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Modifications of surface materials and their effects on cleanability as studied by radiochemical methods

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ACADEMIC DISSERTATION

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CONTENTS

ABSTRACT

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Modifications of surface materials and their effects on cleanability have important impacts in many fields of activity. In this study the primary aim was to develop radiochemical methods suitable for evaluating cleanability in material research for different environments. Another aim was to investigate the effects of surface modifications on cleanabilitity and surface properties of plastics, ceramics, concrete materials and also their coatings in conditions simulating their typical environments. Several new ^{51}Cr and ^{14}C labelled soils were developed for testing situations.

The new radiochemical methods developed were suitable for examining different surface materials and different soil types, providing quantitative information about the amount of soil on surfaces. They also take into account soil soaked into surfaces. The supporting methods colorimetric determination and ATP bioluminescence provided semi-quantitative results. The results from the radiochemical and supporting methods partly correlated with each other.

From a material research point of view numerous new materials were evaluated. These included both laboratory-made model materials and commercial products. Increasing the amount of plasticizer decreased the cleanability of poly(vinyl chloride) (PVC) materials. Microstructured surfaces of plastics improved the cleanability of PVC from particle soils, whereas for oil soil microstructuring reduced the cleanability. In the case of glazed ceramic materials, coatings affected the cleanability. The roughness of surfaces correlated with cleanability from particle soils and the cleanability from oil soil correlated with the contact angles. Organic particle soil was removed more efficiently from TiO_2-coated ceramic surfaces after UV-radiation than without UV treatment, whereas no effect was observed on the cleanability of oil soil. Coatings improved the cleanability of concrete flooring materials intended for use in animal houses.

Keywords: radiochemistry, ^{51}Cr, ^{14}C, gammaspectrometry, liquid scintillation counting, plastic, ceramic, concrete, cleaning, soiling

FOREWORD

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Jenni Määttä

ABBREVIATIONS

AFM	Atomic force microscopy
ATP	Adenosine triphosphate
Benzoflex®	Plasticizer, diethylene glycol dibenzoate, triethylene glycol dibenzoate, bis (2-ethylhexyl) adipate, diethylene glycol monobenzoate
cpm	Counts per minute
DHP	Plasticizer, di-isohexyl phthalate
DIHP	Plasticizer, di-isoheptyl phthalate
DINP	Plasticizer, di-isononyl phthalate
DOP	Plasticizer, dioctyl phthalate
dpm	Disintegrations per minute
E	Colour value of surface, calculated from L*a*b* values
EC-decay	The process of electron capture
ELPI	Elinympäristön pintojen hallinta (Control of surfaces in everyday life) –project
FTIR	Fourier transform infrared spectroscopy
GM-detector	Geiger-Müller detector
Half life, $T_{½}$	The time for the radioactivity of a radioelement to decay to one-half of its original value
Hexamoll® DINCH	Plasticizer, di-isonyl-cyclohexane-1,2-dicarboxylate
HPGe	High purity Ge-crystal
Inorganic particle soil	Radiochemical model soil containing labelled chromium oxide
LSC	Liquid scintillation counter
MMM	Ministry of Agriculture and Forestry
NaI(Tl)	Sodium-iodine-thallium activated