al., 2006; Schrick et al., 2004), ionic strength (Xu & Zhao, 2005), pH (Li et al., 2006; Xu & Zhao, 2005), concentration of contaminant, mixing (Varanasi et al., 2007) and/or reaction time (Chang et al., 2007b; Lin et al., 2005).

The most investigated nanoparticles are iron and clay based particles. Iron was already successfully applied in field-scale pilot studies for groundwater remediation (Elliott & Zhang, 2001; Zhang, 2003). Nanoscale iron particles provide a large flexibility for in situ applications because they are very effective for the transformation and detoxification of many contaminants which are common in the environment (Zhang, 2003) and iron and iron oxides itself are common in geological environments, also in nanoparticulate forms (Madden & Hochella, 2005). Investigations were performed for various forms of iron like zero-valent iron, iron oxides or coated iron. The properties of nanoscale iron-based materials were reviewed recently by Li et al. (2006) and for zero-valent iron nanoparticles the characteristics were examined by Sun et al. (2006).

Clay minerals are natural minerals in soils and they interact with almost all anthropogenic contaminants in the environment (Murray, 2000; Yaron-Marcovich et al., 2005). For environmental application they are modified, for example in their cationic characteristics, in changing from hydrophilic to hydrophobic or in constructing interlayers (Yaron-Marcovich et al., 2005). The resulting materials were not always nanosized. Modified clay materials were able – among other applications – to immobilize contaminants in soils, to degrade organic toxic chemicals, to purify waste water, to prevent groundwater pollution, and they could be applied in more environmentally benign agricultural chemicals (Yaron-Marcovich et al., 2005).

Research in case of soil remediation is ongoing for organic contaminants and metals. Studies were shown in the following sections.

6.3.1 Organic compounds

A lot of research has been conducted about the treatment of organic soil contaminants such as polycyclic aromatic hydrocarbons (PAH), chlorinated hydrocarbons (CH), polychlorinated biphenyls (PCB) and estrogen (17 β -estradiol) with nanoparticles. The studies are listed in Table 6.3.

Table 6.3: Research focus on nanoparticles for remediation of soils contaminated with organic pollutants. PAH = polycyclic aromatic hydrocarbons, CH = chlorinated hydrocarbons, PCB = polychlorinated biphenyls, 7 β -estradiol = estrogene.

group	contaminant	nanoparticles	size	surface area [m ² /g]	concentration	mechanism	soil	source
pesticides	metolachlor, alachlor, atrazine, pendimethalin, chlorpyrifos	nZVI		2.55	>1000 mg metolachlor, >55 mg alachlor, >64 mg atrazine, >35 mg pendimethalin, and >10 mg chlorpyrifos/kg soil; destruction of >60% by Fe0 5%(w/w), >90% when 2% (w/w) Al ₂ (SO ₄) ₃ was added to the Fe0	destruction	soil with 2.6% organic matter	Shea, Machacek & Comfort (2004)
PAH	pyrene	nZVI	50-80	140.8	100 mg pyrene/kg soil; up to 60% removal of pyrene	reaction in soil-water-iron interphase	clay loam with 2.19% organic matter	Chang et al. (2005)
PAH	pyrene	nZVI	200-300	21.1	0.00625-0.15 g iron/g soil; ~62% removal of pyrene in soil by 0.15g iron/g soil	reaction in soil-water-iron interphase	clay loam with 2.19% organic matter	Chang et al. (2007b)
PAH	naphthalene	surface modified smectite (montmorillonite)	A few tenth to a few hundreds in width and length; ~1 nm in thickness	700-900	the suitable amount of adsorbent (smectite) was determined to allow 30-80% uptake of naphthalene initially added	sorption (it can sorb 1180 mg naphthalene/kg at the equilibrium concentration of 1 mg/L	no soil	Yuan (2004)
endocrine-disrupting chemical	17 β -estradiol	smectite			4.3 μ g/mL 17 β -estradiol and 25 mg smectite (+ 7.8 mL deionised water, 200 μ L methanol solution)	sorption (it can remove 98% of 17 β -estradiol from a solution after 4h of reaction)		Yuan (2004)

ff Table 6.3: Research focus on nanoparticles for remediation of soils contaminated with organic pollutants. PAH = polycyclic aromatic hydrocarbons, CH = chlorinated hydrocarbons, PCB = polychlorinated biphenyls, 7 β -estradiol = estrogene.

group	contaminant	nanoparticles	size [nm]	surface area [m ² /g]	concentration	mechanism	soil	source
PCB		Fe, Fe ₂ O ₃ , V ₂ O ₅ /TiO ₂ particles	<100 (Fe); 5-25 (Fe ₂ O ₃); ? (V ₂ O ₅ /TiO ₂)		1g Fe/10 g soil; max. destruction of 98% in the presence of air at 300 °C; at room temperature 38% destruction	destruction; dechlorination (surface reaction): mixing and thermal treatment	original contaminated soil (10.35% C) and filter cake from the original contaminated soil (12.55% C)	Varanasi, Fullana & Sidhu (2007)
CH	penta-chlorophenol	nZVI	10-90	30.9	1000 mg PCP/kg soil; 1wt% nZVI; decay ~40%	oxidation with 1 wt% H ₂ O ₂	clay soil, alluvial soil, laterite soil	Liao et al. (2007)
CH	trichloroethylene	palladized iron (Fe-Pd) stabilized with sodium carboxymethyl cellulose	4.3+/-1.8		ratio of Fe (0.1 g/L) to TCE was 1.17; nearly all of the TCE was destroyed	degradation	without soil; transport test in soil column with loamy sand soil -> 98% of the stabilized Fe-Pd was transported through the soil (with water), whereas the non-stabilized Fe-Pd particles were retained on the top soil bed.	He et al. (2007)
CH	trichloroethylene	anionic, hydrophilic carbon (Fe/C) and poly(acrylic acid)-supported (Fe/PAA) nZVI	carbon: 50-200; Fe: aggregates of 30-100	20-30 Fe/PAA	5 mg iron /mL	dehalogenation	sand, loam, sandy loam, clay loam	Schrick et al. (2004)
CH	7 chlorinated ethanes	Pd/Fe bimetallic	<100; 0.1-1% Pd	33.5	5 g Fe/L; 20 μ L of chlorinated ethane, 50 mL aqueous solution (containing 0.25 g of Pd/Fe); 20-30 mg/L chlorinated ethanes (initial conc.)	hydrodechlorination; surface mediated reaction	no soils	Lien & Zhang (2005)

Table 6.4: Research focus on nanoparticles for remediation of soils contaminated with metals.

group	contaminant	nanoparticles	size [nm]	surface area [m ² /g]	concentration	mechanism	soil	source
heavy metal	Cu	allophane		700-900	uptake of 4448 mg Cu/kg allophane at pH 5.5 and equilibrium concentration of 10 mg Cu/L; mixtures containing 100 mg allophane, 0.036-1.5 mM Cu, and 2 mM CaCl ₂	sorption (cation-exchange reaction and specific complexation between metal ions and the (OH)Al(OH) ₂ groups of allophane)		Yuan (2004)
metal ions	Mn ²⁺	hematite	7.3+/-1.9 (thickness ~1.5); 36.7+/-13.2 (thickness ~8)	210; 40	7 or 9 ppm Mn	oxidation of Mn ²⁺ (aq)		Madden & Hochella (2005)
metal ions	Cu ²⁺	hematite	7 (height 1.4); 25 (height 4.8); 88	188; 62; 9.1	0.25, 0.85 bzw. 0.6 and 0.85	sorption		Madden, Hochella & Luxton (2006)
heavy metal	Pb ²⁺	poly(amidoamine) dendrimers			590 mg lead/kg (sandy soil); 965 mg/kg (clay soil); 1600 mg lead/kg soil; removal of lead: max. 92%, 47%, 73%; retained dendrimers and Pb: ~97%	soil washing; extraction	Sandy soil, clay soil, weathered field-contaminated clay soil	Xu & Zhao (2006)
heavy metal	Cu ²⁺	poly(amidoamine) dendrimers	50 Å		90% Cu removed with 0.1% dendrimers; 4 mg Cu ²⁺ /L and 400 g soil	extraction	Sandy soil; 0.43% organic matter	Xu & Zhao (2005)
metals and metalloids	As(V), Cu(II), Hg(II), Zn(II)	Fe oxides, oxyhydroxides, hydrous oxides (FeOX); synthetic goethite; nanogoethite	5, 25, 75			sorption		Waychunas, Kim & Banfield (2005)

ff Table 6.4: Research focus on nanoparticles for remediation of soils contaminated with metals.

group	contaminant	nanoparticles	size [nm]	surface area [m ² /g]	concentration	mechanism	soil	source
heavy metal	Cu(II)	iron phosphate (vivianite): Fe ₃ (PO ₄) ₂ x 8H ₂ O	8.4+/-2.9		666.4 mg Cu/kg CS soil, 639.2 mg Cu/kg NS soil, 458.8 mg Cu/kg AS soil	immobilization; reduction of leaching	topsoil of acidic, neutral and calcareous soils; 0.34, 0.52, 0.70% C org	Liu & Zhao (2007)
heavy metal	chromate Cr(VI)	stabilized ZVI			0.12 g ZVI/L for 90% Cr(VI) reduction; 83 mg Cr(VI)/kg dry soil	reductive immobilization (reduction of Cr(VI) to Cr(III))	Sandy loam soil, 0.43% org. matter	Xu & Zhao (2007)

6.3.2 Metals

Table 6.4 shows experimental results for the treatment of metal polluted soils. Mainly iron based nanoparticles were studied for this application. Only one study was found reporting the use of allophane, a hydrous aluminosilicate, and one that of poly(amidoamine) dendrimers.

6.3.3 Potential application of nanoparticles for soil remediation in Switzerland

The use of nanoparticles for soil remediation is merely a matter of time. In the United States, the U.S. Environmental Protection Agency (USEPA) is involved in several projects to investigate the effectiveness of nanoparticles for environmental cleanup in groundwater (Lam et al., 2006). In Switzerland methods for soil remediation using nanoparticles are in discussion, but specific applications are not planned (Reusser, 2007, personal communication). To Reusser (2007, personal communication) the main problem is that there are too many unknowns at these methods at the time.

At 3,000 to 4,000 Swiss sites the clean-up values were exceeded and therefore a remediation is needed (Hammer & Wenger, 2001; Reusser, 2007, personal communication). Main sources of the pollution are landfills, industry and accidents (Hammer & Wenger, 2001). Reusser (2007, personal communication) estimates that at a fifth of these sites the soil has to be remediated. The sites were mainly allocated at the densely populated Swiss middle land and polluted by heavy metals especially by lead. Only a few sites may be cleaned up by methods using nanoparticles (Reusser, 2007, personal communication).

6.4 Automotive equipment

Nanotechnology is widely used and further research is ongoing for automotive applications. With more than five million passenger cars in Switzerland (BFS, 2007d) and further millions of utility vehicles there is much potential for applications.

Of all applications found, four main fields were identified for releasing significant amounts of nanoparticles to the soil: Catalytic converters, two regeneration systems for diesel particulate filters, tyres and automotive coatings. These systems are analysed in the following sections, followed by a brief discussion of future developments.

6.4.1 Catalytic converters

Automotive catalytic converters convert the pollutants hydrocarbons, carbon monoxide and nitrogen oxides produced during the combustion process in motor vehicles to nitrogen, carbon dioxide and water by oxidation and reduction, respectively.

A catalytic converter consists of a base composed of a temperature stable ceramic or metallic substrate, a washcoat, mainly aluminium, zirconium, cerium, barium, strontium, praseodymium, lanthanum, and/or silicon in oxidised form, and catalytic active substances like platinum, palladium, rhodium and – rarely – other platinum group metals carried by the washcoat (Winkler, 2007, personal communication). Depending on the kind of fuel, the formation of the catalytically active substances changes. So, rhodium is not applied in diesel catalytic converters because of the high oxygen concentration and when petrol is used, the percentage of rhodium increases due to its efficient methane reduction potential.

A catalytic converter of a main passenger car contains about 1.75 to 2 g of precious metals (Jarvis, Parry & Piper, 2001; Umweltbundesamt Dessau, 2006). Winkler (2007, personal communication) estimated the cluster size of those platinum group elements (PGE) in the range of 10 to 50 nm and another analysis of catalyst surfaces reported a particle size of the PGE of 1.6 nm (McCabe & Kisenyi, 1995, in Jarvis, Parry & Piper, 2001).

The main function of the washcoat is to stabilise the finely dispersed catalyst material against sintering (Görsmann, 2005). As a maximal surface area of the washcoat is aimed for (normally about a few hundred m²/g), the loading of the material is between 3 and 300 g/dm³ catalyst volume with typical metal loadings of 0.1 to 10 g/dm³ catalyst volume (Görsmann, 2005). The oxides of the washcoat are agglomerated and, depending on the process, sintered together, so that they are neither nano- nor microparticulate (Winkler, 2007, personal communication). Emissions caused by the washcoat were therefore not considered in this work, although they were observed.

Because precious metals are highly chemically stable, they are not converted during application in catalytic converters. Losses of platinum group elements because of evaporation is little, occurring at temperatures above 900 °C which can be reached in catalytic converters (Palacios et al., 2000). The predominant part of catalytic active metals is emitted due to mechanical or thermal erosion and is present as nanocrystals in particulate form (Barefoot, 1999; Palacios et al., 2000; Rauch et

al., 2000). The amount of the emitted particulate platinum varies between 90 and 99%, the amounts of particulate Rh and Pd are often lower (Artelt et al., 1999; Moldovan et al., 2002). Particulate platinum group elements are emitted in nanoparticulate form bound to a substrate, often aluminium of the washcoat (Ely et al., 2001; Moldovan et al., 2002). These platinum group elements containing particles were expected to have diameters of some micrometers (Artelt et al., 1999; Konig et al., 1992), and significant amounts of the precious metals are expected to be released as catalyst fragments by malfunction of catalysts (Artelt et al., 1999; Hagelucken, 1995). These findings are supported by platinum distribution studies where a platinum concentration in soils above background level was not observed at sites far from traffic lanes (Fragnière et al., 2005; Zereini et al., 1997). Emissions of platinum group elements from catalysts are depending on converter brands, engine types, converter age, and driving conditions (Artelt et al., 1999; Ulrich, 2007, personal communication).

The calculation of the total amounts of nanoparticulate platinum group elements released by catalytic converters in Switzerland for the year 2006 were derived from literature data with use of equation 6-1.

$$PGE_{\text{emitted}} = \text{mileage}_{\text{catalyst}} * (\text{rate}_{\text{catalyst}} * PGE_{\text{catalyst}} / \text{age}_{\text{catalyst}})$$

6-1

where

PGE_{emitted} is the total amount of PGE released by catalytic converters in Switzerland for the year 2006 [kg/y];

$\text{mileage}_{\text{catalyst}}$ is the part of the total mileage driven by vehicles with catalytic converters [vehicle km/y];

$\text{rate}_{\text{catalyst}}$ is the rate of PGE which gets emitted per catalytic converter [];

PGE_{catalyst} is the amount of PGE in a catalytic converter [kg];

$\text{age}_{\text{catalyst}}$ is the mileage of an ordinary catalytic converter during service life [km]

For the realistic scenario calculations were conducted on the basis of the information of Cowley (1997, in Jarvis, Parry & Piper, 2001) that 20 to 30% of a catalysts PGE were recovered during the recycling process and 70 to 80% get lost during life time ($\text{rate}_{\text{catalyst}} = 0.7$ is assumed; see Figure 6.2). With a catalyst reaching the end of life, $\text{age}_{\text{catalyst}}$, after 80,000 km and five years, respectively (Jarvis et al., 2001), and a PGE amount, PGE_{catalyst} , of 2 g in a new catalyst an emission rate of 17.5 µg/vehicle km is resulting and multiplied with the mileage driven with catalysts, $\text{mileage}_{\text{catalyst}} = 46,605,251,436$ km (derivation see chapter 5.2.2), in total 816 kg is emitted in Switzerland in the year 2006.

The worst case scenario (see Figure 6.2) is based on the highest amount of PGE emission possible, 2 g per catalyst and 25 µg/vehicle km, which leads to a Pt to Pd/Rh ratio of 2:3 for a Pt emission rate of 10 µg/vehicle km, the highest rate found in literature (Helmers, Mergel & Barchet, 1994, in Helmers, 1996). Thereby an amount of PGE released in Switzerland per year of 1,165 kg is resulting.

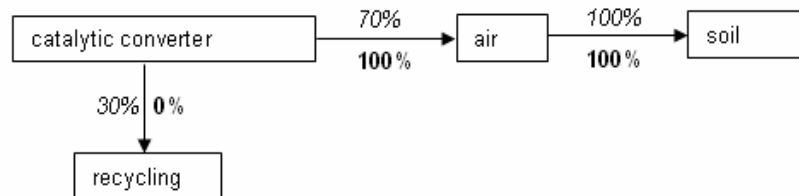


Figure 6.2: Flow chart for the worst case (**bold**) and the realistic (*italic*) scenario of platinum group element fluxes from catalytic converters to the soil.

For spatial distribution of the released PGE the following assumptions were made:

- The total amount of PGE released by catalysts, $PGE_{emitted}$, is deposited on soil,
- the total amount of PGE is emitted in nanoparticulate form bound to substrate, and therefore distributed homogeneously in soil near traffic lane (values for $volume_{bulk\ particles\ distribution\ national\ or\ other\ roads}$ and derivation see Table 5.2,
- the part of the mileage driven on national roads is calculated in chapter 5.2, equations 5-1 and 5-2, and resulting mileage for national and other roads are shown in Table 5.4.

With these assumptions concentrations for soils beside national and other roads could be calculated for the realistic and the worst case scenario using equation 6-2:

$$PGE_{conc\ soil} = PGE_{emitted} * rate_{mileage\ national\ or\ other\ roads} / volume_{bulk\ particles\ distribution\ national\ or\ other\ roads} \quad \mathbf{6-2}$$

where

$PGE_{conc\ soil}$ is the yearly increase of the concentration of PGE in soil [$kg/m^3/y$];

$PGE_{emitted}$ is the total amount of PGE released by catalytic converters in Switzerland for the year 2006 [kg/y];

$rate_{mileage\ national\ or\ other\ roads}$ is the part of the total mileage driven on national and other roads, respectively [];

$volume_{bulk\ particles\ distribution\ national\ or\ other\ roads}$ is the soil volume contaminated with PGE beside national and other roads, respectively [m^3]

As soil depth 20 cm was chosen as Zereini et al. (1997) showed that Pt of catalytic converters was deposited mainly in the upper 4 cm and from 20 cm downwards no Pt was found anymore.

All results are shown in Table 6.5.

Table 6.5: Realistic and worst case scenario for total amounts and the increase in concentrations per year for platinum group element (PGE) emissions from catalytic converters.

	realistic scenario	worst case scenario
total amount of PGE released [kg/y]	816	1,165
PGE emitted per vehicle km [$\mu\text{g}/\text{km}$]	18	25
Yearly concentration increase of PGE at national roads [$\mu\text{g}/\text{m}^3/\text{y}$]	0.24	0.35
Yearly concentration increase of PGE at national roads [$\mu\text{g}/\text{kg}/\text{y}$]	0.0046	0.0066
Yearly concentration increase of PGE at other roads [$\mu\text{g}/\text{m}^3/\text{y}$]	0.017	0.025
Yearly concentration increase of PGE at other roads [$\mu\text{g}/\text{kg}/\text{y}$]	$3.3 \cdot 10^{-4}$	$4.8 \cdot 10^{-4}$

A study investigating concentrations of PGE in air showed increasing concentrations in air and it was assumed that a part of the emitted particles remains airborne (Zereini et al., 2001). Other studies on the distribution of PGE indicated transport distances far away from the road with decreasing concentrations with greater distance from the road (Zereini et al., 2004). Even in snow of Greenland and of the Alps elevated concentrations of PGE were monitored (Barbante et al., 1999; Barbante et al., 2001). Rauch et al. (2005) found that weathering conditions influence heavily the atmospheric residence time and environmental fate of PGE. Such influences are not considered in this work but these have to be kept in mind for interpretation of the resulting amounts of PGE emitted.

Values for the release of PGE from catalytic converters reported in literature are usually in the range of ng per vehicle km. Artelt et al. (1999) measured 9 to 124 ng/km and Moldovan et al. (2002) measured on average 5.4 to 111.5 ng/km Pt, 7.2 to 54.2 ng/km Pd and 2.2 to 76.9 ng/km Pd for various test arrangements. Only few data are reported to be in the microgram range such as Helmers, Mergel & Barchet (1994, in Helmers, 1996) with 4-10 $\mu\text{g}/\text{km}$. With 17.5 and 25 $\mu\text{g}/\text{km}$ for realistic and worst case scenario, respectively, the values obtained in this work are much higher. If these values are compared to concentrations observed in soils near motorways, usually less than several hundred μg per kg soil (e.g., Schäfer & Puchelt, 1998; Whiteley & Murray, 2003; Zereini et al., 1997), the concentration values calculated in this work are rather low with 1 to 1.5 $\mu\text{g}/\text{kg}$ soil for PGE levels at national roads. For this calculation the PGE were distributed in an area of 1 m x 1 m x 0.04 m because the highest PGE concentrations were measured in the uppermost 4 cm soil in a distance of 1 m to the traffic lane (Zereini et al., 1997). The resulting concentration was multiplied with 20, as catalysts have been in use since about 20 years. 1 $\mu\text{g}/\text{kg}$ was found by Zereini et al. (1997) as the Pt background concentration in the uppermost soil layer.

The toxicity of platinum compounds was investigated and it was found that they are highly cytotoxic and strong allergens (see Palacios et al., 2000). Also plant uptake and accumulation of PGE was investigated. In metallic form platinum is not bioavailable (Barefoot, 1999; Palacios et al., 2000). But in the study of Lustig et al. (1996) it was found that platinum in tunnel dust formed more organic species in soil when extracted with organic solvents than from other sources, and the Pt was

more bioavailable. Experiments with complexing agents have shown that the Pt released from catalytic converters was mobilized because of oxidation of Pt(0). This behavior was strongest with the nanocrystalline pore size and the ultrafine dispersion of Pt in tunnel dust (Palacios et al., 2000). In a review paper Ek, Morrison & Rauch (2004) stated that Pd is more and Rh is less bioavailable than Pt.

A new development in the catalyst industry is the “intelligent catalyst”, a palladium-containing perovskite catalyst with the self-regenerative function of Pd (Tan et al., 2006; Tanaka et al., 2006). The coating Pd particles of this catalyst remain nanosized (range of 1 nm or less) in contrast to the Pd particles on Al₂O₃, which increase in size up to 120 nm (Tan et al., 2006; Tanaka et al., 2006). This development was a reaction to the increasing demand on Pd, needed to achieve the emission reduction goals.

6.4.2 Coated diesel particulate filters and fuel borne catalysts

Diesel particulate filters are applied to control emissions of particulate matter from diesel engines. In Switzerland filters are required by law for busses, construction machines on construction sites and vehicles for underground or indoor use (Mayer, Ulrich, 2007, personal communications). For retrofitting of these vehicles only proofed filter systems are permitted (Mayer, 2006a) while for new vehicles the VERT¹ conditions have to be met. To meet the demands on particulate matter emissions retrofitting is afforded to a number of vehicles without authoritative filter regulation and in car manufacture today most manufacturers offer vehicle models with diesel particulate filter as original equipment (Blessing, 2007, personal communication). For heavy duty vehicles (>3,500 kg) without particulate filter obligation, often a Denox catalytic converter is used instead of a particulate filter to meet the emission guidelines (Jenk, 2007, personal communication).

During vehicle use soot is deposited on the particulate filter and regeneration occurs when a given backpressure is reached after several operating hours and mileage, respectively. By filter systems with onboard regulation, the soot on the filter is burned by the system itself and a manual cleansing of the particulate filter is only needed after about 80,000 km because of the ashes on the filter which are not burnable. Since around the year 2002 filter systems were developed using additives as fuel borne catalysts to lower the ignition temperature for filter regeneration and for two to three years systems with catalytic coatings on the particulate filter have been available (Ulrich, 2007, personal communication). Ashes recovered by cleansing of the filter are disposed in waste incineration plants so long as the amounts remain small (BAFU, 2006a).

Fuel borne catalysts

As fuel borne catalysts (FBC) the metals cerium, iron, copper, strontium, and platinum are applied. All of them but cerium are added as organo-metallic components. Cerium is used as colloidal cerium oxide clusters in the nanoparticulate size range. Common to all of these additives is their even

¹ VERT: „Verminderung der Emissionen von Realmaschinen im Tunnelbau“ (egl. reduction of diesel engine emissions at tunnel construction sites)

distribution which guarantees their function. All additives are in form of metal oxides when entering the environment.

Due to the properties of additives (e.g., reduction of pinking at petrol engines, reduction of soot building in motors and heating installations or keep clean of motors; Mayer, 2007, personal communication), they are widely used in diesel as well as in petroleum and fuel oils. But when no particle filters were installed, the total amount of additives would be emitted to the environment. In this thesis application of fuel additives without filter is not considered because no data were found. Nevertheless, a great influence on the amount of potentially emitted nanoparticles could be attributed to them. In a web search most products that were found seemed to consist of organic ingredients and a widely used one was urea¹. One product that was found contained cerium oxide, reducing fuel consumption². For another cerium oxide containing product, the usage as fuel additive without filter was clearly rejected because of its negative influence on the environment³ (Lemaire, 1999).

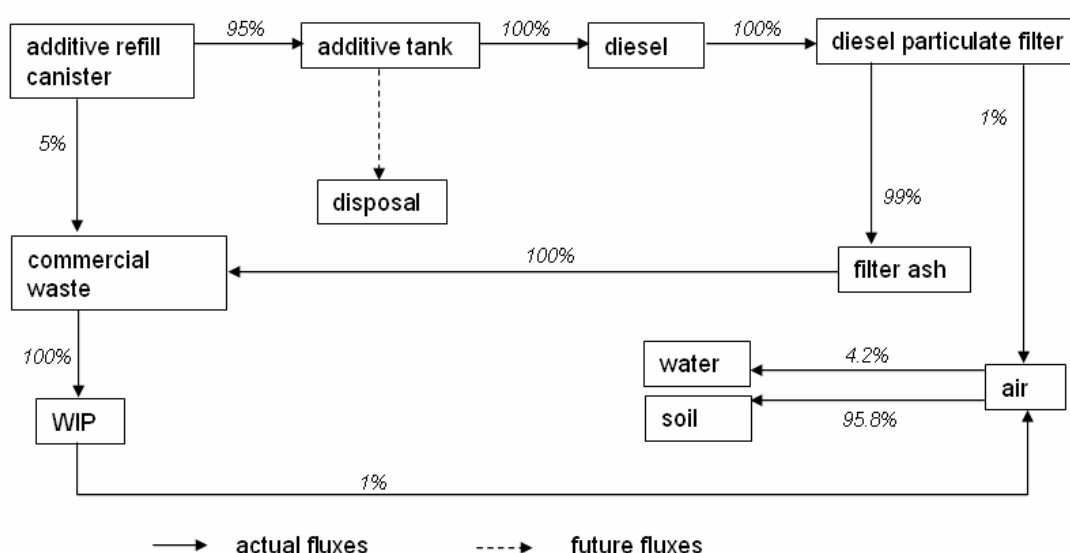


Figure 6.3: Flow chart for nanoparticles fluxes from fuel additives to the soil.

For modelling the fluxes of nanoparticles released from fuel borne catalysts to the soil (see Figure 6.3), the following assumptions were made:

- 5% of the additives remain in the refill canisters and are disposed,
- no FBC get lost on the way between additive tank and diesel particulate filter,

¹ AdBlue, BASF, <http://www.adblue-swiss.ch/>

² Envirox, Oxonica, http://www.oxonica.com/energy/energy_home.php

³ Eolys, Rhodia, http://www.rhodia-ec.com/images/events_press/documentation_pdf/eolys_all.pdf

- no emissions occur during the filter cleansing process (with air or water),
- the total amount of the released additives are deposited on the water or soil surface,
- no vehicles with FBC regenerated filter are disposed at the time (because of the age of these filters only accident vehicles may be disposed).

At the time 85% of the cars equipped with filters use FBC for regeneration (Mayer, 2006b). The other 15% have installed most likely systems of coated filters combined with oxidation catalysts. For heavy duty vehicles regeneration systems with electrical heating of the filter seem to be common, especially for busses and ships, but detailed information was not received. Therefore the distribution was assumed to be similar to the distribution of approved filter systems in the VERT-list (Mayer, 2006a), 29.7% each for systems with catalytic coating and additives. The total amount of additives used for DPF regeneration (FBC consumption_{tot}) was calculated with the following equations 6-3 and 6-4:

$$\begin{aligned} \text{FBC consumption}_{\text{tot}} = & \text{FBC consumption}_{\text{passenger car}} + \text{FBC consumption}_{\text{heavy duty onroad}} \\ & + \text{FBC consumption}_{\text{heavy duty offroad}} \end{aligned} \quad \mathbf{6-3}$$

where

$$\text{FBC consumption}_x = \text{diesel consumption}_{\text{DPF } x} * \text{conc FBC}_x * \text{rate}_{\text{DPF } x \text{ with FBC}} \quad \mathbf{6-4}$$

where

FBC consumption_{tot} is the total amount of FBC used for DPF regeneration in Switzerland in 2006 [kg/y];

FBC consumption_{passenger car} is the amount of FBC used by passenger cars [kg/y];

FBC consumption_{heavy duty onroad} is the amount of FBC used by heavy duty onroad vehicles [kg/y];

FBC consumption_{heavy duty offroad} is the amount of FBC used by heavy duty offroad vehicles [kg/y];

x means passenger car, heavy duty onroad and heavy duty offroad, respectively

diesel consumption_{DPF x} is the part of diesel consumed by passenger cars, heavy duty onroad vehicles and heavy duty offroad vehicles, respectively, with DPF [kg/y];

conc FBC_x is the concentration of FBC in fuel used for filter regeneration in passenger cars, heavy duty onroad vehicles and heavy duty offroad vehicles, respectively [mg/kg];

rate_{DPF x with FBC} is the part of DPF used by passenger cars, heavy duty onroad vehicles and heavy duty offroad vehicles, respectively, regenerated with FBC []

Where *rate*_{DPF passenger car with FBC} is 85% and *rate*_{DPF heavy duty onroad/offroad with FBC} 29.7%, and values for diesel consumption_{DPF x} are shown in chapter 5.2 with the according derivation. For *conc FBC*_{passenger car} the values 10 mg/kg and 12 mg/kg were used for the realistic and the worst case scenario,

respectively, for $conc\ FBC_{heavy\ duty\ onroad/offroad}$ 20 mg/kg and 50 mg/kg, respectively. These values for additive concentrations were chosen based on the data shown in Table 6.6.

Table 6.6: Data on additive concentrations added to diesel fuel.

description	additive concentration	source
cerium additive	50 ppm	Khair, Lemaire & Fischer (2000, in HEI, 2001)
additive	10-50 µg/g	Heeb et al. (2005)
FBC reduction	From 25 mg/kg to <10 mg/kg	Mayer (2006b)
additive	10-50 mg/kg	Ulrich & Wichser (2003)
dosing Eolys 2 (Rhodia) passenger cars	10-12 mg/kg Ce/Fe	Rocher (2007, personal communication)
dosing Eolys 2 (Rhodia) heavy duty and retrofit	20 mg/kg	Rocher (2007, personal communication)
dosing Eolys (Rhodia) busses	50 mg/kg	Lemaire (1999)

For additives, several values were reported about the release of so called secondary emissions through the filter to the environment. They range from 0.001 to 0.01% for cerium oxide and cerium iron mixed additives (Heeb, 1998, in HEI, 2001; Heeb et al., 2005; Lemaire, 1999; Mayer, 2007, personal communication; Ulrich & Wichser, 2003) and only few larger values were found (Heeb, 1998; Ulrich & Wichser, 2003). As for cars cerium oxide is commonly used and guidelines restrict the secondary emissions of most other vehicle categories to 1% (Mayer, 2006a), 1% was chosen as an adequate emission rate.

It was assumed that all particles released by vehicles with FBC regenerated DPF are evenly deposited on the Swiss soil surface. The results are shown in Table 6.7.

Table 6.7: Realistic and worst case scenario for total amounts of nanoparticles released to soils and yearly concentration increase expected in soils from fuel borne catalysts (FBC).

	realistic scenario	worst case scenario
total amount of FBC used [kg/y]	1000	2100
total amount of FBC released [kg/y]	10	21
Yearly concentration increase of FBC in Switzerland [µg/m ³ /y]	0.0012	0.0026
Yearly concentration increase of FBC in Switzerland [µg/kg/y]	$9.2 \cdot 10^{-7}$	$2 \cdot 10^{-6}$

According to information on the market share and the amount of the fuel born catalyst Eolys sold in Switzerland by Rhodia (Rocher, 2007, personal communication), the whole amount of additives used in Switzerland should be higher than what resulted from the model. There may be two rea-

sons for the difference: The number of filters or the concentration of additives may be larger or additives could be used otherwise, for example in petrol engines, in ship motors or heating installations.

As the installation of diesel particulate filter is a newer development, the model in Figure 6.3 is a temporary one. Changes will come with respect to more efficient, longer lasting filters, and filters using less metal resources. Also a trend to coated filters is recognizable.

Changes will also occur in the application of cerium and other rare earth elements. These elements are currently applied in lighters, carbon arc lamps, glass additives, ceramics, abrasives, permanent magnets, and in the washcoat of three-way catalysts (Hedrick, 1998, in HEI, 2001; Winkler, personal communication, 2007) and the demand for rare earth metals is expected to continue increasing (HEI, 2001). Future uses may be for fuel cells, and nanoparticulate rare earth may be used more often.

The distribution of fuel borne catalyst emission is modelled evenly on Swiss surface. But in reality higher concentrations can be expected close to roadways as it is shown by Ward (1990, in HEI, 2001) who measured concentrations of cerium of 38 mg/kg as background level in Great Britain, and concentrations of 47 to 136 mg/kg near a motorway with heavy traffic. The size of particles released through diesel particulate filters is expected of the same size range as measured by Pattas et al. (1992, in HEI, 2001) on the filter inlet area, 20 to 150 nm, for particles deposited near the source (Samaras, 1994, in HEI, 2001). Pattas et al. (1992, in HEI, 2001) observed cerium oxide particles in the filter inlet area which had a highly aggregated composition. Cerium is expected to be present in the environment as cerium oxide and smaller amounts as phosphates and sulphates (HEI, 2001).

Cerium oxide deposited on soil is most likely taken up by direct soil ingestion. A review of studies investigating toxicity of orally administered cerium concluded that cerium is poorly absorbed by the digestive tract and therefore exposition to cerium by food is not likely to be a major concern (HEI, 2001). Two newer studies showed toxicity of cerium oxide on cultured human lung cancer cells and gram-negative bacteria, respectively (Lin et al., 2006; Thill et al., 2006).

Catalytic coatings

In catalytic coatings of diesel particulate filters vanadium, wolfram, palladium, and platinum are commonly used (Ulrich, 2007, personal communication) with documented particle size distribution between 20 and 40 nm (Villani et al., 2006b). Abrasion per area might be in a similar range than the emissions from catalytic converters, but the total filter area is much larger due to the larger filter size (Ulrich, 2007, personal communication). In filter systems with catalytic coatings used by cars, usually an oxidation catalyst is installed upstream of the particulate filter (Joubert & Seguelong, 2004; Blessing, 2007, personal communication). Data found on metal load and volume of coated diesel particulate filters are shown in Table 6.8.

Table 6.8: Data of metal load and volume of coated diesel particulate filters (from Joubert & Seguelong, 2004). DOC = diesel oxidation catalyst; PGE = platinum group elements; DPF = diesel particulate filter; 1 ft = 30.48 cm.

description	metal load	volume
PGE on catalytic coating of cars	30-40 g/ft ³	2.5 L
PGE on catalytic coating of cars	< 90 g/ft ³	4.7 L
Pt-loaded DOC upstream of DPF	> 120 g/ft ³	2.5 L
DOC	90-140 g/ft ³	
Pt-DPF wash coating	30-90 g/ft ³	

As described above it is assumed, that 15% of all passenger cars equipped with particulate filter are regenerated with catalytic coating ($rate_{passenger\ car\ with\ CC} = 0.15$) and for heavy duty vehicles it is approximated that filter equipment is equal distributed to the filter systems proved which were listed in the VERT filter list, $rate_{DPF\ heavy\ duty\ with\ CC} = 0.297$ (Mayer, 2006a).

No data were found on the abrasion rate of catalytic coating and therefore the same strategy was followed that was used to calculate the emissions from catalytic converters (see chapter 6.4.1 and Figure 6.4) with a release rate, $rate_{emitted}$, of 1% similar to the release of fuel borne catalyst.

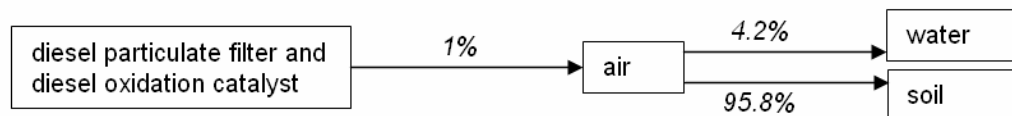


Figure 6.4: Flow chart for emissions of catalytic coating to the soil.

The following equations 6-5, 6-6 and 6-7 were used to calculate the emissions of catalytic coatings to the environment ($CC_{emitted}$):

$$CC_{emitted} = CC_{emitted\ passenger\ car} + CC_{emitted\ heavy\ duty} \quad 6-5$$

$$CC_{emitted\ passenger\ car} = mileage_{CC} / age_{CC} * CC_{passenger\ car\ tot} * rate_{emitted} \quad 6-6$$

$$CC_{emitted\ heavy\ duty} = rate_{DPF\ heavy\ duty\ with\ CC} * (diesel\ consumption_{DPF\ heavy\ duty\ onroad} + diesel\ consumption_{DPF\ heavy\ duty\ offroad}) * CC_{emitted\ passenger\ car} / rate_{passenger\ car\ with\ CC} * diesel\ consumption_{DPF\ passenger\ car} \quad 6-7$$

where

$CC_{emitted}$ is the total amount of catalytic coating released to the environment [kg/y];

$CC_{\text{emitted passenger car}}$ is the amount of catalytic coating released by passenger cars [kg/y];

$CC_{\text{emitted heavy duty}}$ is the amount of catalytic coating released by heavy duty vehicles [kg/y];

mileage_{CC} is the mileage driven with vehicles with coated DPF [km/y];

age_{CC} is the mileage of an ordinary coated DPF during service life [km]

$CC_{\text{passenger car tot}}$ is the whole amount of catalytic coatings used in DPF of passenger cars in Switzerland [kg];

$\text{rate}_{\text{emitted}}$ is the part of catalytic coating emitted [];

$\text{rate}_{\text{DPF heavy duty with CC}}$ is the part of DPF of heavy duty vehicles regenerated by catalytic coating [];

$\text{diesel consumption}_{\text{DPF heavy duty onroad}}$ is the total amount of diesel fuel used by heavy duty onroad vehicles with DPF [kg];

$\text{diesel consumption}_{\text{DPF heavy duty offroad}}$ is the total amount of diesel fuel used by heavy duty offroad vehicles with DPF [kg];

$\text{rate}_{\text{passenger car with CC}}$ is the part of passenger cars with DPF regenerated with catalytic coating [];

$\text{diesel consumption}_{\text{DPF passenger car}}$ is the amount of diesel fuel used by passenger cars with DPF [kg]

It was assumed that coated diesel particulate filters reach the same age than catalytic converters, $\text{age}_{CC} = 80,000$ km. For the realistic scenario the metal load of the coating, $CC_{\text{passenger car tot}}$, was assumed to be 0.0141 kg, corresponding to a 2.5 L DPF with 40 g/ft³ platinum load linked with a 2.5 L DOC with 120 g/ft³ platinum load. For the worst case scenario it was assumed that the filter system was coated with 0.0273 kg Pt, corresponding to the load expected for a 4.7 L DPF with 90 g/ft³ Pt linked with a DOC with 140 g/ft³ (see Table 6.8). All other parameters were derived in chapter 5.2. All results are assembled in Table 6.9.

Table 6.9: Realistic and worst case scenario for total amounts of nanoparticles released from catalytic coatings (CC) to soils and yearly concentration increase expected in soils.

	realistic scenario	worst case scenario
total amount of CC used [kg/y]	127	244
total amount of released CC [kg/y]	1.3	2.4
yearly concentration increase of CC in Switzerland [$\mu\text{g}/\text{m}^3/\text{y}$]	0.00015	0.00030
yearly concentration increase of CC in Switzerland [$\mu\text{g}/\text{kg}/\text{y}$]	$1.2 \cdot 10^{-7}$	$2.3 \cdot 10^{-7}$

Catalytic coatings for lowering the ignition temperature for soot oxidation are a newer development and accordingly research on appropriate material for washcoat and catalytic active substances is in progress. Tschamber et al. (2007) investigated recently two catalysts, Pt/Al₂O₃ and Ru/NaY, for soot oxidation and the results showed that Pt did not oxidise carbon while Ru lead to significantly better soot oxidation. Another study showed that Ru oxidizes soot also in the absence of NO_x at

temperatures where Pt remains inactive (Villani et al., 2006a). Ag was also investigated as an active catalytic agent with higher oxidation level of carbon black than Pt, both on Al₂O₃ substrate (Villani, Brosius & Martens, 2005). Ag is used in nitrated form and forms very tiny particles. Further potassium (An & McGinn, 2006; Nejar & Illan-Gomez, 2007) and cobalt (Sui, Yu & Zhang, 2007) were studied as potential catalytic active substances in diesel particulate filter regeneration.

6.4.3 Tyres

The main compounds of tyres are rubber, filler and materials for stability like steel, rayon or nylon (RVS, 2007, personal communication). Tyres of vehicles for offroad use contain more steel than tyres for road wear (Wertstoff-Börse GmbH, 2003). As filler, carbon black and silica are most common. In road wear, the amount of carbon black in the filler is higher to ensure good grip. A higher amount of silica in the tyre treads improves tear resistance and creates less lumping and more resistance to cutting (Sellers & Toonder, 1965, in Semaan et al., 2002). These are qualities wished for tyres used offroad. Furthermore, tyres contain additives such as softening agents and chemicals for vulcanization (sulphur and zinc oxide) (RVS, 2007, personal communication). The model composition of new and discarded tyres is shown in Table 6.10. Because tyre formulations have been secret, little is known on ingredients of tyre tread and several assumptions had to be made.

Table 6.10: Percentage of substances in new and discarded tyres.

	new tyre [%] (RVS, 2007, personal communication)	discarded tyre [%] (BAFU, 2006b)
rubber	48	47
steel	15	16.5
textiles	5	5.5
filler	22	21.5
carbon black ^a	18.42	18.85
silica ^a	3.15	3.08
zinc oxide	1	1
sulphur	1	1
additives	8	7.5

^a Division of filler into carbon black and silica (each 50%) for heavy duty offroad, agricultural and industrial vehicles.

Carbon black enhances tensile strength, modulus, abrasion and tear resistance of rubber (Studebaker, 1957, in Semaan et al., 2002). The carbon black particles used in tyre industries are in the range of 1 to 500 nm with a typical diameter of 20 to 26 nm (Semaan, Quarles & Nikiel, 2002).

Zinc oxide (ZnO) is used in the range of several nm to a few μm and its surface size has a big influence on vulcanization (Gent, 1992, in Semaan et al., 2002). During pyrolysis ZnO is partially transformed into solid ZnS (Aylón et al., 2007). Adachi & Tainosho (2004) measured an average size of $0.52 \mu\text{m}$ for ZnO particles in tyre dust. In a web review one supplier of nanoparticulate ZnO (nZnO) could be found arguing that cross-linking properties and wear depending properties get improved by use of nZnO in tyre rubber (Shanxi Four High Nanotechnology Company Limited).

One product was found in the web with ultrafine silica (nSiO_2) as filler combined with ultrafine polymers¹. Polymers are not considered further as their employment is assumed to be an exception. SiO_2 on the other side is more likely used in a nanosized range. The silica used in tyres is fumed of silicon tetrachloride (Semaan et al., 2002). As silica is very stable under pyrolysis conditions it is likely that it is present unchanged in tyre dust (Aylón et al., 2007).

Emissions of nanoparticles from tyres are expected during use, recycling and disposal (see Figure 6.5). The emissions during use are mainly due to abrasion of tyre tread and consisting of rubber blend which may contain nanosized carbon black, silica, and zinc oxide. The degree of abrasion depends primarily on vehicle speed, whereby abrasion increases with increasing speed, but also on tyre composition and pavement (Dahl et al., 2006). Per year, approximately 5,000 t (realistic scenario) to 10,443 t (maximal scenario) of tyre dust is produced in Switzerland (see Table 6.11). The realistic scenario was calculated from the average tyre composition of new and discarded tyres and the average amount of discarded tyres in Switzerland of 50,000 to 52,000 t of tyres per year (BAFU, 2006b; RVS, 2007, personal communication) with equations 6-8 to 6-12. The worst case scenario calculated with equations 6-13 to 6-16 depends on the only mass related data found on abrasion, 0.07 g/km for passenger cars and 1 g/km for heavy duty vehicles (van Basshuysen & Schäfer, 2007). Emissions during use of other tyre parts than tyre tread are assumed to be negligible.

$$\text{tyre abrasion}_{\text{realistic}} = \text{tyres}_{\text{new tot}} - \text{textiles} - \text{steel} - \text{rubber}_{\text{old}} \quad \mathbf{6-8}$$

where

$$\text{textiles} = \text{rate}_{\text{textiles old}} * \text{tyres}_{\text{old tot}} \quad \mathbf{6-9}$$

$$\text{steel} = \text{rate}_{\text{steel old}} * \text{tyres}_{\text{old tot}} \quad \mathbf{6-10}$$

$$\text{rubber}_{\text{old}} = \text{tyres}_{\text{old tot}} - \text{steel} - \text{textiles} \quad \mathbf{6-11}$$

$$\text{tyres}_{\text{new tot}} = (\text{textiles} + \text{steel}) * 5 \quad \mathbf{6-12}$$

where

tyre abrasion_{realistic} is the amount of tyre tread abraded in the realistic scenario in Switzerland per year [t/y];

¹ S.drive, Yokohama Tire, <http://www.yokohama.ca/en/article.php?story=20070328082246174>

$tyres_{new\ tot}$ is the weight of the discarded tyres in new conditions [t/y];

$textiles$ is the amount of textile material in the tyres discarded in Switzerland per year [t/y];

$steel$ is the amount of steel in the tyres discarded in Switzerland per year [t/y];

$rubber_{old}$ is the amount of rubber material in the tyres discarded in Switzerland per year [t/y];

$rate_{textiles\ old}$ is the part of the discarded tyres consisting of textile materials [];

$tyres_{old\ tot}$ is the amount of tyres discarded in Switzerland per year [t/y];

$rate_{steel\ old}$ is the part of the discarded tyres consisting of steel []

Thereby $tyres_{old\ tot}$ is 50,000 t, $rate_{steel\ old}$ is 0.165, and $rate_{textiles\ old}$ is 0.055.

$$\begin{aligned} tyre\ abrasion_{worst\ case} = & tyre\ abrasion_{passenger\ car} + tyre\ abrasion_{heavy\ duty\ onroad} \\ & + tyre\ abrasion_{heavy\ duty\ offroad} \end{aligned} \quad \mathbf{6-13}$$

where

$$tyre\ abrasion_{passenger\ car} = rate_{passenger\ car} * mileage_{private\ traffic} \quad \mathbf{6-14}$$

$$tyre\ abrasion_{heavy\ duty\ onroad} = rate_{heavy\ duty\ onroad} * mileage_{heavy\ duty\ onroad} \quad \mathbf{6-15}$$

$$\begin{aligned} tyre\ abrasion_{heavy\ duty\ offroad} = & rate_{heavy\ duty\ offroad} \\ & * diesel\ consumption_{heavy\ duty\ offroad\ tot} / diesel\ consumption_{heavy\ duty\ offroad} \end{aligned} \quad \mathbf{6-16}$$

where

$tyre\ abrasion_{worst\ case}$ is the amount of tyre tread abraded in the worst case scenario in Switzerland per year [t/y];

$tyre\ abrasion_{passenger\ car}$ is the amount of tyre tread of the worst case scenario abraded by passenger cars [t/y];

$tyre\ abrasion_{heavy\ duty\ onroad}$ is the amount of tyre tread of the worst case scenario abraded by heavy duty onroad vehicles [t/y];

$tyre\ abrasion_{heavy\ duty\ offroad}$ is the amount of tyre tread of the worst case scenario abraded by heavy duty offroad vehicles [t/y];

$rate_{passenger\ car}$ is the tyre material abraded per km of passenger cars [t/km];

$mileage_{private\ traffic}$ is the mileage driven by private private traffic [km/y];

$rate_{heavy\ duty\ onroad}$ is the tyre material abraded per km of heavy duty onroad vehicles [t/km];

$mileage_{heavy\ duty\ onroad}$ is the mileage driven by heavy duty onroad vehicles [km/y];

$rate_{heavy\ duty\ offroad}$ is the tyre material abraded per km of heavy duty offroad vehicles [t/km];

$diesel\ consumption_{heavy\ duty\ offroad\ tot}$ is the total amount of diesel fuel used by heavy duty offroad vehicles [t/y];

$diesel\ consumption_{heavy\ duty\ offroad}$ is the amount of diesel fuel used for a km by heavy duty offroad vehicles [t/km]

Thereby $rate_{passenger\ car} = 0.07\ g/km$, $rate_{heavy\ duty\ onroad} = 1\ g/km$, $rate_{heavy\ duty\ offroad} = 0.5\ g/km$, and $diesel\ consumption_{heavy\ duty\ offroad} = 0.3\ L/km$.

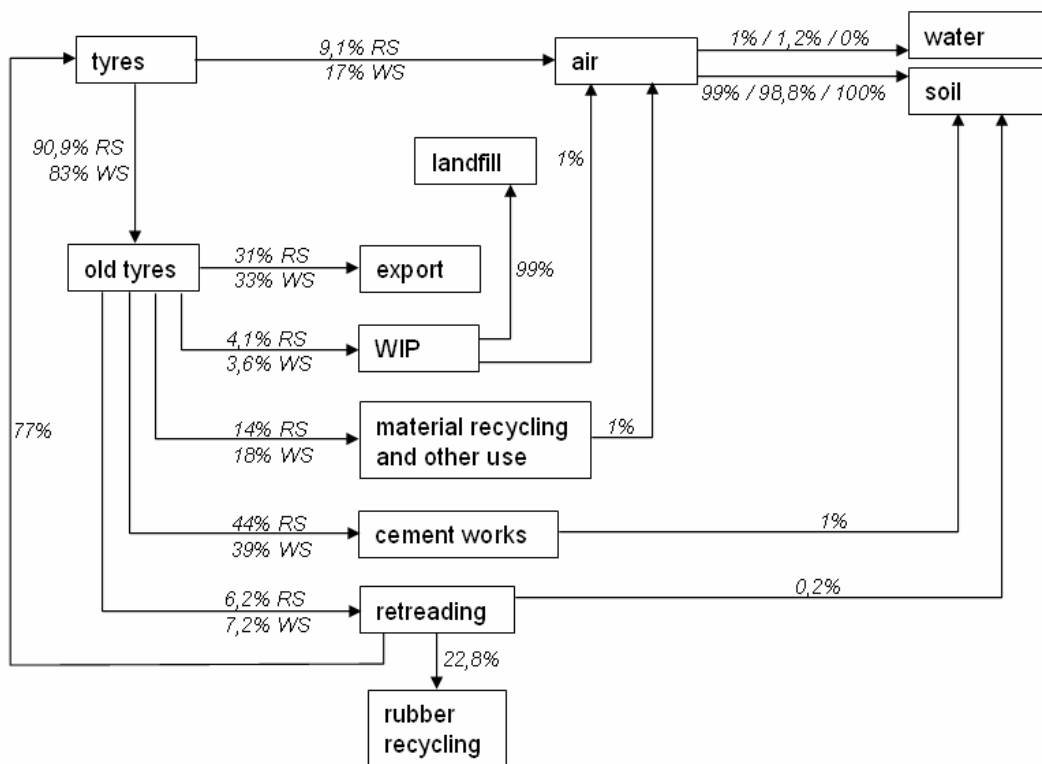


Figure 6.5: Flow chart for emissions of nanoparticulate tyre material to the soil. RS = realistic scenario; WS = worst case scenario; three numbers mean carbon black / nano zinc oxide / nano silica.

The nanoparticulate part of tyre abrasion is calculated with equations 6-17 to 6-19.

$$nZnO = rate_{nZnO} * amount_{ZnO} * rate_{material\ saving} \quad 6-17$$

$$nSiO_2 = rate_{nSiO_2} * rate_{offroad+agricultural+industrial\ vehicles} * rate_{silica} * amount_{SiO_2} \quad 6-18$$

$$CB = (1 - rate_{offroad+agricultural+industrial\ vehicles} + rate_{offroad+agricultural+industrial\ vehicles} * rate_{silica}) * amount_{CB} \quad 6-19$$

where

$nZnO$ is the amount of $nZnO$ in abraded tyre tread [t/y];

$rate_{nZnO}$ is the nanosized part of ZnO [];

$amount_{ZnO}$ is the total amount of ZnO abraded [t/y];

$rate_{material\ saving}$ is the ZnO savings by application of $nZnO$ instead of bulk sized ZnO [];

$nSiO_2$ is the amount of $nSiO_2$ in abraded tyre tread [t/y];

$rate_{nSiO_2}$ is the nanosized part of SiO_2 [];

$rate_{offroad+agricultural+industrial\ vehicles}$ is the part of the tyre tread abraded by offroad, agricultural and industrial vehicles [];

$rate_{silica}$ is the part of the whole filler material consisting of silica [];

$amount_{SiO_2}$ is the total amount of SiO_2 abraded [t/y];

CB is the amount of CB in abraded tyre tread [t/y];

$amount_{CB}$ is the total amount of carbon black abraded [t/y]

Thereby $rate_{nZnO}$ and $rate_{nSiO_2}$ are assumed to be 0.01 and 0.1, respectively, and $rate_{material\ saving}$ is 0.1 as 90% of ZnO can be saved due to nanoparticulate ZnO (RVS, 2007, personal communication). The amounts of ZnO , SiO_2 , and CB in tyre abrasion were calculated with the information in Table 6.10 and are 63 and 130 kg/y for ZnO , 200 and 410 t/y for SiO_2 , and 1,200 and 2,500 t/y for CB for realistic and worst case scenario, respectively. As described above, SiO_2 is usually used in tyres for offroad use and for that $rate_{offroad+agricultural+industrial\ vehicles} = 0.29$ is included, the fraction of tyre abrasion by agricultural, industrial and offroad vehicles. For all these vehicles it is assumed that half of CB is substituted for silica ($rate_{silica} = 0.5$).

As the most important disposal routes BAFU (2006b) and RVS (2007, personal communication) named the use as alternative fuel in cement works, retreading, material recycling, and the disposal in waste incineration plants. In the amount referred to by BAFU (2006b) and RVS (2007, personal communication), disused tyres which fulfil the conditions of Swiss law to be further used as second hand tyres, are included, too, but this fact is not considered in the calculation as it would not influ-

ence the results much. Profile tyres are mostly contained in the amount of 15,000 to 18,000 t of tyres exported (estimation of the year 2001; Hauser, 2007, personal communication) and therefore leaving the system boundary of this model. Disposal in landfills is forbidden in Switzerland, and will soon be forbidden in the European Union as well (Council Directive 1999/31/EC). Calculations of emissions due to the following discarding processes are similar calculated as shown for tyre abrasion and all results are assembled in Table 6.11.

During storage of waste tyres nanoparticulate emissions caused of weather impacts with adjacent dislocation via water or air are expected. These emissions are assumed to be of little importance and not considered further.

In Switzerland 3,000 to 4,000 t of discarded tyres are retreaded per year (estimation of the year 2001; Hauser, 2007, personal communication). Especially for highly used heavy duty tyres retreadment is a common habitude. Retreads cause the same emissions as new tyres during use and these are considered implicitly in annual abrasion. For tyre retreading the old rubber material is removed first and small injuries at the carcass are sanded, producing rubber scraps of 1 to 5 mm (Zehnder, 2007, personal communication). These scraps are sucked off and supplied to material recycling, e.g. for rubber mats, sports fields or pavement (Wiederkehr, Zehnder, 2007, personal communications). No relevant emissions to the environment are expected by retreading companies because of a filter (Wiederkehr, Zehnder, 2007, personal communications). Further, rubber compounds used in tyre industry must not lead to particulate matter emissions during use and consequently during retreading, too (Wiederkehr, 2007, personal communication). For calculation it was assumed that the same amount that has been abraded is removed for retreading (700 t for realistic and 900 t for worst case scenario) and 1% of this removed material is released to the environment.

Emissions from cement works are not expected because of the high temperatures (1,450°C) during sintering. 21,326 t old tyres (cemsuisse, 2006) were combusted at 1,000°C. The dust generated during the combustion process is mixed with the raw mix and is sintered. Particular emissions measured in the flue gas are 5 mg/Nm³ but these do not contain particles of old tyres (Widmer, 2007, personal communication). Before combustion the material has probably to be shredded to small pieces and for this process an emission rate of 1% was assumed.

As mentioned in chapter 5.1, emissions of waste incineration plants to the environment are confined to emissions to the air, approximately 1% of the nanoparticulate fraction or less. The combustion temperature of WIPs (> 850°C) leads to complete combustion of the rubber material, so that the nanoparticulate fraction at the end of the combustion process is composed of silica and possibly ZnO. 2,000 t of old tyres are combusted per year in Switzerland (estimation of the year 2001; Hauser, 2007, personal communication). It is assumed that no particles get lost inside the WIP and nSiO₂ and nZnO were emitted to the air as free nanoparticles, aggregated or bound to other particles.

Of 7,000 to 10,000 t of discarded tyres nothing is known on their further fate (estimation of the year 2001; Hauser, 2007, personal communication). A part of it will be recycled to rubber granulate and powder as there is one fabricating tyre granulate in Switzerland (Hauser, 2007, personal communication). For the calculation an emission rate of 1% was assumed.

Table 6.11: Realistic (RS) and worst case (WS) scenario for total amounts and concentrations of carbon black (nCB), nanosized silica (nSiO₂), and nanosized zinc oxide (nZnO) in tyre abrasion and emissions during disposal processes.

	nCB emitted [t/y]		nZnO emitted [t/y]		nSiO ₂ emitted [t/y]	
	CB RS	CB WS	nZnO RS	nZnO WS	nSiO ₂ RS	nSiO ₂ WS
tyre abrasion	1,200	2,500	0.063	0.13	20	41
WIP ^a	0	0	2.5*10 ⁻⁴	2.5*10 ⁻⁴	0.062	0.062
cement works ^a	39	39	0.0029	0.0029	0.66	0.66
retreading	1.3	1.7	8.8*10 ⁻⁵	1.1*10 ⁻⁴	0.022	0.028
unknown	13	18	8.8*10 ⁻⁴	0.0013	0.22	0.31
total	1,253.3	2,558.7	0.067118	0.13456	21.522	42.06

^a only one scenario, because there was only one value for the amount of tyres disposed.

For modelling soil contamination with nanoparticulate emissions of tyre material, it was assumed that the whole amount of material released is deposited on soil. Further the emission sources were divided into three categories with emissions to the whole surface area of Switzerland (WIP, unknown disposal, and abrasion of offroad, agricultural and industrial vehicles), emissions near roads (tyre abrasion without offroad, agricultural and industrial vehicles), and punctual soil contamination (cement works, retreading). The reason for that is the large size of particles emitted by tyre abrasion and fabrication of tyre scraps. All results are shown in Table 6.12.

For modelling the deposition around the eight cement works in Switzerland, deposition within a radius of 500 m was assumed, resulting in an area of 6,283,184 m² and a soil mass of 8,168,139,200 kg. Probably there are more retreading companies and therefore the concentrations of tyre material around them are much smaller and possibly old tyres are delivered to cement works in scraps, yet. SiO₂ is in the model only used in offroad, agricultural, and industrial tyres and therefore no emissions occur on roads. The part of tyres containing silica is 29% (see equation 6-18 above).

Table 6.12: Yearly concentration increases and allocation of nZnO, nSiO₂, and nCB in soils. RS = realistic scenario; WS = worst case scenario.

	CB RS	CB WS	nZnO RS	nZnO WS	nSiO ₂ RS	nSiO ₂ WS
conc. soil ^a [$\mu\text{g}/\text{m}^3/\text{y}$]	25	50	0.0054	0.0060	2.4	5.0
conc. soil ^a [$\mu\text{g}/\text{kg}/\text{y}$]	0.19	0.38	$4.2 \cdot 10^{-6}$	$4.6 \cdot 10^{-6}$	0.0018	0.0038
conc. national roads ^b [$\mu\text{g}/\text{m}^3/\text{y}$]	7,300	15,000	0.34	0.71	0	0
conc. national roads ^b [$\mu\text{g}/\text{kg}/\text{y}$]	5.6	12	$2.6 \cdot 10^{-4}$	$5.5 \cdot 10^{-4}$	0	0
conc. other roads ^b [$\mu\text{g}/\text{m}^3/\text{y}$]	550	1,200	0.030	0.056	0	0
conc. other roads ^b [$\mu\text{g}/\text{kg}/\text{y}$]	0.42	0.92	$2.3 \cdot 10^{-5}$	$4.3 \cdot 10^{-5}$	0	0
conc. point sources ^c [$\mu\text{g}/\text{m}^3/\text{y}$]	?	31,000	?	2.3	?	520
conc. point sources ^c [$\mu\text{g}/\text{kg}/\text{y}$]	?	24	?	0.0018	?	0.4

^a Emissions of WIP, unknown disposal, and tyre abrasion offroad+agricultural+industrial; ^b Emissions of tyre abrasion less offroad+agricultural+industrial; ^c emissions of cement works and retreading

In addition to the recycling methods described above, two more recycling methods were found by literature and web review. A company in the European Union fabricates carbon black from discarded tyres (CBp Carbon Industries Inc, 2007) and a future use may be the production of multi-walled carbon nanotubes by injecting tyre powder into an electric arc (Murr et al., 2005). In the European Union discarding of used tyres in landfills will be forbidden soon (Council Directive 1999/31/EC), and this fact may lead to changes in allocation of scraped tyres. In Switzerland especially imports and exports may alter.

Tyre abrasion in Germany has been estimated to be between 55 and 657 kg/km/yr (Muschack, 1990). If compared with the model results the average abrasion of 70 to 140 kg/km/yr is within the range reported for Germany, whereby values are much higher for national roads and slightly lower for other roads.

For abraded tyre tread fragments, a mass based size distribution of 1 to 100 μm was reported by Schultz (1994) and Dahl et al. (2006) measured an average particle number diameter of 15 to 50 nm. The modelled emission allocation may therefore not represent reality, because a smaller mass fraction of tyre dust may get transported longer distances or remain airborne, although most of the particle mass is deposited near the source.

Zinc in tyre tread is mostly in the form of ZnO or ZnS and only a small part forms chelates with accelerators (Fauser et al., 1999). In tyre wear debris zinc is multiangular and has a diameter of 1 μm or less (Adachi & Tainosho, 2004). The fate and effect of tyre zinc in soils was investigated in a soil column experiment by Smolders & Degryse (2002). They concluded that zinc was released of tyre tread particles within a year, but leaching was not elevated compared to reference. Further they observed a higher nitrification potential which was attributed to higher pH levels in soils with tyre

debris. This findings support the observation of elevated zinc levels near traffic lanes by Sadiq et al. (1989). No evidence has been found that nZnO behaves in a similar way in soils.

nSiO₂ and nZnO have antibacterial properties producing reactive oxygen species (Adams et al., 2006b) and therefore sever ecosystem health implications are feared. Studies on (nanoscale) ZnO and SiO₂ in water suspension showed toxic effects on bacteria and eukaryotes, increasing with particle concentration (Adams et al., 2006a; Adams et al., 2006b). Chang et al. (2007a) reported that silica nanoparticles were not cytotoxic at low dosages, but effects were observed at high dosages. And a study on particle size effects on toxicity showed milder effects on fibrogenesis in rats by nanosized than by microsized SiO₂ (Chen et al., 2004). Surface depending toxicity of quartz particles was demonstrated by Warheit et al. (2007) in a pulmonary assay on rats. For carbon black toxic effects are observed primarily by inhalation exposure (Gilmour et al., 2004; Koike & Kobayashi, 2006; Stone et al., 1998). Oxidative stress in alveolar epithelia cells and alveolar macrophages was revealed greater for smaller carbon black particles and it is assumed that it is mediated by surface functions of carbon black (Koike & Kobayashi, 2006; Stone et al., 1998).

Cornelissen et al. (2005) found that organic chemicals adsorb to carbon black and other carbonaceous materials partly resulting in much higher adsorption quantities than in soils without carbonaceous materials.

6.4.4 Automotive coatings, sealings and paints

Products of this category promise that no more water and dirt will adhere to automotive glass, paint, plastic and metal. Sealed surfaces shall get scratch resistant and existing scratches should become invisible. Further the car body will be protected against corrosion.

For conducting an emissions calculation two main difficulties occurred in this product group: First, a huge palette of products is offered by many small companies and a centralized sales market is lacking as products get sold on the internet, at tradeshowes and in shops with specialized or general assortment. Secondly, on the products or on the web sites, ingredients and mechanisms of action are seldom declared in a helpful way.

For all these reasons, the division of products containing nanoparticles or not was approximated by the method described in chapter 5.3 with the keyword *versiegelung* (egl. sealing, coating). Products considered were sealings, coatings or paints for automotive use.

The output of the web search was mainly composed of glass, paint, wheel, plastic and metal sealings for private use. Self-cleaning or easy-to-clean was a frequent attribute to the products, which was ascribed to the so called Lotus-effect (see chapter 6.5.1). Further, "nano" was used for ultra thin layers mostly of molecules adhesive on one side and hydrophobic on the other. Nanoparticles were mentioned in explanations of the lotus-effect and of products for scratch resistance. Explicitly declared were ceramic, polymers, diamonds, silver, silica, and glass nanoparticles, but rarely and without concentrations.

Conventional sealings contain Teflon, silicone, acryl, wax, and polymers for achieving the desired properties. Siloxane, silane, and permanon were also not treated as nanoparticles (for explanation see chapter 6.5.1).

The results of the web search were then used for an estimation of the total amount of nanoparticles contained in automotive sealings. Because of the broad product and sales range, official or centrally collected data of the product field were missing and therefore the total amount of these products applied in Switzerland was missing, too. Based on one declaration of the amount of easy to clean products for automotive paint and the market share of the company in this specific market sector (Koch, 2007, personal communication), a total amount of 400 t was calculated for Switzerland. Under the assumption that 8 m² of the surface of a car is painted ($area_{vehicle}$) and 13 g/m² of the sealing is applied ($sealing\ per\ m^2$) two times per year ($rate_{applications}$), 1.92 million vehicles were treated in Switzerland each year (see equation 6-20). If all these vehicles were treated with glass sealing (4 m² glass per vehicle, 8,6 g/m² sealing application) and wheel sealing (24 g/wheel sealing application), too, additionally 132 t of glass and 370 t of wheel sealing would be applied (calculation with equation 6-20). As the amount of sealing used, the average amount from all articles found (see annex 3) was taken.

$$\text{amount}_{\text{vehicles}} = \frac{\text{sealing}_{\text{paint or glass or wheel}}}{(\text{rate}_{\text{applications}} * \text{sealing per m}^2 \text{ or sealing per wheel} * \text{area}_{\text{vehicle}})} \quad \mathbf{6-20}$$

where

$\text{amount}_{\text{vehicles}}$ is the number of vehicles treated with sealing [y^{-1}];

$\text{sealing}_{\text{paint or glass or wheel}}$ is the amount of sealing used in Switzerland per year to seal paint, glass and wheels, respectively [t/y];

$\text{rate}_{\text{applications}}$ is the rate of applications per year [];

sealing per m^2 or sealing per wheel is the amount of sealing applied to a m² or a wheel [t/m^2 or $t/wheel$];

$\text{area}_{\text{vehicle}}$ is the area sealed [m^2] or the number of wheels []

The web search showed that 40% (realistic scenario) to 70% (maximal scenario) of these sealings contain nanoparticles ($rate_{NP}$) and 1% of the product weight is supposed to consist of nanoparticles ($concentration_{NP}$), as this concentration was declared by Koch (2007, personal communication) for one product. It thus follows with equation 6-21 that 2.6 to 4.5 t of nanoparticles were applied in sealings for automotive use.

$$NP_{tot} = (sealing_{paint} + sealing_{glass} + sealing_{wheel}) * rate_{NP} * concentration_{NP} \quad 6-21$$

where

NP_{tot} is the total amount of nanoparticles used in sealings [t/y];

$sealing_{paint}$ is the amount of sealing applied on paint [t/y];

$sealing_{glass}$ is the amount of sealing applied on glass [t/y];

$sealing_{wheel}$ the amount of sealing applied on wheels [t/y];

$rate_{NP}$ is the part of sealing containing nanoparticles [];

$concentration_{NP}$ is the concentration of nanoparticles in sealings [t/t];

A flow chart for nanoparticulate emissions is shown in Figure 6.6. According to an appraisal for one product containing $nSiO_2$ by Koch (2007, personal communication), the nanoparticles are abraded by water and air within half a year along with the cementing agent. For the emission calculation it is assumed that 20% remain on the vehicle, 30% go to the soil via air and 50% go to the soil by water runoff. Further it is estimated that 5% remain in the package and are disposed. Approximately half of the products found in the web are applied with spray (often polished with rag) and the other half as fluid (polished with rag) (data see annex 3). By application with spray 30 to 50% get lost to the environment (Koch, 2007, personal communication). For calculation it is assumed that 40% of the total amount of nanoparticles goes directly to the air. Thus, the resulting emissions to the soil are realistically 2.0 t and maximally 3.5 t of nanoparticles per year calculated with equations 6-22 to 6-25.

$$NP_{soil} = 0.8 * NP_{vehicle} + 0.958 * NP_{air} \quad 6-22$$

where

$$NP_{vehicle} = 0.55 * (NP_{tot} - NP_{WIP})/2 + 0.95 * NP_{tot}/2 \quad 6-23$$

$$NP_{air} = 0.4 * (NP_{tot} - NP_{wip})/2 + 0.01 * NP_{WIP} \quad 6-24$$

$$NP_{WIP} = 0.05 * NP_{tot} \quad 6-25$$

where

NP_{soil} is the amount of nanoparticles reaching soil [t/y];

$NP_{vehicle}$ is the amount of nanoparticles applied on vehicles [t/y];

NP_{air} is the amount of nanoparticles released to the air [t/y];

NP_{tot} is the total amount of nanoparticles used in sealings [t/y];

NP_{WIP} is the amount of nanoparticles incinerated [t/y]

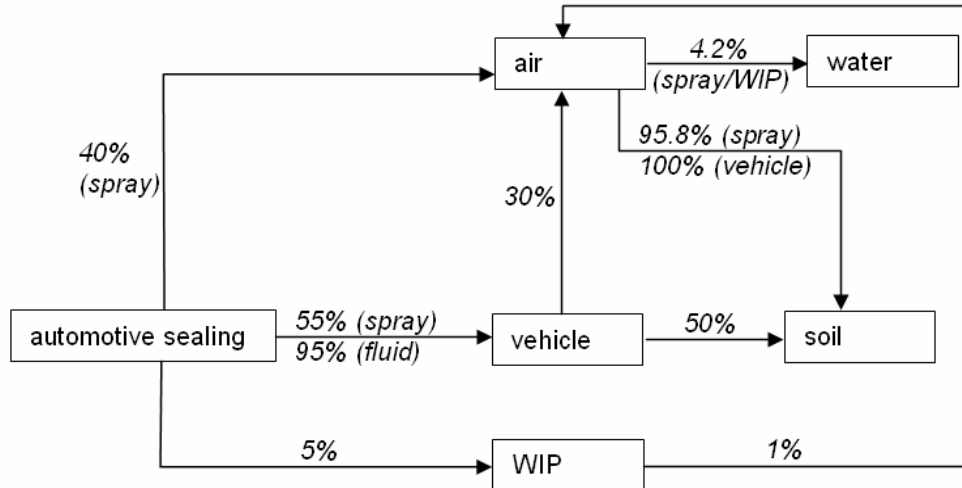


Figure 6.6: Flow chart for emissions of nanoparticulate automotive sealing to the soil.

When spraying liquid coating material on surfaces, droplets or aerosols are formed which may get transported over a certain distance. A main part will be deposited in vicinity, another part will be deposited far away and a third part will remain in air. The spreading is heavily depending on the kind of spray, the coated object and the application attitude. Nothing is known to the author about emissions from the coated vehicle. It is assumed that the hardened material gets released at surface areas where the coating is breached or adhesion get lost. Then the coatings flake off by wind, water or hits of pebbles or branches. A part might be released in soluble form. To simplify matters, it is assumed that all emissions reach the soil. A major part is therefore assumed to be deposited beside roads, the coating particles emitted of the vehicle, and a smaller part gets evenly distributed by air, the emissions by WIP and spray. The resulting concentrations in soil were calculated with equations 6-26 to 6-28:

$$\text{conc}_{\text{soil CH}} = \text{NP}_{\text{air}} / \text{area}_{\text{CH}} \tag{6-26}$$

$$\text{conc}_{\text{national roads}} = 0.8 * \text{NP}_{\text{vehicle}} * \text{rate}_{\text{national roads}} / \text{area}_{\text{bulk material}} + \text{conc}_{\text{soil CH}} \tag{6-27}$$

$$\text{conc}_{\text{other roads}} = 0.8 * \text{NP}_{\text{vehicle}} * \text{rate}_{\text{other roads}} / \text{area}_{\text{other roads}} + \text{conc}_{\text{soil CH}} \tag{6-28}$$

where

$\text{conc}_{\text{soil CH}}$ is the yearly increase in concentration of nanoparticles in Swiss soils [$\text{t}/\text{m}^3/\text{y}$]

NP_{air} is the amount of nanoparticles released to the air [t/y];

area_{CH} is the area of Switzerland [km^2];

$\text{conc}_{\text{national roads}}$ is the yearly increase in concentration of nanoparticles in soils beside national roads [$\text{t}/\text{m}^3/\text{y}$];

$\text{NP}_{\text{vehicle}}$ is the amount of nanoparticles applied on vehicles [t/y];

$\text{rate}_{\text{national roads}}$ is the part of the total mileage driven on national roads [];

$area_{\text{bulk material}}$ is the area on which bulk particles are distributed beside roads [km^2];

$conc_{\text{other roads}}$ is the yearly increase in concentration of nanoparticles in soils beside other roads [$\text{t}/\text{m}^3/\text{y}$];

$rate_{\text{other roads}}$ is the part of the total mileage driven on other roads [];

$area_{\text{other roads}}$ is the area beside other roads on which nanoparticles are distributed [km^2]

All results are shown in Table 6.13.

Table 6.13: Realistic and worst case scenario for total amounts of nanoparticles (NP) released from automotive coatings and yearly concentration increases expected in soils.

	realistic scenario	worst case scenario
total amount of coating used [t/y]	649	649
total amount of NP [t/y]	2.60	4.54
conc. of NP in Swiss soils [$\text{mg}/\text{m}^3/\text{y}$]	0.079	0.14
conc. of NP in Swiss soils [$\text{mg}/\text{kg}/\text{y}$]	$6.1 \cdot 10^{-5}$	$1.1 \cdot 10^{-4}$
conc. of NP at national roads [$\text{mg}/\text{m}^3/\text{y}$]	11	20
conc. of NP at national roads [$\text{mg}/\text{kg}/\text{y}$]	0.0085	0.015
conc. of NP at other roads [$\text{mg}/\text{m}^3/\text{y}$]	0.90	1.6
conc. of NP at other roads [$\text{mg}/\text{kg}/\text{y}$]	$6.9 \cdot 10^{-4}$	0.0012

Scratch resistant clear coats as they were applied during serial-production by DaimlerChrysler (Mercedes-Benz, 2007) might have a different emission pattern. These coatings are a part of automotive paint and may keep their function over the whole lifetime of the vehicle. To improve scratch resistance of automotive paint, four techniques are used, one of them containing nanoparticles (SiO_2 , aluminium oxide, barium sulphate) (Schulz, 2007). Also nanodiamonds are investigated for increasing the life of automotive paints and their emission pattern may be similar to scratch resistant clear coats (Vogt, 2004). According to Schrand et al. (2007), nanodiamonds are not cytotoxic.

6.4.5 Automotive light-weight construction

Nanocomposite materials offer the possibilities of weight savings and therefore energy savings. For example polymers can be loaded with inorganic nanoparticles (e.g., nanoclay, carbon nanotubes, carbon nanofibers), whereas much less filler is needed than in using conventional materials like glass fibres or graphite (DaimlerChrysler, 2007; Garcés et al., 2000; Lloyd & Lave, 2003). It is estimated, that nanocomposite plastic parts offer weight savings of 25% over highly filled plastics and as much as 80% over steel (Garcés et al., 2000). Further advantages are a better quality of the surface and of working properties (DaimlerChrysler, 2007). Approved properties desired by the

automotive industries like dimensional stability, stiffness and toughness do not get lost and are achieved with smaller amounts of nanoparticles than of bulk fillers (DaimlerChrysler, 2007; Garcés et al., 2000). The heat-distortion temperature seems to get higher for nanocomposite materials as in an example is shown (Garcés et al., 2000). And another advantage is the improved scratch and mar resistance of nanocomposites (Garcés et al., 2000), which is described more precisely in chapter 6.4.4.

Thermoplastic nanocomposites with nanoflakes are applied by General Motors Corp. for smaller automotive parts (Presting & König, 2003) and in Germany a project in the same area has been in work since two years, managed by DaimlerChrysler and promoted by the German Bundesministerium für Bildung und Forschung (DaimlerChrysler, 2007). These new light-weight materials are not yet used for exposed automotive parts and therefore today's potential emissions are assumed to be negligible.

6.5 Building materials and coatings

6.5.1 Coatings and sealings

Coatings

Surface coatings are made for protection of objects or for facilitating maintenance. The term “nano” is widely used in this field meaning ultra thin layers, nanoparticles or nanostructures, and nanoparticles refer to metals, metal oxides, ceramics, or silicone. The latter have hydrophobic properties and are well described in Kastien (2003). Silicones are compounds of silica and organic components of which two forms are used widely today, silanes and siloxanes. A silane is a singular molecule of a silane (SiH_4) with three alcoholic groups; a siloxane is composed of several silanes. Silanes are highly volatile and therefore often mixed with siloxanes, which have a less efficient penetration capability but lower vapour pressure. Siloxanes and silanes are not treated as nanoparticles here. Often named on the product description is the so called Lotus-effect, a self-cleaning effect originally observed on some plant leaves (Barthlott & Neinhuis, 1997). The adhesion of dirt is minimized by a nanostructured surface and the water takes the dirt with it (Nees-Institut, 2007). Often products with self-cleaning (Lotus-effect) or easy-to-clean effect are made of silicones. Products with Lotus-effect are nearly exclusively for exterior use (Sto, 2006).

According to Christinger (2007, personal communication) nanoscale silica gels (aerosil) have been used in paint manufacturing for many years. Sto (2006) mentioned that nanoscale silica gels as a new development for cementing technology are mostly used outdoors. nSiO_2 is also added in anti-graffiti paint.

TiO_2 is primarily used as white pigment. A newer development is its application for self-cleaning properties due to the UV-light interaction in the nanoparticulate size range. This effect is also observable in micro-sized TiO_2 , but nTiO_2 is clear and does not form a milky fog as micro-sized TiO_2 (Christinger, 2007, personal communication). Likewise nAg is used in paints for its biocidal effects and nZnO is possibly used for UV-protection of coated materials. Transparent Fe_2O_3 pigments with needles of 50 to 100 nm length and 2 nm width are applied in wood scumble to protect against UV-light (Verband der deutschen Lackindustrie e. V.). Also used for UV-protection are CaCO_3 particles of 4 to 8 nm size and carbon black as a black pigment (Christinger, 2007, personal communication).

Only little information was received on the nanoparticulate content of coatings. Therefore the approximation described in chapter 5.3 was taken to estimate the amounts of products containing nanoparticles. Of the product sites found in the web search with Google and the keyword *farb* (e.g. paint) 16.7% contained most likely products with nanoparticles and another 27.8% may contain nanoparticles, too. These results were taken for the realistic and the worst case scenario. As average concentration of nanoparticles in products, 0.5% was taken, assumed from declarations found in the web.

The VSLF (2006) estimated that the Swiss inland market volume in 2005 was 87,290 t for paint and lacquer for construction, industrial and corrosion paint, wood paint, and wood protection and care products. Because no declaration was made whether the paint was for interior or exterior use half of the paint was assumed to be for exterior use. With equation 6-29, 36 and 97 t of nanoparticles were contained in paints on the Swiss market for the realistic and the worst case scenario, respectively.

$$NP_{\text{tot}} = \text{paint}_{\text{tot}} / 2 * \text{rate}_{\text{NP}} * \text{conc}_{\text{NP}}$$

6-29

where

NP_{tot} is the total amount of nanoparticles applied in paints in Switzerland [t/y];

$\text{paint}_{\text{tot}}$ is the total amount of paint used in Switzerland per year [t/y];

rate_{NP} is the part of paint containing nanoparticles [];

conc_{NP} is the average concentration of nanoparticles in paint [kg/kg]

In Figure 6.7 the expected mass fluxes are charted. For the time until building surfaces are painted again, 20 years was used, based on a declaration by Christinger (2007, personal communication) that facades are impregnated all 10 to 20 years. For the age of buildings 100 years was taken. Furthermore, it was assumed that during surface preparation all abraded coating material is disposed in the WIP, in dry form or as slurry, and all but 5% of the coating material is released within 20 years. Emissions to the air were assumed to be smaller than for automotive coatings because the painted objects do not move. It was assumed that unpolluted water is drained as this is the main disposal path proposed by the GSchG (1991), though in reality rain water is often lead to the STP, especially in urban area.

Literature on emission calculation was not found for particle release and methods for estimation of released VOC seemed not adequate enough.

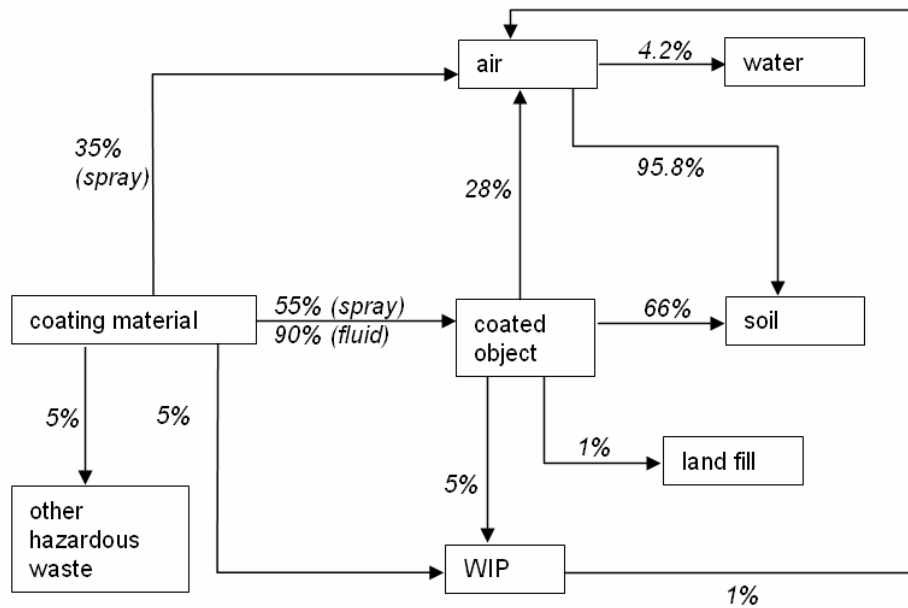


Figure 6.7: Flow chart for emissions of nanoparticular coating material to soils.

Total amounts of nanoparticles emitted to the soil are calculated with equations 6-30 to 6-33:

$$NP_{soil} = rate_{object/soil} * NP_{object} + rate_{air/soil} * NP_{air} \tag{6-30}$$

where

$$NP_{air} = rate_{spray/air} * NP_{tot} / 3 + rate_{object/air} * NP_{object} + rate_{WIP} * NP_{WIP} \tag{6-31}$$

$$NP_{WIP} = rate_{coating/WIP} * NP_{tot} + rate_{object/WIP} * NP_{object} \tag{6-32}$$

$$NP_{object} = rate_{spray/object} * NP_{tot} / 3 + 2/3 * NP_{tot} * rate_{coating/object} \tag{6-33}$$

where

NP_{soil} is the amount of nanoparticles deposited on soil [t/y];

$rate_{object/soil}$ is the rate of nanoparticles transfer from object to soil [];

NP_{object} is the amount of nanoparticles applied on the coated object [t/y];

$rate_{air/soil}$ is the rate of nanoparticle transfer from air to soil [];

NP_{air} is the amount of nanoparticles released to the air [t/y];

$rate_{spray/air}$ is the rate of nanoparticle transfer from spraying to air [];

NP_{tot} is the total amount of nanoparticles applied in paints in Switzerland [t/y];

$rate_{object/air}$ is the rate of nanoparticle transfer from object to air [];

$rate_{WIP}$ is the rate of nanoparticles released from WIP [];

NP_{WIP} is the amount of nanoparticles incinerated in the WIP [t/y];

$rate_{coating/WIP}$ is the rate of nanoparticle transfer from total coating material to WIP [];

$rate_{object/WIP}$ is the rate of nanoparticle transfer from object to WIP [];

$rate_{spray/object}$ is the rate of nanoparticle transfer from spraying to object [];

$rate_{coating/object}$ is the rate of nanoparticle transfer from total coating material to object []

For NP_{soil} , 30.6 t/y were received for the realistic scenario and 81.5 t/y for the worst case. The distribution was modelled in two ways. It was assumed that particles released to the air were distributed evenly in Switzerland. That seemed plausible because emissions occur at several sites widely distributed in Switzerland and particles are smaller than particles falling to the soil directly. Resulting concentrations of nanoparticles in the soil are $5.9 \cdot 10^{-5}$ and $1.6 \cdot 10^{-4}$ $\mu\text{g}/\text{m}^3/\text{y}$ for realistic and worst case scenario. On the other hand particles washed off by rain and bulk particles flaked off will not be transported wide distances by air. Concentrations of nanoparticles in the soil could not be calculated as the coated surface area was not known. Approximately 1.65 $\text{g}/\text{m}^3/\text{y}$ and 2.1 $\text{mg}/\text{kg}/\text{y}$ soil, respectively, can be expected under assumption that coated objects were on average 10 m tall, 100 g paint are applied per m^2 and all particles get distributed within 10 m distance to the coated object.

Table 6.14: Realistic and worst case scenario for total amounts of nanoparticles released from coatings to soils and yearly increase in concentration expected for soil.

	realistic scenario	worst case scenario
total amount of coating used [t/y]	87,290	87,290
total amount of NP [t/y]	36	97
total amount of NP in Swiss soils [t/y]	30.6	81.5
conc. of NP in Swiss soils [$\mu\text{g}/\text{m}^3/\text{y}$]	$5.9 \cdot 10^{-5}$	$1.6 \cdot 10^{-4}$
conc. of NP in Swiss soils [$\mu\text{g}/\text{kg}/\text{y}$]	$4.5 \cdot 10^{-8}$	$1.2 \cdot 10^{-7}$
conc. of NP in soils near coated objects [$\text{g}/\text{m}^3/\text{y}$]	1.65	1.65
conc. of NP in soils near coated objects [$\text{g}/\text{kg}/\text{y}$]	0.0021	0.0021

Particles emitted from coated objects because of abrasion are most likely in the micrometer size. The particles are bound in cementing agents or released in agglomerated form (Christinger, Knoll, 2007, personal communications). At Bioni CS GmbH currently a study is in progress examining the emissions from coatings (Knoll, 2007, personal communication).

According to Christinger (2007, personal communication), it depends mostly on the feedstock suppliers whether nanoparticles were employed or not. Because of limited potential for application in

the sectors of pigments, where the optimal particle size ranges from 200 to 400 nm, nanoparticles are most likely applied with new functions, provided by TiO₂ or potentially dendrimers (Kastien, 2006).

Sealings

Coatings included in this part are sealings for glass, stone, metal, plastics, concrete, and ceramic, and protection products against corrosion. Nanoparticles found were aluminium, silica, and polymers in hydrophobic sealing, impregnations, and cleaning agents, and TiO₂ applied on roofs and glass for waterproofing.

For this category a web search was conducted with the same strategy as described in chapter 5.3. The search was done with Google in the global web and with the keywords *beschichtung* OR *imprägnierung* OR *versiegelung*. Of twenty web sites, 9 (45%) contained products with nanoparticles, 1 (5%) contained possibly nanoparticles and 10 (50%) did not contain nanoparticles.

Because no data on sales market volume was received, only a qualitative discussion of the emissions is possible. Emissions are similar to the one of automotive sealing and paints. Figure 6.8 shows the fluxes of nanoparticles of the coated product to the environment.

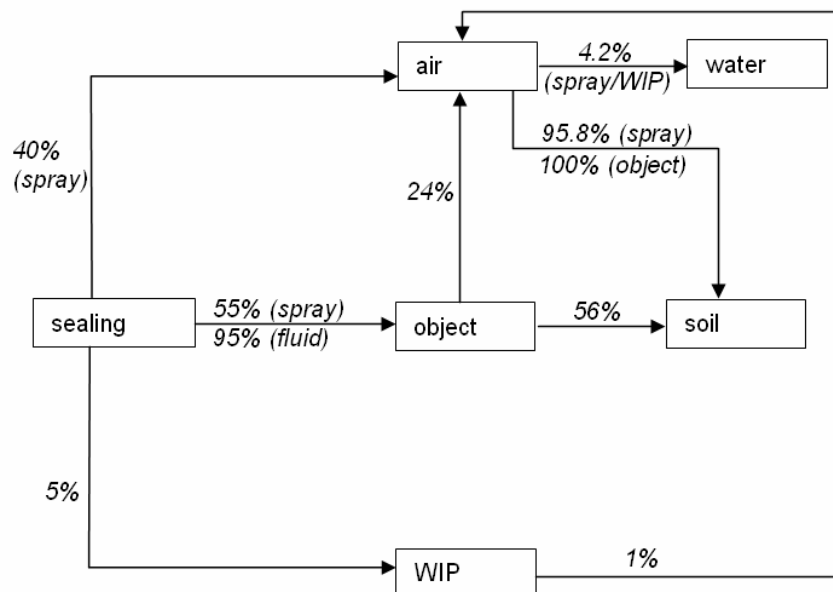


Figure 6.8: Flow chart for emissions of nanoparticulate sealing to the soil.

The short term durability of glass coatings could be explained with the penetration depth which is smaller on surfaces with low absorbency, small pore size, and small pore number (Kastien, 2003). And products with silanes last shorter than other hydrophobic coatings due to decomposition by UV-light and vaporization (Kastien, 2003). Further emissions are depending on pigment-volume concentration, cementing agent, and whether the coating is bright or matt (Christinger, 2007, personal communication).

6.5.2 Building materials

Concrete

$n\text{SiO}_2$ is possibly added to concrete for better durability due to water blocking and improved mechanical properties because of the higher density of the particle packing (Mann, 2006). One supplier of concrete additives was found in the web. The ingredient was not specified but its use against corrosion suggests that it is a product containing $n\text{SiO}_2$ ¹.

Research on $n\text{Fe}_2\text{O}_3$ addition is ongoing showing benefits of increasing strength and a possibility to monitor stress levels by measuring the electrical resistance (Mann, 2006). The sterilizing and self-cleaning properties of $n\text{TiO}_2$ are used in cements, too, in projects around the world (Mann, 2006). CNTs (1%w) may improve mechanical properties, but several problems by adding CNT are not solved yet (Mann, 2006). Further, research has been done on several coatings with self-healing or protective properties, and on nanoparticulate sensors incorporated into concrete or spread onto the surface for monitoring use (Mann, 2006).

Coatings of concrete are included in the previous section. Nanoparticulate emissions of concrete are assumed to be small, mostly because long lasting corrosion inhibition is achieved. But if nanoparticles get applied on a grand scale, the potential for generation of emissions must not be neglected.

Steel

Research on copper nanoparticles has shown that these are able to smooth the steel surface with the consequence of less stress risers and fatigue cracking (Mann, 2006). Stronger cables may be achieved by refinement of cementite particles and delay fracture problems may be solved by vanadium and molybdenum nanoparticles (Mann, 2006). Magnesium and calcium nanoparticles are used in another research project for increasing weld toughness to avoid cracking (Mann, 2006).

In a product described in the Nanoforum Report (Mann, 2006), unspecified nanoparticles were incorporated in the steel matrix for a steel of high strength with high ductility². The steel was proposed for use in sports, lightweight construction, security and safety (Sandvik, 2007). These are speciality goods and emissions to the soil will be small.

¹ Beton-Additive, nano4home, http://www.nano4home.de/Beton_Additiv.html

² Nanoflex, Sandvik, <http://www.smt.sandvik.com/nanoflex>

6.6 Other fields leading to nanoparticles fluxes to the soil

6.6.1 Water and air

Environmental compartments are not isolated but substances get transported between them. Fluxes from other compartment to the soil were not included in this work because first the sources emitting nanoparticles to them must be known and no study has modelled nanoparticles in environmental compartments so far. Thus, these immission sources are only briefly discussed here.

Nanoparticles can get from water and air to the soil compartment. Airborne particles are deposited by precipitation or under dry conditions and are expected to originate mainly from WIP, traffic, industry, and possibly sprays. Transport by air can lead to distribution of some particles to fare distances of the source.

As it is investigated by Müller (2007), water can get contaminated with nanoparticles. These nanoparticles originate primarily from house sewage and the concentrations found in water depend on the presence and the filtration efficiency of sewage treatment plants. Further sources could be soils (erosion, leaching, run off) and air deposition. These nanoparticles may get into soils by flooding, diffusion, and irrigation. In Switzerland agricultural soils are irrigated partly with river water, mainly in regions with market gardening or dry climate conditions.

6.6.2 Foodstuff, textiles, cosmetics and sports goods

Direct input of nanoparticles by foodstuff, textiles, cosmetics and sports goods is small due to processes leading to contamination and/or abundance of nanoparticles applied in those categories.

Information on application of nanotechnology in the food sector are only sparsely available but it is mentioned that at the time most implementations affect packaging (ETC Group, 2004; Joseph & Morrison, 2006). For food itself nanosized additives were produced and possibly nanoparticles were used for functional food (e.g., encapsulation for delivery) (ETC Group, 2004; Joseph & Morrison, 2006). Packaging is not likely to have a direct contact to soil because it is incinerated. Nanoparticles in food may be recovered in sewage sludge or in water if consumed and food waste is delivered to WIP or composted, the latter leading to direct contamination of soil.

Emissions of particles from textiles occur during entire life cycle whereby also nanoparticles may be released. During use textiles degrade causing emissions (Köhler et al., 2007). It is expected that textiles loose most material during the washing processes and are therefore transported to the STP, and only few material is released directly to the soil by abrasion processes. Textiles are recycled, exported, resold, or processed to building material or renewed to fibre (Köhler et al., 2007). A major part of textiles in Switzerland is incinerate at the end of life (Köhler et al., 2007).

Cosmetics, sunscreens and most other products for personal care are available with nanoparticulate ingredients (Gleiche, Hoffschulz & Lenhert, 2006; Miller, 2006). In sunscreens nanoscale TiO₂ and ZnO are most common. Like textiles a major part of products for personal care ends up in the STP due to washing and can be found in sewage sludge or water or is directly released to lakes or riv-

ers. A small amount may remain in the package and is incinerated, and a further small part is expected to reach soil by direct contact.

Nanoparticles are used in sporting goods in the form of nanocomposites (see WWI database¹). These products are normally incinerated at the end of their life or the material is recycled. During use only small amounts of nanoparticulate emissions are expected. One product found in the WWI database¹, that is most likely ending up directly on the soil is a ski wax. If this product or similar applications of nanoparticles get common, then the situation needs to be newly evaluated.

All those consumer products mentioned could lead to serious environmental contamination also affecting soil if nanoparticles were not captured at STP and WIP and if they were applied in a large scale.

6.6.3 Sewage sludge, combustion, electronics, landfills, irrigation

All themes discussed in this subchapter are of smaller concern for Switzerland but they are supposed to be of major concern in other regions of the world.

In Switzerland, the application of sewage sludge on soils as fertilizer is forbidden since 2007 (Laube & Vonplon, 2004). All sludge in Switzerland is thermally recycled in sludge combustors, waste incineration plants or cement works, and temporarily export is possible with allowance (Laube & Vonplon, 2004). Nanoparticles which are removed in STPs are present in the sewage sludge and therefore transported to the soil if applied as fertilizer.

A promising application of nanotechnology and nanoparticles are electronics. A part of the Swiss electronic waste is exported for material recovery (Morf & Taverna, 2004) and the working and handling conditions, especially in developing countries are bad. Among other problems, this may lead to soil contamination by nanoparticles in those countries.

STPs are standard in most industrial countries. Without them very much material containing nanoparticles may get released to the water. Waterborne nanoparticles can then be transported to the soil by irrigation.

Further sources of nanoparticles can be landfills. If wastes are landfilled, nanoparticles may leach out of products. Often landfills are ignited and burned and thus nanoparticles may be released to air and soil.

¹ A Nanotechnology Consumer Products Inventory, Woodrow Wilson International Center for Scholars; <http://www.nanotechproject.org/44/consumer-nanotechnology>

7 Discussion

In this study products were identified which are expected to have a major impact on soil ecosystem pollution with engineered or unintentionally produced nanoparticles. These are catalytic converters, fuel borne catalysts, catalytic coatings of diesel particulate filters, tyres, automotive and other coatings, sealings, biocides, fertilizers and nanoparticles used for soil remediation. The pathways of material flow were drawn and quantified, resulting in total expected amounts of nanoparticles reaching the soil surface within one year. Further, nanoparticle concentrations supposed to be found in soils were calculated. The main results are summarised in Table 7.1 and Table 7.2.

Table 7.1: Total amounts (t/y) of nanoparticles released to soils by the applications discussed in this work.

source	nanoparticulate ingredients	amount of nanoparticles deposited on soil [t/y]	
		realistic scenario	worst case scenario
catalytic converters	PGE (mainly Pt, Pd, Rh)	0.816	1.165
fuel borne catalysts	CeO, Fe, Cu, Sr, Pt	0.010	0.021
coated DPFs	Pt, Pd, V, W	0.0013	0.0024
tyres	CB, nZnO, nSiO ₂	1,275	2,601
automotive coatings	nSiO ₂ , diamond, nAg, ceramics, glass, polymers	2.60	4.54
coatings	nTiO ₂ , nSiO ₂ , nAg, nZnO, Fe ₂ O ₃ , CaCO ₃ , ceramics	36	97

Table 7.2: Yearly increase in concentrations of nanoparticles in soils of Switzerland from the different sources.

source	Switzerland		national roads		other roads		point sources	
	[µg/kg/y]		[µg/kg/y]		[µg/kg/y]		[µg/kg/y]	
	RS	WS	RS	WS	RS	WS	RS	WS
catalytic converters	--	--	0.0046	0.0066	3.3*10 ⁻⁴	4.8*10 ⁻⁴	--	--
fuel borne catalysts	9.2*10 ⁻⁷	2*10 ⁻⁶	--	--	--	--	--	--
coated DPFs	1.2*10 ⁻⁷	2.3*10 ⁻⁷	--	--	--	--	--	--
tyres	0.19	0.38	5.6	12	0.42	0.92	?	24
automotive coatings	0.061	0.11	8.5	15	0.69	1.2	--	--
coatings	4.5*10 ⁻⁸	1.2*10 ⁻⁷	--	--	--	--	2,100	2,100
total	0.25	0.49	14	27	1.1	2.1	2,100	2,100

As shown in Table 7.1, the amounts of nanoparticles emitted by tyres are by far the highest with more than 1000 tonnes of nanoparticles released to the soil per year. The nanoparticulate ingredient of tyre dust is mainly composed of carbon black and silica and to a smaller amount of zinc oxide. Coatings are another product field supposed to emit high amounts of nanoparticles. In this category several forms of nanoparticles are used but silica and titanium dioxide are ubiquitous. Also nano silver and zinc oxide are supposed to be often applied. Both tyres and coatings do most likely not emit free nanoparticles but bulk fragments in which nanoparticles are embedded. According to several persons working with those materials, they are intentionally made not to release fine particles and therefore further research is needed on the degradation of these materials for evaluating their potential exposure to soils (Christinger, Knoll, Wiederkehr, personal communications, 2007).

Nanoparticles originating from catalytic converters and catalytic coatings are expected to be released in purer form, but aggregated and bound to the substrate (washcoat). Only fuel borne catalysts are likely to leave as nanoparticles or very small agglomerates. Fuel borne catalysts for diesel particle filter regeneration are not expected to be released in amounts exceeding the presented levels much, but it has to be kept in mind that the same or similar products may be applied for other reasons without filter. For PGE and cerium oxide, studies have shown higher concentrations in soils near traffic sources than background levels (Ward, 1990, in HEI, 2001; Zereini et al., 1997), indicating accumulation over longer time frames.

Looking at the allocation of emitted nanoparticles (see Table 7.2), it becomes clear that exposure is highest in densely populated regions. Concentrations are expected to be highest besides traffic lanes and close to point sources such as cement works. Diffuse emissions cause much lower concentration levels. Concentrations in urban areas are expected to be higher than the model values because roads cross each other and buildings are standing closer, generating a higher impact on a smaller soil area.

A thorough assessment of the exposure of soils to nanoparticles by the investigated products is not possible at present because too little is known about the behaviour of these nanoparticles in soils. Therefore studies on mobility, transformation and degradation are needed for such materials and also an analysis of the uptake into plants and soil organisms.

Direct human exposure to contaminated soil occurs mainly through the dermal and oral pathway. Uptake of nanoparticles by the digestive system is primarily depending on the uptake of nanoparticles by plants, as well as the digestion mechanisms, and practically all people are exposed. Soil uptake is small but children staying on polluted lands may be affected to a relevant amount. Observations of nanoparticle uptake over the intestinal tract have been presented, but excretion seems to be efficient (Meili et al., 2007). Dermal uptake of nanoparticles from soil is restricted to people in direct contact with soil e.g., gardeners, farmers or part-time gardeners, but at the time no study has confirmed the uptake of nanoparticles through skin (Meili et al., 2007). Most research has been focused on inhalation and pulmonary effects which are supposed to affect humans most (SCENIHR, 2006).

The application of nanoparticles is only at the beginning and rapid changes are foreseeable. To date developments are under way in the product categories plant protection products and coatings.

These have to be reassessed after a certain time. Both fields are supposed to have a major potential to pollute soil. Characteristics of plant protection products are their direct and unhindered release on plants and soils, resulting in a high exposure potential for soils. Similarly nanoparticles containing fertilizers may affect soils, but in this field the research is less advanced and the advantage of nanoparticular ingredients is less obvious. The potential addition of nanoparticles to coatings depends on the development of ingredients with new and convincing properties.

Applications of nanoparticles that have been on the market for many years are carbon black and silica in tyres and platinum group elements in catalytic converters. These materials are not held back by any filter and are therefore a direct and relevant source for soil contamination. (Eco)toxicological studies have shown toxic effects of such materials (Adams et al., 2006a; Adams et al., 2006b; Chang et al., 2007a; Chen et al., 2004; Gilmour et al., 2004; Koike & Kobayashi, 2006; Stone et al., 1998). It is not evident that the particles used in tyres and coatings presents a health risk for humans or ecosystems because it depends on the nanoparticle form and functionalization.

The data obtained in this work by modelling represent not reality in detail, but show tendencies. Because the goal of this thesis was not to derive absolute values and the given time frame was limited, the work was done without a statistical validation. Here a qualitative validation assessment shall be held.

The data basis needed for modelling fluxes of nanoparticles to the soil are scanty, even data on common processes like traffic or emissions from coatings are not completely available. Today no guideline limits the use of the term "nano" nor provides a declaration of nanoparticular ingredients. Therefore it is possible that some products by mistake are supposed to contain or not to contain nanoparticles (Thomas et al., 2006). Likewise only products known to contain nanoparticles were included in the models and the possibility has to be taken into account that certain applications were not considered causing emissions of nanoparticles to the soil. Data provided by contacted persons differed in terms of quality and precision and personal values partially influenced the answers. Lacking definitions and business secrets made interrogations even more difficult. It was conspicuous that persons manufacturing nanoparticle containing products or selling them, often knew rather little, implicating only a limited information transfer from the nanoparticle or ingredients manufacturer.

To model the fluxes of nanoparticles, the methods were chosen to achieve the most realistic amount of released nanoparticles possible (see also SCENIHR, 2006), but because of the difficulties mentioned above for some product categories, an approximation had to be used with limited explanatory power, a web search based approach. In the worst case scenario the calculated amounts of nanoparticles are most likely overestimated. Due to lacking data a future scenario was not modelled as it would need additionally a probability assessment. The modelling is mass-based due to the fact that data on particle numbers were only rarely available although particle number and surface area were stated to be more adequate than particle mass (Meili et al., 2007; SCENIHR, 2006). Urgently methods have to be developed which allow comparing results from different studies, because the studies available today used various materials, methods and concentrations.

The knowledge about the behaviour of nanoparticles in soils is currently insufficient to model nanoparticle fluxes through soils. Because (bio)accumulation, degradation or transformation influence nanoparticle exposure to a high degree, further research is needed in this direction for a thorough exposure assessment. The behaviour of colloids and soil organisms like bacteria or viruses can help to understand a part of the behavior of nanoparticle but the influence of the surface modifications and functionalizations changes the characteristics of the nanomaterials. Also exchange rates between environmental compartments have been studied seldom. These studies would be necessary for assessing the role of the soil compartment with respect to nanoparticle behavior in the whole environment. The model used in this study indicates that the pathway through air is the main route of nanoparticles transfer to the soil. Leaching and groundwater movement are likely to lower nanoparticles concentrations in soils and may therefore serve as source of nanoparticles for water.

To assess the risks of nanoparticles for soil ecosystems, further research is also necessary on the toxicity of nanoparticles to organisms and especially soil microorganisms as these are the basis of the food webs (Lecoanet & Wiesner, 2004). Up to date only one study has been published investigating impacts of nanoparticles on soil organisms, showing only low toxicity (Gardiner et al., 1996). The toxic effects on water organisms have been more extensively investigated, mostly indicating toxicity at high concentrations (e.g., Oberdörster, 2004; Oberdörster, Oberdörster & Oberdörster, 2005).

Nanoparticles are handled as a new chance for goods and applications with environmental benefits. But on the other hand, increasingly evidence is found that nanoparticles can have toxic impacts on organisms. Therefore it has to be considered if there are alternatives to nanoparticle applications and if these are more environmentally friendly. The benefits and disadvantages of conventional and nanotechnological applications have to be weighted up against each other. For example, additives for filter regeneration lead to less combustion derived emissions, but small amounts of fuel borne catalysts are emitted. Additives used without filter reduce fuel consumption but all additives are released to the environment. Similarly the use of nanoparticles for soil remediation can reduce the risks of pollutions but on the other hand the used nanomaterial will in most cases remain in soil or water.

In this diploma thesis it was found that the exposure of soils to contaminations with engineered and unintentionally produced nanoparticles is rather low to date, though several nanoparticulate forms are released in large amounts. Because of the developmental state of several applications and the persistency of nanoparticles in soils, the risk of exposure of soils with nanoparticles will potentially rise and an early restriction of the impacts is important to these sensitive ecosystems. For a thorough exposure assessment further studies are needed, most urgently investigations on degradation, transformation, accumulation, and mobility of nanoparticles in soils and on appropriate methods. Additional product fields should be examined closer to identify and assess the other potential nanoparticles applications and their effect on soils.

8 Bibliography

- ADACHI, K. & TAINOSHO, Y. (2004). Characterization of heavy metal particles embedded in tire dust. *Environment International* **30**, 1009-1017.
- ADAMS, L. K., LYON, D. Y. & ALVAREZ, P. J. J. (2006a). Comparative eco-toxicity of nanoscale TiO₂, SiO₂, and ZnO water suspensions. *Water Research* **40**, 3527-3532.
- ADAMS, L. K., LYON, D. Y., MCINTOSH, A. & ALVAREZ, P. J. J. (2006b). Comparative toxicity of nano-scale TiO₂, SiO₂ and ZnO water suspensions. *Water Science & Technology* **54**, 327-334.
- ALLIANZ & OECD. Small sizes that matter: Opportunities and risks of nanotechnologies. Report in co-operation with the OECD International Futures Programme (ed. C. Lauterwasser), pp. 45, München, Germany.
- AN, H. M. & MCGINN, P. J. (2006). Catalytic behavior of potassium containing compounds for diesel soot combustion. *Applied Catalysis B-Environmental* **62**, 46-56.
- ARTELT, S., KOCK, H., KONIG, H. P., LEVSEN, K. & ROSNER, G. (1999). Engine dynamometer experiments: platinum emissions from differently aged three-way catalytic converters. *Atmospheric Environment* **33**, 3559-3567.
- ASTRA. (2006). Verkehrsentwicklung und Verfügbarkeit der Nationalstrassen. Jahresbericht 2006. Bundesamt für Strassen (ed.), pp. 16, Berne.
- AYLÓN, E., MURILLO, R., FERNÁNDEZ-COLINO, A., ARANDA, A., GARCÍA, T., CALLÉN, M. S. & MASTRAL, A. M. (2007). Emissions from the combustion of gas-phase products at tyre pyrolysis. *J. Anal. Appl. Pyrolysis* **79**, 210-214.
- BAFU. (2006a). Einsatz von Partikelfiltersystemen in Bussen. Empfehlungen für Nachrüstung und Betrieb. Umwelt-Wissen Nr. 0608, Berne.
- BAFU. (2006b). Vollzugshilfe für die Entsorgung von Altreifen (Vollzugshilfe Altreifen). Bereinigter Entwurf Stand 14. März 2006. Bundesamt für Umwelt (ed.), Berne, pp. 17.
- BARBANTE, C., COZZI, G., CAPADAGLIO, G., VAN DE VELDE, K., FERRARI, C., VEYSSEYRE, A., BOUTRON, C. F., SCARPONI, G. & CESCONE, P. (1999). Determination of Rh, Pd, and Pt in polar and alpine snow and ice by double-focusing ICPMS with microconcentric nebulization. *Anal. Chem.* **71**, 4125-4133.
- BARBANTE, C., VEYSSEYRE, A., FERRARI, C., VAN DE VELDE, K., MOREL, C., CAPODAGLIO, G., CESCONE, P., SCARPONI, G. & BOUTRON, C. (2001). Greenland snow evidence of large scale atmospheric contamination for platinum, palladium, and rhodium. *Environ. Sci. Technol.* **35**, 835-839.
- BAREFOOT, R. R. (1999). Distribution and speciation of platinum group elements in environmental matrices. *Trends Anal. Chem.* **18**, 702-707.
- BARTHLOTT, W. & NEINHUIS, C. (1997). Purity of the sacred lotus, or escape from contamination in biological surfaces. *Planta* **202**, 1-8.
- BFE. (2006). Schweizerische Gesamtenergiestatistik 2006 - Statistique globale suisse de l'énergie 2006 (ed. Bundesamt für Energie), Berne.
- BFS. (2006a). Fahrzeugbewegungen und Fahrleistungen im Güterverkehr. Bundesamt für Statistik, Neuchâtel.: <http://www.bfs.admin.ch/bfs/portal/de/index/themen/11/04/blank/key/02.html> (july 2007).
- BFS. (2006b). Fahrzeugbewegungen und Fahrleistungen im Personenverkehr. Bundesamt für Statistik, Neuchâtel.: <http://www.bfs.admin.ch/bfs/portal/de/index/themen/11/04/blank/key/01.html> (july 2007).
- BFS. (2007a). Mobilität und Verkehr. Taschenstatistik 2007 (ed. Eidgenössisches Departement des Innern, Bundesamt für Statistik), pp. 30, Neuchâtel.
- BFS. (2007b). *Mobilität und Verkehr. Taschenstatistik 2007*, Neuchâtel.

- BFS. (2007c). Schiffsbestände nach Bootskategorien, Entwicklung. Bundesamt für Statistik, Neuchâtel:
http://www.bfs.admin.ch/bfs/portal/de/index/themen/11/03/blank/key/fahrzeuge_schiffsverkehr.html (september 2007).
- BFS. (2007d). Strassenfahrzeugbestand nach Fahrzeuggruppe und Fahrzeugart 1990 - 2006. Bundesamt für Statistik, Neuchâtel:
http://www.bfs.admin.ch/bfs/portal/de/index/themen/11/03/blank/key/fahrzeuge_strasse/bestand.html (july 2007).
- BFS. (2007e). Strassenfahrzeuge in der Schweiz. Inverkehrsetzung neuer Strassenfahrzeuge 2006. Bundesamt für Statistik, Neuchâtel:
http://www.bfs.admin.ch/bfs/portal/de/index/themen/11/03/blank/key/fahrzeuge_strasse/inverkehrsetzung.html (july 2007).
- BFS. (2007f). Superweb. Bundesamt für Statistik, Neuchâtel:
<http://www.bfs.admin.ch/bfs/portal/de/index/infothek/superweb.html> (august 2007).
- BFS. (2007g). Taschenstatistik der Schweiz 2007 (ed. Bundesamt für Statistik), pp. 34, Neuchâtel.
- BLESSING, R. & BURGNER, A. (2004). 9. Berichterstattung im Rahmen der Energieverordnung über die Absenkung des spezifischen Treibstoff-Normverbrauchs von Personenwagen 2004. AutoSchweiz (ed.), pp. 26, Berne.
- BLW. (2007). Pflanzenschutzmittelverzeichnis. Bundesamt für Landwirtschaft, Berne:
http://www.psa.blw.admin.ch/index_de_3_1.html (july 2007).
- BORM, P. J. A. & DONALDSON, K. (2007). An introduction to particle toxicology: From coal mining to nanotechnology. In *Particle Toxicology*, pp. 1-424.
- BRUNNER, T. J., WICK, P., MANSER, P., SPOHN, P., GRASS, R. N., LIMBACH, L. K., BRUININK, A. & STARK, W. J. (2006). In vitro cytotoxicity of oxide nanoparticles: comparison to asbestos, silica, and the effect of particle solubility. *Environ. Sci. Technol.* **40**, 4374-4381.
- CBP CARBON INDUSTRIES INC. (2007): <http://www.cbpcarbon.com> (september 2007).
- CEMSUISSE. (2006). Jahresbericht - Rapport annuel 2006: <http://www.cemsuisse.ch> (september 2007).
- CHANG, J. S., CHANG, K. L. B., HWANG, D. F. & KONG, Z. L. (2007a). In vitro cytotoxicity of silica nanoparticles at high concentrations strongly depends on the metabolic activity type of the cell line. *Environmental Science & Technology* **41**, 2064-2068.
- CHANG, M.-C., SHU, H.-Y., HSIEH, W.-P. & WANG, M.-C. (2007b). Remediation of soil contaminated with pyrene using ground nanoscale zero-valent iron. *J. Air & Waste Manage. Assoc.* **57**, 221-227.
- CHANG, M.-C., SHU, H.-Y., HSIEH, W.-P. & WANG, M.-C. (2005). Using nanoscale zero-valent iron for the remediation of polycyclic aromatic hydrocarbons contaminated soil. *J. Air & Waste Manage. Assoc.* **55**, 1200-1207.
- CHEN, Y., CHEN, J., DONG, J. & JIN, Y. (2004). Comparing study of the effect of nanosized silicon dioxide and microsized silicon dioxide on fibrogenesis in rats. *Toxicol. Ind. Health* **20**, 21-27.
- CORNELISSEN, G., GUSTAFSSON, O., BUCHELI, T. D., JONKER, M. T. O., KOELMANS, A. A. & VAN NOORT, P. C. M. (2005). Extensive sorption of organic compounds to black carbon, coal, and kerogen in sediments and soils: Mechanisms and consequences for distribution, bioaccumulation, and biodegradation. *Environ. Sci. Technol.* **39**, 6881-6895.
- COWLEY, A. (1997). *Platinum 1997*. Interim Review, Johnson Matthey, pp. 28.
- DAHL, A., GHARIBI, A., SWIETLICKI, E., GUDMUNDSSON, A., BOHGARD, M., LJUNGMAN, A., BLOMQUIST, G. & GUSTAFSSON, M. (2006). Traffic-generated emissions of ultrafine particles from pavement-tire interface. *Atmospheric Environment* **40**, 1314-1323.
- DAIMLERCHRYSLER. (2007). Leichter bauen mit Nanos. In *DaimlerChrysler Hightech Report* **1**, 39-41.

- EK, K. H., MORRISON, G. M. & RAUCH, S. (2004). Environmental routes for platinum group elements to biological materials - a review. *Sci. Total Environ.* **334-335**, 21-38.
- EL-NAHHAL, Y., UNDABEYTIYA, T., POLUBESOVA, T., MISHAEL, Y. G., NIR, S. & RUBIN, B. (2001). Organo-clay formulations of pesticides: reduced leaching and photodegradation. *Applied Clay Science* **18**, 309-326.
- ELLIOTT, D. W. & ZHANG, W.-X. (2001). Field assessment of nanoscale bimetallic particles for groundwater treatment. *Environ. Sci. Technol.* **35**, 4922-4926.
- ELY, J. C., NEAL, C. R., KULPA, C. F., SCHNEEGURT, M. A., SEIDLER, J. A. & JAIN, J. C. (2001). Implications of platinum-group element accumulation along US roads from catalytic-converter attrition. *Environmental Science & Technology* **35**, 3816-3822.
- ETC GROUP. (2004). Down on the farm. The impact of nano-scale technologies on food and agriculture, pp. 68, Ottawa.
- FAUSER, P., TJELL, J. C., MOSBAEK, H. & PILEGAARD, K. (1999). Quantification of tire-tread particles using extractable organic zinc as tracer. *Rubber Chemistry and Technology* **72**, 969-977.
- FRAGNIÈRE, C., HALDIMANN, M., EASTGATE, A. & KRÄHENBÜHL, U. (2005). A direct ultratrace determination of platinum in environmental, food and biological samples by ICP-SFMS using a desolvation system. *J. Anal. At. Spectrom.* **20**, 626-630.
- GARCÉS, J. M., MOLL, D. J., BICERANO, J., FIBIGER, R. & MCLEOD, D. G. (2000). Polymeric nanocomposites for automotive applications. *Adv. Mater.* **12**, 1835-1839.
- GARDINER, K., CALVERT, I. A., VAN TONGEREN, M. J. A. & HARRINGTON, J. M. (1996). Occupational exposure to carbon black in its manufacture: Data from 1987 to 1992. *Annals of Occupational Hygiene* **40**, 65-77.
- GENT, A. N. (1992). *Engineering with rubber* (ed. Rubber division of the Am Chem Soc). Hanser, New York.
- GILMOUR, P. S., ZIESENIS, A., MORRISON, E. R., VICKERS, M. A., DROST, E. M., FORD, I., KARG, E., MOSSA, C., SCHROEPEL, A., FERRON, G. A., HEYDER, J., GREAVES, M., MACNEE, W. & DONALDSON, K. (2004). Pulmonary and systemic effects of short-term inhalation exposure to ultrafine carbon black particles. *Toxicol. Appl. Pharmacol.* **195**, 35-44.
- GLEICHE, M., HOFFSCHULZ, H. & LENHERT, S. (2006). Nanotechnology in consumer products. In *Nanoforum Report* (ed. Nanoforum), pp. 30.
- GÖRSMANN, C. (2005). Catalytic coatings for active and passive diesel particulate filter regeneration. *Monatsheft für Chemie* **136**, 91-105.
- HAGELUKEN, C. (1995). Recycling of car exhaust catalysts - situation and prospects in Europe. *Metall* **49**, 486-490.
- HAMMER, B. & WENGER, C. (2001). Altlasten: erfassen, bewerten, sanieren. Bundesamt für Umwelt, Wald und Landschaft, pp. 39, Berne.
- HE, F., ZHAO, D. Y., LIU, J. C. & ROBERTS, C. B. (2007). Stabilization of Fe-Pd nanoparticles with sodium carboxymethyl cellulose for enhanced transport and dechlorination of trichloroethylene in soil and groundwater. *Ind. Eng. Chem. Res.* **46**, 29-34.
- HEDRICK, J. B. (1998). Rare earths. In *Minerals Yearbook*, vol I: Metals and Minerals, pp 61.1-61.14. US Geological Survey, Reston VA edition.
- HEEB, N. V. (1998). Influence of particulate trap systems on the composition of diesel engine exhaust gas emissions. In *Research Report* (ed. EMPA), Dübendorf.
- HEEB, N. V., ULRICH, A., EMMENEGGER, L., CZERWINSKI, J., MAYER, A. & WYSER, M. (2005). Secondary emissions risk assessment of diesel particulate traps for heavy duty applications. *SIAT* **165**.
- HEI. (2001). Evaluation of human health risk from cerium added to diesel fuel. Communication 9 (ed. Health Effects Institute), pp. 57, Boston.
- HELMERS, E. (1996). Elements accompanying platinum emitted from automobile catalysts. *Chemosphere* **33**, 405-419.

- HELMERS, E., MERGEL, N. & BARCHET, R. (1994). Platinum in ash from sewage sludge incinerators and in grass. *UWSF-Z. Umweltchem. Ökotox.* **6**, 89-101.
- HUND-RINKE, K. & SIMON, M. (2006). Ecotoxic effect of photocatalytic active nanoparticles TiO₂ on algae and daphnids. *Environmental Science and Pollution Research* **13**, 225-232.
- IVES, K. J. (1975). *The scientific basis of filtration. NATO Advanced Study Institute Series E*, vol. 2, Noordhoff, Leiden.
- JARVIS, K. E., PARRY, S. J. & PIPER, J. M. (2001). Temporal and spatial studies of autocatalyst-derived platinum, rhodium, and palladium and selected vehicle-derived trace elements in the environment. *Environ. Sci. Technol.* **35**, 1031-1036.
- JOSEPH, T. & MORRISON, M. (2006). Nanotechnology in agriculture and food. In *Nanoforum Report* (ed. Nanoforum), pp. 14.
- JOUBERT, E. & SEGUELONG, T. (2004). Diesel particulate filters market introduction in Europe: review and status. In *Deer Conference 2004*. Aquis & Aquis (ed.). U.S. Department of Energy, Energy Efficiency and Renewable Energy: http://www1.eere.energy.gov/vehiclesandfuels/pdfs/deer_2004/session12/2004_deer_seguelong2.pdf (august 2007).
- KARATHANASIS, A. D. (1999). Subsurface migration of copper and zinc mediated by soil colloids. *Soil Science Society of America Journal* **63**, 830-838.
- KASTIEN, H. (2003). Hydrophobierung mineralischer Oberflächen. In *applic. SVLFC*: <http://www.svlfc.ch/aktuell.html> (september 2007).
- KASTIEN, H. (2006). Möglichkeiten und Grenzen der Nanotechnologie in der Lackindustrie. Schweizerische Vereinigung der Lack- und Farben-Chemiker. Schweizerischer Verband der Lack- und Farbenfabrikanten: <http://www.svlfc.ch/aktuell.html> (september 2007).
- KHAIR, M., LEMAIRE, J. & FISCHER, S. (2000). Achieving heavy-duty diesel NOx/PM levels below the EPA 2002 standards: An integrated solution. *SAE Technical Paper* **1**.
- KÖHLER, A. R., SOM, C., HELLAND, A. & GOTTSCHALK, F. (2007). Studying the potential release of carbon nanotubes throughout the application life cycle. *Journal of Cleaner Production* **in press**.
- KOIKE, E. & KOBAYASHI, T. (2006). Chemical and biological oxidative effects of carbon black nanoparticles. *Chemosphere* **65**, 946-951.
- KONIG, H. P., HERTEL, R. F., KOCH, W. & ROSNER, G. (1992). Determination of platinum emissions from a 3-way catalyst-equipped gasoline-engine. *Atmospheric Environment Part a-General Topics* **26**, 741-745.
- KRETZSCHMAR, R., BARMETTLER, K., GROLIMUND, D., YAN, Y. D., BORKOVEC, M. & STICHER, H. (1997). Experimental determination of colloid deposition rates and collision efficiencies in natural porous media. *Water Resources Research* **33**, 1129-1137.
- KRETZSCHMAR, R., BORKOVEC, M., GROLIMUND, D. & ELIMELECH, M. (1999). Mobile subsurface colloids and their role in contaminant transport. In *Advances In Agronomy, Vol 66*, vol. 66. *Advances In Agronomy*, pp. 121-193.
- KRETZSCHMAR, R., ROBARGE, W. P. & AMOOZEGAR, A. (1994). Filter efficiency of 3 saporlites for natural clay and iron-oxide colloids. *Environmental Science & Technology* **28**, 1907-1915.
- LAI, F., WISSING, S. A., MULLER, R. H. & FADDA, A. M. (2006). Artemisia arborescens L essential oil-loaded solid lipid nanoparticles for potential agricultural application: Preparation and characterization. *Aaps Pharmscitech* **7**.
- LAM, C. W., JAMES, J. T., MCCLUSKEY, R., AREPALLI, S. & HUNTER, R. L. (2006). A review of carbon nanotube toxicity and assessment of potential occupational and environmental health risks. *Critical Reviews In Toxicology* **36**, 189-217.
- LAUBE, A. & VONPLON, A. (2004). Klärschlamm Entsorgung in der Schweiz - Mengen- und Kapazitätserhebung. In *Umwelt-Materialien Nr. 181* (ed. Bundesamt für Umwelt, Wald und Landschaft), pp. 47, Berne.

- LEAD, J. R. & WILKINSON, K. J. (2006). Aquatic colloids and nanoparticles: Current knowledge and future trends. *Environmental Chemistry* **3**, 159-171.
- LECOANET, H. F. & WIESNER, M. R. (2004). Velocity effects on fullerene and oxide nanoparticle deposition in porous media. *Environmental Science & Technology* **38**, 4377-4382.
- LEMAIRE, J. (1999). Eolys Fuel-Borne Catalyst for diesel particulates abatement: a key component of an integrated system. In *DieselNet Technical Report*, DieselNet: <http://www.dieselnet.com/papers/9909rhodia/> (september 2007).
- LI, Z.-Z., CHEN, J.-F., LIU, F., LIU, A.-Q., WANG, Q., SUN, H.-Y. & WEN, L.-X. (2007). Study of UV-shielding properties of novel porous hollow silica nanoparticle carriers for avermectin. *Pest Manag. Sci.* **63**, 241-246.
- LI, Z.-Z., XU, S.-A., WEN, L.-X., LIU, F., LIU, A.-Q., WANG, Q., SUN, H.-Y., YU, W. & CHEN, J.-F. (2006). Controlled release of avermectin from porous hollow silica nanoparticles: Influence of shell thickness on loading efficiency, UV-shielding property and release. *Journal of Controlled Release* **111**, 81-88.
- LIAO, C. J., CHUNG, T. L., CHEN, W. L. & KUO, S. L. (2007). Treatment of pentachlorophenol-contaminated soil using nano-scale zero-valent iron with hydrogen peroxide. *Journal Of Molecular Catalysis A-Chemical* **265**, 189-194.
- LICK, C. (2007). BASF Pflanzenschutz bietet aktuelle und innovative Beiträge zum Technologietransfer. Presse-Information 7. März 2007. BASF: http://www.agro.basf.com/p02/AP-In-net/en_GB/function/conversions:/publish/content/PressReleases_Folder/deutsch/news_release_2007-03-07_de.pdf (september 2007).
- LIEN, H. L. & ZHANG, W. X. (2005). Hydrodechlorination of chlorinated ethanes by nanoscale Pd/Fe bimetallic particles. *J. Environ. Eng.* **131**, 4-10.
- LIN, C.-C., CHEN, S.-J., HUANG, K.-L., HWANG, W.-I., CHANG-CHIEN, G.-P. & LIN, W.-Y. (2005). Characteristics of metals in nano/ultrafine/fine/coarse particles collected beside a heavily trafficked road. *Environ. Sci. Technol.* **39**, 8113-8122.
- LIN, W., HUANG, Y. W., ZHOU, X. D. & MA, Y. (2006). Toxicity of cerium oxide nanoparticles in human lung cancer cells. *Int. J. Toxicol.* **25**, 451-547.
- LIU, F., WEN, L.-X., LI, Z.-Z., YU, W., SUN, H.-Y. & CHEN, J.-F. (2006). Porous hollow silica nanoparticles as controlled delivery system for water-soluble pesticide. *Materials Research Bulletin* **41**, 2268-2275.
- LIU, R. & ZHAO, D. (2007). In situ immobilization of Cu(II) in soils using a new class of iron phosphate nanoparticles. *Chemosphere* **68**, 1867-1876.
- LLOYD, S. M. & LAVE, L. B. (2003). Life cycle economic and environmental implications of using nanocomposites in automobiles. *Environ. Sci. Technol.* **37**, 3458-3466.
- LUSTIG, S., ZANG, S., MICHALKE, B., SCHRAMMEL, P. & BECK, W. (1996). Transformation behaviour of different platinum compounds in a clay-like humic soil: speciation investigations. *The Science of the Total Environment* **188**, 195-204.
- MADDEN, A. S. & HOCELLA, M. F. (2005). A test of geochemical reactivity as a function of mineral size: Manganese oxidation promoted by hematite nanoparticles. *Geochim. Cosmochim. Acta* **69**, 389-398.
- MADDEN, A. S., HOCELLA, M. F. & LUXTON, T. P. (2006). Insights for size-dependent reactivity of hematite nanomineral surfaces through Cu²⁺ sorption. *Geochim. Cosmochim. Acta* **70**, 4095-4104.
- MANN, S. (2006). Nanotechnology and construction. In *Nanoforum Report* (ed. Nanoforum), pp. 55.
- MASCIANGIOLI, T. & ZHANG, W. X. (2003). Environmental technologies at the nanoscale. *Environ. Sci. Technol.* **37**, 102A-108A.
- MAWDSLEY, J. L., BARDGETT, R. D., MERRY, R. J., PAIN, B. F. & THEODOROU, M. K. (1995). Pathogens in livestock waste, their potential for movement through soil and environmental-pollution. *Applied Soil Ecology* **2**, 1-15.

- MAYER, A. (2006a). *Filterliste BAFU/Suva. Geprüfte und erprobte Partikelfilter-Systeme für die Nachrüstung von Dieselmotoren. Stand: Dezember 2006.* Bundesamt für Umwelt, Berne, and Schweizerische Unfallversicherungsanstalt Suva, Luzerne, pp. 33.
- MAYER, A. (2006b). PFS-news 2006. Retrofit- and OEM-applications. Arbeitskreis Partikel-Filter-Systemhersteller: <http://www.akpf.org/pubs.html> (july 2007).
- MAYER, A. (2007). Retrofitting off-road engines. In *Seminar on DPF particle filter retrofitting Diesel engines*, Munich. Arbeitskreis Partikel-Filter-Systemhersteller: <http://www.akpf.org/pubs.html> (august 2007).
- MCCABE, R. W. & KISENYI, J. M. (1995). *Chem. Ind.* **15**, 605-608.
- MCGECHAN, M. B. (2002). Transport of particulate and colloid-sorbed contaminants through soil, part 2: Trapping processes and soil pore geometry. *Biosystems Engineering* **83**, 387-395.
- MCGECHAN, M. B. & LEWIS, D. R. (2002). Transport of particulate and colloid-sorbed contaminants through soil, part 1: General principles. *Biosystems Engineering* **83**, 255-273.
- MEILI, C., WIDMER, M., HUSMANN, F., GEHR, P., BLANK, F., RIEDIKER, M., SCHMID, K., STARK, W. & LIMBACH, L. (2007). Synthetische Nanomaterialien. Risikobeurteilung und Risikomanagement. Grundlagenbericht zum Aktionsplan. (ed. BAFU and BAG), pp. 284, Berne.
- MERCEDES-BENZ. (2007): http://www.mercedes-benz.ch/content/switzerland/mpc/mpc_switzerland_website/de/home_mpc.html (september 2007).
- MILLER, G. (2006). Nanomaterials, sunscreens and cosmetics: small ingredients big risks. Friends of the Earth Australia and United States (ed.), pp. 29.
- MOLDOVAN, M., PALACIOS, M. A., GOMEZ, M. M., MORRISON, G., RAUCH, S., MCLEOD, C., MA, R., CAROLI, S., ALIMONTI, A., PETRUCCI, F., BOCCA, B., SCHRAMMEL, P., ZISCHKA, M., PETERS-SON, C., WASS, U., LUNA, M., SAENZ, J. C. & SANTAMARIA, J. (2002). Environmental risk of particulate and soluble platinum group elements released from gasoline and diesel engine catalytic converters. *Science Of The Total Environment* **296**, 199-208.
- MORF, L. & TAVERNA, R. (2004). Metallische und nichtmetallische Stoffe im Elektronikschrott. Schriftenreihe Umwelt Nr. 374, Bundesamt für Umwelt, Bern, pp 134.
- MÜLLER, N. (2007). Nanoparticles in the environment - risk assessment based on exposure-modelling, ETH Zürich and EMPA, pp 97.
- MURR, L. E., BROWN, D. K., ESQUIVEL, E. V., PONDA, T. D., MARTINEZ, F. & VIRGEN, A. (2005). Carbon nanotubes and other fullerenes produced from tire powder injected into an electric arc. *Materials Characterization* **55**, 371-377.
- MURRAY, H. H. (2000). Traditional and new applications for kaolin, smectite, and palygorskite: a general overview. *Applied Clay Science* **17**, 207-221.
- MUSCHACK, W. (1990). Pollution of street run-off by traffic and local conditions. *Science of the Total Environment* **93**, 419-431.
- NANOSYS GMBH. (2005). Nano-Argentum 10. Technisches Merkblatt: <http://www.nanosys.ch/tedablas/d/nanoargentum230905.pdf> (september 2007).
- NAVROTSKY, A. (2000). Nanomaterials in the environment, agriculture, and technology (NEAT). *Journal of Nanoparticle Research* **2**, 321-323.
- NEES-INSTITUT. (2007). Lotus-Effect. Nees-Institut für Biodiversität der Pflanzen der Universität Bonn: <http://www.lotus-effekt.de/> (august 2007).
- NEJAR, N. & ILLAN-GOMEZ, M. J. (2007). Performance of potassium-promoted catalysts for NO_x and soot removal from simulated diesel exhaust. *Topics in Catalysis* **42-43**, 277-282.
- NYER, E. K. & VANCE, D. B. (2001). Nano-scale iron for dehalogenation. *Ground Water Monit. Rem.* **21**, 41-46.
- O'MELIA, C. R. (1980). Aquasols - the behavior of small particles in aquatic systems. *Environ. Sci. Technol.* **14**, 1052-1060.

- OBERDÖRSTER, E. (2004). Manufactured nanomaterials (Fullerenes, C-60) induce oxidative stress in the brain of juvenile largemouth bass. *Environ. Health Perspect.* **112**, 1058-1062.
- OBERDÖRSTER, E., MCCLELLAN-GREEN, P. & HAASCH, M. L. (2006). Ecotoxicity of engineered nanomaterials. In *Nanomaterials - Toxicity, health and environmental issues* (ed. Kumar). Wiley-VCH, Weinheim.
- OBERDÖRSTER, E., ZHU, S. Q., BLICKLEY, T. M., MCCLELLAN-GREEN, P. & HAASCH, M. L. (2006). Ecotoxicology of carbon-based engineered nanoparticles: Effects of fullerene (C-60) on aquatic organisms. *Carbon* **44**, 1112-1120.
- OBERDÖRSTER, G., OBERDÖRSTER, E. & OBERDÖRSTER, J. (2005). Nanotoxicology: an emerging discipline evolving from studies of ultrafine particles. *Environ. Health Perspect.* **113**, 823-839.
- OBERDÖRSTER, G., SHARP, Z., ATUDOREI, V., ELDER, A., GELEIN, R., LUNTS, A., KREYLING, W. & COX, C. (2002). Extrapulmonary translocation of ultrafine carbon particles following whole-body inhalation exposure of rats. *J. Toxicol. Environ. Health A* **65**, 1531-1543.
- PALACIOS, M., GOMEZ, M. M., MOLDOVAN, M., MORRISON, G., RAUCH, S., MCLEOD, C., MA, R., LASERNA, J., LUCENA, P., CAROLI, S., ALIMONTI, A., PETRUCCI, F., BOCCA, B., SCHRAMMEL, P., LUSTIG, S., ZISCHKA, M., WASS, U., STENBOM, B., LUNA, M., SAENZ, J. C. & SANTAMARIA, J. (2000). Platinum-group elements: quantification in collected exhaust fumes and studies of catalyst surfaces. *Science Of The Total Environment* **257**, 1-15.
- PATTAS, K., SAMARAS, Z., SHERWOOD, D., UMEHARA, K., CANTIANI, C., AGUERRE CHARIOL, O., BARTHE, P. & LEMAIRE, J. (1992). Cordierite filter durability with cerium fuel additive: 100,000 km of revenue service in Athens. *SAE Technical Paper* **920363**.
- PRESTING, H. & KÖNIG, U. (2003). Future nanotechnology developments for automotive applications. *Material Science and Engineering C* **23**, 737-741.
- RAHE, T. M., HAGEDORN, C., MCCOY, E. L. & KLING, G. F. (1978). Transport of antibiotic-resistant escherichia-coli through Western Oregon hillslope soils under conditions of saturated flow. *Journal Of Environmental Quality* **7**, 487-494.
- RAUCH, S., HEMOND, H. F., BARBANTE, C., OWARI, M., MORRISON, G. M., PEUCKER-EHRENBRINK, B. & WASS, U. (2005). Importance of automobile exhaust catalyst emissions for the deposition of platinum, palladium, and rhodium in the Northern Hemisphere. *Environmental Science & Technology* **39**, 8156-8162.
- RAUCH, S., MOTELICA-HEINO, M., MORRISON, G. M. & DONARD, O. F. X. (2000). Critical assessment of platinum group element determination in road and urban river sediments using ultrasonic nebulisation and high resolution ICP-MS. *Journal Of Analytical Atomic Spectrometry* **15**, 329-334.
- SADIQ, M., ALAM, I., ELMUBAREK, A. & ALMOHDHAR, H. M. (1989). Preliminary evaluation of metal pollution from wear of auto tires. *Bulletin of Environmental Contamination and Toxicology* **42**, 743-748.
- SAMARAS, Z. (1994). Cerium based fuel additive for the effective reduction of diesel particulate emissions: assessment of its environmental effects. In *Final Report prepared for Rhône-Poulenc Project "Diesel Propre"* (ed. Rhône-Poulenc), Courbevoie Ceux, France.
- SANDVIK. (2007). Sandvik Materials Technology: <http://www.smt.sandvik.com/> (september 2007).
- SCENIHR. (2006). *Modified Opinion (after public consultation) on The appropriateness of existing methodologies to assess the potential risks associated with engineered and adventitious products of nanotechnologies*. Adopted by the SCENIHR during the 10th plenary meeting of 10 March 2006 after public consultation. Scientific Committee on Emerging and Newly Identified Health Risks (ed.), pp. 79.
- SCHÄFER, J. & PUCHELT, H. (1998). Platinum-Group-Metals (PGE) emitted from automobile catalytic converters and their distribution in roadside soils. *Journal of Geochemical Exploration* **64**, 307-314.

- SCHEFFER, F. & SCHACHTSCHABEL, P. (2002). *Lehrbuch der Bodenkunde*, 15th edition. Spektrum Akademischer Verlag GmbH, Heidelberg, pp. 593.
- SCHRAND, A. M., HUANG, H. J., CARLSON, C., SCHLAGER, J. J., OSAWA, E., HUSSAIN, S. M. & DAI, L. M. (2007). Are diamond nanoparticles cytotoxic? *Journal of Physical Chemistry B* **111**, 2-7.
- SCHRICK, B., HYDUTSKY, B. W., BLOUGH, J. L. & MALLOUK, T. E. (2004). Delivery vehicles for zerovalent metal nanoparticles in soil and groundwater. *Chem. Mater.* **16**, 2187-2193.
- SCHULTZ, E. (1994). Size fractionated determination of black carbon particles in airborne dust originating from highway traffic. *The Science of the Total Environment* **146/147**, 289-296.
- SCHULZ, D. (2007). Kleine Kratzer heilen von selbst. In *Industrie Anzeiger*. **36**, 62: http://www.industrieanzeiger.de/ia/live/fachartikelarchiv/ha_artikel/detail/31186958.html (september 2007).
- SELLERS, J. W. & TOONDER, F. E. (1965). *Reinforcement of elastomers*, J. Wiley and Sons edition, New York.
- SEMAAN, M. E., QUARLES, C. A. & NIKIEL, L. (2002). Carbon Black and silica as reinforcers of rubber polymers: Doppler broadening spectroscopy results. *Polymer Degradation and Stability* **75**, 259-266.
- SHANXI FOUR HIGH NANOTECHNOLOGY COMPANY LIMITED: <http://www.fhnm.com/english/cpzt1.htm> (september 2007).
- SHEA, P. J., MACHACEK, T. A. & COMFORT, S. D. (2004). Accelerated remediation of pesticide-contaminated soil with zerovalent iron. *Environmental Pollution* **132**, 183-188.
- SMOLDERS, E. & DEGRYSE, F. (2002). Fate and effect of zinc from tire debris in soil. *Environmental Science & Technology* **36**, 3706-3710.
- STO. (2006). Nanopartikel. Anwendungen und Risiken. Presentation at Ministerium für Arbeit und Soziales, Stuttgart.
- STONE, V., SHAW, J., BROWN, D. M., MACNEE, W., FAUX, S. P. & DONALDSON, K. (1998). The role of oxidative stress in the prolonged inhibitory effect of ultrafine carbon black on epithelial cell function. *Toxicology in Vitro* **12**, 649-659.
- STUDEBAKER, M. (1957). *Rubber Chem Technol* **30**, 1400.
- SUI, L., YU, L. Y. & ZHANG, Y. H. (2007). Catalytic combustion of diesel soot on Co-Sr-K catalysts. *Energy & Fuels* **21**, 1420-1424.
- SUN, Y. P., LI, X. Q., CAO, J. S., ZHANG, W. X. & WANG, H. P. (2006). Characterization of zerovalent iron nanoparticles. *Adv. Coll. Interface Sci.* **120**, 47-56.
- SUVA (2006). http://www.suva.ch/home/unternehmen/spezialthema/dossier_partikelfilter.htm (july 2007).
- TAN, I., TANIGUCHI, M., TANAKA, H., UENISHI, M., KAJITA, N., NISHIHATA, Y., MIZUKI, J. & NIIHARA, K. (2006). The self-regenerative "intelligent" catalyst for automotive emissions control. *Key Engineering Materials* **317-318**, 833-836.
- TANAKA, H., UENISHI, M., TANIGUCHI, M., TAN, I., NARITA, K., KIMURA, M., KANEKO, K., NISHIHATA, Y. & MIZUKI, J. (2006). The intelligent catalyst having the self-regenerative function of Pd, Rh and Pt for automotive emissions control. *Catalysis Today* **117**, 321-328.
- TCS & BFE. (2007). Verbrauchskatalog (ed. TCS), pp. 130, Emmen.
- THILL, A., ZEYONS, O., SPALLA, O., CHAUVAT, F., ROSE, J., AUFFAN, M. & FLANK, A. M. (2006). Cytotoxicity of CeO₂ nanoparticles for Escherichia coli. Physico-chemical insight of the cytotoxicity mechanism. *Environ. Sci. Technol.* **40**, 6151-6156.
- THOMAS, T., THOMAS, K., SADRIEH, N., SAVAGE, N., ADAIR, P. & BRONAUGH, R. (2006). Research strategies for safety evaluation of nanomaterials, part VII: Evaluating consumer exposure to nanoscale materials. *Toxicol. Sci.* **91**, 14-19.
- TONG, Z., BISCHOFF, M., NIES, L., APPLIGATE, B. & TURCO, R. F. (2007). Impact of fullerene (C60) on a soil microbial community. *Environ. Sci. & Technol.* **41**, 2985-2991.

- TRATNYEK, P. G. & JOHNSON, R. L. (2006). Nanotechnologies for environmental cleanup. *nano today* **1**, 44-48.
- TSCHAMBER, V., JEGUIRIM, M., VILLANI, K., MARTENS, J. & EHRBURGER, P. (2007). Comparison of the activity of Ru and Pt catalysts for the oxidation of carbon by NO₂. *Applied Catalysis B-Environmental* **72**, 299-303.
- ULRICH, A. & WICHSER, A. (2003). Analysis of additive metals in fuel and emission aerosols of diesel vehicles with and without particle traps. *Anal. Bioanal. Chem.* **377**, 71-81.
- UMWELTBUNDESAMT DESSAU. (2006). Edelmetall-Emissionen aus Pkw-Katalysatoren, Dessau.
- VAN BASSHUYSEN, R. & SCHÄFER, F. (ed.). motorlexikon.de: <http://motorlexikon.de/?l=5437&K=schmier%F6l> (september 2007).
- VANDERGHEYNST, J., SCHER, H., GUO, H.-Y. & SCHULTZ, D. (2007). Water-in-oil emulsions that improve the storage and delivery of the biolarvacide *Lagenidium giganteum*. *BioControl* **52**, 207-229.
- VARANASI, P., FULLANA, A. & SIDHU, S. (2007). Remediation of PCB contaminated soils using iron nano-particles. *Chemosphere* **66**, 1031-1038.
- VBSA. (2007). Der VBSA stellt sich vor. Verband der Betriebsleiter und Betreiber Schweizerischer Abfallbehandlungsanlagen: http://www.vbsa.ch/index.html?&page_id=21&node=14&level=0&l=2 (september 2007).
- VERBAND DER DEUTSCHEN LACKINDUSTRIE E. V. Jahresbericht 2005/2006 (ed. Verband der deutschen Lackindustrie e. V.), pp. 43: <http://www.lackindustrie.de/start.asp> (august 2007).
- VILLANI, K., BROSIUS, R. & MARTENS, J. A. (2005). Catalytic carbon oxidation over Ag/Al₂O₃. *Journal of Catalysis* **236**, 172-175.
- VILLANI, K., KIRSCHHOCK, C. E. A., LIANG, D., VAN TENDELOO, G. & MARTENS, J. A. (2006a). Catalytic carbon oxidation over ruthenium-based catalysts. *Angewandte Chemie-International Edition* **45**, 3106-3109.
- VILLANI, K., VERMANDEL, W., SMETS, K., LIANG, D., VAN TENDELOO, G. & MARTENS, J. A. (2006b). Platinum particle size and support effects in NO_x mediated carbon oxidation over platinum catalysts. *Environmental Science & Technology* **40**, 2727-2733.
- VOGT, B. (2004). Nanodiamonds increase the life of automotive paints. *Industrial Diamond Review* **3**, 30-31.
- VSLF. (2006). Entwicklung des schweizerischen Inland-Marktvolumens von Lacken, Farben, kunststoffgebundenen Putzen und Druckfarben (Schätzung), pp. 1. Verband Schweizerischer Lack- und Farbenfabrikanten.
- WARD, N. I. (1990). Multielement contamination of British motorway environments. *Sci Total Environ* **93**, 393-401.
- WARHEIT, D. B., WEBB, T. R., COLVIN, V. L., REED, K. L. & SAYES, C. M. (2007). Pulmonary bioassay studies with nanoscale and fine-quartz particles in rats: toxicity is not dependent upon particle size but on surface characteristics. *Toxicol. Sci.* **95**, 270-280.
- WAYCHUNAS, G. A., KIM, C. S. & BANFIELD, J. F. (2005). Nanoparticulate iron oxide minerals in soils and sediments: unique properties and contaminant scavenging mechanisms. *J. Nanopart. Res.* **7**, 409-433.
- WEN, L.-X., LI, Z.-Z., ZOU, H.-K., LIU, A.-Q. & CHEN, J.-F. (2005). Controlled release of avermectin from porous hollow silica nanoparticles. *Pest Manag. Sci.* **61**, 583-590.
- WERTSTOFF-BÖRSE GMBH. (2003). *Altireifenentsorgung in der Schweiz*: <http://www.wertstoffboerse.ch> (july 2007).
- WHITELEY, J. D. & MURRAY, F. (2003). Anthropogenic platinum group element (Pt, Pd and Rh) concentrations in road dusts and roadside soils from Perth, Western Australia. *Science Of The Total Environment* **317**, 121-135.
- XU, Y. & ZHAO, D. (2007). Reductive immobilization of chromate in water and soil using stabilized iron nanoparticles. *Water Research* **41**, 2101-2108.

- XU, Y. & ZHAO, D. (2006). Removal of lead from contaminated soils using poly(amidoamine) dendrimers. *Ind. Eng. Chem. Res.* **45**, 1758-1765.
- XU, Y. H. & ZHAO, D. Y. (2005). Removal of copper from contaminated soil by use of poly(amidoamine) dendrimers. *Environ. Sci. Technol.* **39**, 2369-2375.
- YARON-MARCOVICH, D., CHEN, Y., NIR, S. & PROST, R. (2005). High resolution electron microscopy structural studies of organo-clay nanocomposites. *Environmental Science & Technology* **39**, 1231-1238.
- YUAN, G. D. (2004). Natural and modified nanomaterials as sorbents of environmental contaminants. *J. Environ. Sci. Health A* **39**, 2661-2670.
- ZEREINI, F., ALT, F., MESSERSCHMIDT, J., VON BOHLEN, A., LIEBL, K. & PUTTMANN, W. (2004). Concentration and distribution of platinum group elements (Pt, Pd, Rh) in airborne particulate matter in Frankfurt am Main, Germany. *Environ. Sci. Technol.* **38**, 1686-1692.
- ZEREINI, F., ALT, F., RANKENBURG, K., BEYER, J.-M. & ARTELT, S. (1997). Verteilung von Platingruppenelementen (PGE) in den Umweltkompartimenten Boden, Schlamm, Strassenstaub, Strassenkehrgut und Wasser. Emission von Platingruppenelementen (PGE) aus Kfz-Abgaskatalysatoren. *Z. Umweltchem. Ökotox.* **9**, 193-200.
- ZEREINI, F., WISEMAN, C., ALT, F., MESSERSCHMIDT, J., MULLER, J. & URBAN, H. (2001). Platinum and rhodium concentrations in airborne particulate matter in Germany from 1988 to 1998. *Environ. Sci. Technol.* **35**, 1996-2000.
- ZHANG, W. X. (2003). Nanoscale iron particles for environmental remediation: An overview. *Journal of Nanoparticle Research* **5**, 323-332.

	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006 (calc)	
public transport	250	263	266	265	264	265	261	261	267	270	275	280	283	287	292		290	
private traffic	44782	45799	45152	44159	45106	46492	47431	48067	49028	50204	51649	52870	54093	54987	56100	56697	56981	
goods traffic	4592	4682	4699	4656	4777	4853	4822	4860	4958	5103	5252	5225	5228	5264	5359	5428	5471	
total																	62742	
	1990	1991	1992	1993	1994	1995	1996	1997	1998	1999	2000	2001	2002	2003	2004	2005	2006	2006 (calc)
national roads	1495	1502	1515	1530	1533	1540	1594	1613	1638	1642	1638	1673	1706	1759	1734	1756	1758	
cantonal roads	18278	18275	18297	18318	18326	18238	18224	18276	18176	18110	18097	18115	18048	18088	18117	18094		18040
municipal roads	51197	51197	51197	51197	51197	51197	51197	51197	51397	51397	51397	51397	51438	51446	51446	51446		51496
total																		

Table A1-1: Data on road length and mileage (BFS, 2006a; BFS, 2006b; BFS, 2007b).

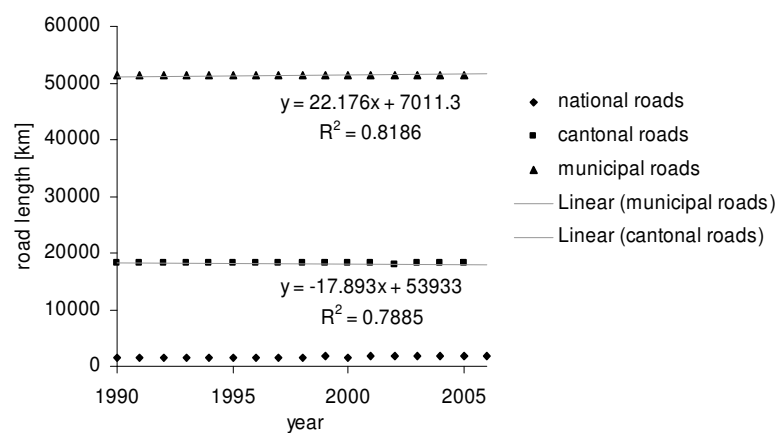


Figure A1-1: Road length 1990 to 2005 (BFS, 2007b).

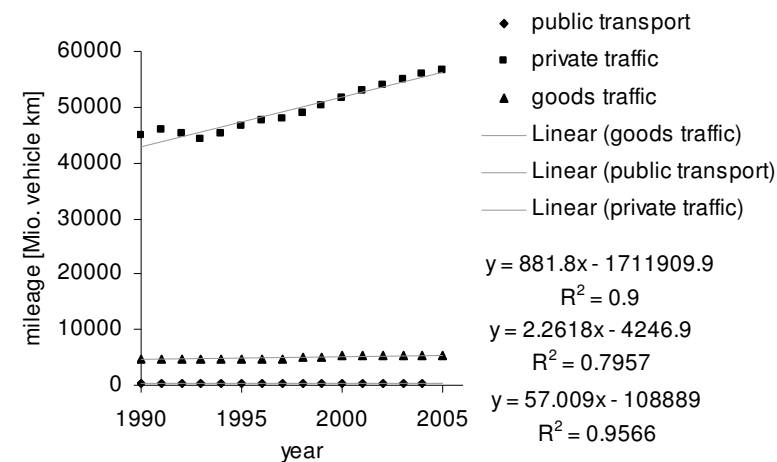


Figure A1-2: Mileage 1990 to 2005 (BFS, 2006a; BFS, 2006b).

Annex 2: Fertilizer

Table A2-1: Patents on fertilizers found in Derwent Innovations Index in ISI Web of Knowledge.				
Title	Inventor/s	Patent Number	Nanoparticles	Fertilizer type
Coated slow-releasing fertilizer and its production	Ying Z. Ying B. Wang B. Hu Y.	CN1854111-A	Inorganic filler (average particle size <1microns) ; polar bonding material	Coated slow-releasing fertilizer
Application of oxide nano rare earth in fertilizer	Wang J. Yang J. Liu X. Fan Y. Wu Y. Zheng W. Zhao F.	CN1686957-A	Nano rare earth	Coated seed, foliage spray, fertilizers
Application of hydroxide of nano rare earth to produce fertilizer products	Wang J. Yang J. Liu X. Fan Y. Wu Y. Zheng W. Zhao F.	CN1686955-A	Hydroxide of nano rare earth	Coated seed, foliage spray, fertilizers
Nano-micron foam plastic mixed polymer fertilizer adhesive coating agent preparation method	Zhang F. Yao C. Wang Y.	CN1631952-A	Nanomicron-submicron foamed plastic organic compound sticker mixed polymer	Cementing agent of cementated fertilizer and enveloping agent of deserted land fertilizer
Nano-sized controlled release fertilizer	Wu X.	CN1594239-A	unclear	Controlled release fertilizer
Production process of nanometer-submicron level PVA mixed polymer as fertilizer cementing and coating agent	Zhang F. Yao Q. Wang Y.	CN1609078-A	Nanometer-submicron level polyvinylalcohol (PVA) mixed polymer solution	Cementing agent for cementing type slow release fertilizer and coating agent for coating type slow release fertilizer
Liquid complex fertilizer which contains nanosilver and allicin and preparation method thereof to provide antibacterial effects thus to increase crop production	Kim W. H.	KR2005000265-A	Nanosilver	Liquid complex fertilizer
Preparation of nanometer-scale olefin/starch mixed polymer fertilizer covering agent	Zhang, F. Wang, Y. Zhang, J.	CN1546543-A	Nano level non-homogeneous phase mixed polymer of hydroxyethyl methacrylate, acrylic nitrile and starch	Slow/controlled release fertilizer
Active nano grade organic fine humic fertilizer and its production	Wu X.	CN1472176-A	Nano-class fermented active organic fertilizer	Active organic fertilizer
Production technology of nano-clay-polyester mixed polymer fertilizer	Zhang, F. Zhao B.	CN1414033-A	Nano-class clay-polyester mixed	Cementing agent for coating

coating cementing agent	Zhang J.		polymer	slow/controlled releasing fertilizer and mixed fertilizer; earth film and soil improver
Production technology of coating cement for nano sulfonate lignin mixture fertilizer	Zhang F. Shi C. Zhao B.	CN1417173-A	Nanometer-level sulfonated lignin mixture water solution	Coating cement for controlled release fertilizer, granulating cement for organic-inorganic composite fertilizer
Process comprises combining soil repairing technique and nanobiological fertilizer to promote growth of microbes, improve soil and remove residual herbicides	Min J. Zou J. Zhu Y	CN1413963-A	Nano-class biological fertilizer	Biological fertilizer to make soil dynamically balanced, promote growth of microbes, improve soil and remove residual herbicides
New method for preparation of controlled release special fertilizer comprises mixing and granulating Ximaxi clay minerals, coating with various fertilizers, trace elements and additives and finally coating with nano-clay	Li Y. Yin G. Liu L.	CN1349958-A	Nano clay	Controlled release special fertilizer
Efficient use of rocks in agriculture – by mixing the pulverised rocks with fertilisers	Koeroesi, F. Marai, G. Horvath, J. Illes, B.	HU62248-T	Colloid particles (1-500nm)	Composite of colloid rock particles mixed and boiled with organic and inorganic fertilisers
Tubular assembly useful for manufacturing e.g. packaging material for liquid chromatography columns, ultrafiltration material or ceramic insulation material comprises phases of nanocrystalline divalent metal ion phosphate	MacPhee C. Wright D.	WO2007003969-A2	Metal nanocrystalline phosphate	Slow release fertilizer
Preparation of a polymer-containing composition useful in e.g. coating ink or cleaning, rubber or resin formulation involves preparing mixture of an inorganic anionic clay and a cyclic monomer; and polymerizing the monomer	Schomaker E. De Vos S. C.	WO2006000550-A1	Polymer-based nanocomposite	Controlled release fertilizer
Production process for mixing polymer of nano-subnano grade marsh dregs-gangue compound	Zhang F. Wang Y. Zhang J.	CN1560191-A	Nano-submicron level pond residues-coal gangue compound hybrid polymer	Sustained/controlled release fertilizer, adhesive coating agent
Drug nanoparticles for manufacturing medical agent, having preset average particle diameter, is formed by irradiating compact of drug powder with laser light, such that drug material is released as finely divided component	Nagare S. Senna M.	WO2004110405-A1	Drug nanoparticles (average diameter of 100nm)	For manufacturing chemical fertilizer
Bioactive agent delivery system useful for delivering bioactive agents such as DNA, and antibiotics, comprises hollow tubular body defining	Dennis D. M. Martin C. R. Rogers R. J.	US2004076681-A1	nanotube (hollow tubular body: max. dimension of less than 10microns;	Delivering of fertilizer, timed release

inner void, comprising first end and second end, and bioactive agent contained within inner void	Stewart J. D.		capped nanotube: max. dimension of less than 100microns)	
Biological organic compound liquid nanofertilizer and preparing process	Ni J.	CN1451636-A	?	Nano-class composite liquid fertilizer
Stable nanoparticulate composition for release of active agents, e.g. drugs, cosmetics or agrochemicals, comprising active agent adsorbed on coupled to nanoparticulate inorganic core	Bosch W. H. Cooper E. R. Matijevic E. Ryde N. P.	WO2003032959-A1	Nanoparticulate inorganic core (particle size <1000nm)	Fertilizer (adsorbed on the core or linked to the core by at least one coupling agent)
Preparation of free nano-sized particles of active agents useful in e.g. pulmonary delivery involves use of an aerosol flow reactor method	Watanabe W. Kauppinen E. Ahonen P. Brown D. Muttonen E.	WO200256866-A	Free nano-sized particle of an active agent	Fertilizer in the form of dry powder, powder dispersed in liquids, or colloidal suspension
Production of nanoparticles used for bioactives, cosmetics, foods or industrial products, by fluid bed spray drying from non-aqueous or mixed solvents	Kerkhof N. J. Ong J. T. H.	WO200145674-A	Nanoparticles of a poorly water soluble or insoluble compound (particle size <1000nm)	fertilizer
Plant growth liquid containing titanium dioxide nanoparticles comprises an aqueous titanium dioxide colloid solution incorporating a surfactant and e.g. bactericidal agents	Lee S. Choi H.	BR200403721-A	Titanium dioxide nanoparticles	Plant growth liquid
Nano diatomite and zeolite ceramic crystal powder, useful e.g. in the manufacture of a plant growth medium, comprises powder of diatomite and powder of zeolite mixed with the diatomite	Yu E. Q.	US2005115469-A1	Nano diatomite and zeolite ceramic crystal powder	Plant growth medium

Annex 3: Sealings

Table A3-1: Products for automotive sealing found in a web search.

product	durability	amount applied	NP concentration	applications mode	source
NANO-line				fluid	http://www.penanoclean.ch/chemische%20nano.htm
All automotive		6.3mL/m ²	Nano-polymers	Spray or rag	http://www.nanotol.de/nano_tol_shop.htm
Wheel and paint sealing	A couple of month	6.7mL/m ²		Spray and rag	http://www.nano-beratung.ch/shop.htm
Paint and paint accelerator (Härter)	Optional application			Spray among others	http://www.nano-beratung.ch/shop.htm
De-mister (Antibeslag)		10mL/m ²		spray	http://www.nanotech.ch/index.php?id=19
Plastic sealing	12Mt or 15000km	15mL /vehicle			http://www.renagate.ch/index.php?id=63
Plastic sealing				spray	http://www.nano-world.ch/autolack.htm
Metal sealing		20mL/m ²		spray	http://www.nano-world.ch/autolack.htm
Glass sealing	1year or 30000km	5mL/m ²		spray	http://www.nanotech.ch/index.php?id=19
Glass sealing	20000km			rag	http://www.nanorein.ch/shop/home.html
Glass sealing	24Mt	20mL/m ²		spray	http://www.nano-nt.ch/NANO-NT-f-uuml;r/Auto-Bike-Felgen:::28_63.html
Glass sealing		10mL/m ²			http://www.nanoproofed.de/reload.html?home.htm
Glass sealing		5-10mL/m ²		Spray, rag	http://www.autonano.de/artikel.php?nummer=6&shopid
Glass sealing		10mL/m ²		rag	http://www.nanoproofed.de/reload.html?home.htm
Glass sealing	1year or 30000km	5mL/m ²		spray	http://www.ac-nano.ch/acnano-autoglasversiegelung-p-17.html
Glass sealing		6.7mL/m ²		fluid	http://www.nanorein.ch/shop/home.html
Glass sealing		10-15mL/m ²		spray	http://www.nanoversiegelung.ch/

Glass sealing	1year	10mL/m ²			http://www.nanoproofed.de/reload.html?home.htm
Glass sealing	8-12Mt or 30000km	1rag / wind screen		rag	http://www.nano-world.ch/autolack.htm
glass sealing		100mL / 2Combis oder Kleinbus		spray	http://www.nano-world.ch/autolack.htm
Glass sealing	12 month or 20000km	6.7mL/m ²		spray	http://www.nano-beratung.ch/shop.htm
Glass sealing	8-12Mt or 20000km	15mL/win d and two other screens; 30mL for a car; 50mL for a van/Com bi		fluid	http://www.nano-world.ch/autolack.htm
Glass sealing		10mL/win d screen		rag	http://www.nanoversiegelung.ch/
Glass sealing		5mL/m ²		rag	http://www.nanotech.ch/index.php?id=19
Glass sealing	1year or 20000km	10mL/m ²			http://www.nano4swiss.ch/index.php?page=shop.browse&category_id=12&option=com_virtuemart&Itemid=26
Paint sealing	1 year or longer lasting			spray	http://www.nano-world.ch/autolack.htm
Paint sealing		10mL/m ²			http://www.nanotech.ch/index.php?id=19
Paint sealing		5mL/m ²		Fluid and rag	http://www.nanotech.ch/index.php?id=19
Paint sealing		5- 10mL/m ²		fluid	http://www.nanoversiegelung.ch/
Paint sealing	6-9Mt	20mL/m ²	Diamant, silber, ke- ramik oder glas	Aerosol spray	http://www.autonano.de/artikel.php?nummer=6&shopid
Paint sealing	12Mt or 15000km	50mL/veh icle			http://www.renogate.ch/index.php?id=63

Paint sealing		10-15mL/m2			http://www.ac-nano.ch/acnano-autoglasversiegelung-p-17.html
Paint sealing	6Mt	0.5L/ 3-4 vehicles		fluid	http://www.nano-nt.ch/NANO-NT-f-uuml;r/Auto-Bike-Felgen:::28_63.html
Wheel sealing	Several month	20mL/m2	Kermik, 10nm durchmesser	spray	http://www.nano-nt.ch/NANO-NT-f-uuml;r/Auto-Bike-Felgen:::28_63.html
Wheel sealing				rag	http://www.nano4swiss.ch/index.php?page=shop.browse&category_id=12&option=com_virtuemart&Itemid=26
Wheel sealing		25mL/wheel		Spray	http://www.nanotech.ch/index.php?id=19
Wheel sealing		20-50mL/wheel		spray	http://www.nanoversiegelung.ch/
Wheel sealing		5-10mL/m2		fluid	http://www.nanoproofed.de/reload.html?home.htm
Wheel sealing		100mL/ 3x4 wheels		spray	http://www.nanorein.ch/shop/home.html
Wheel sealing		100mL/ 4wheels		spray	http://www.nano-world.ch/autolack.htm
Wheel sealing		250mL/3x4 wheels		spray	http://www.autonano.de/artikel.php?nummer=6&shopid
Wheel sealing	12Mt or 15000km	25mL/vehicle			http://www.renagate.ch/index.php?id=63
Wheel sealing		15-75mL/wheel			http://www.nano-concept.ch/automobile/classivo_classic.html
Wheel sealing		25mL/wheel		spray	http://www.ac-nano.ch/acnano-autoglasversiegelung-p-17.html

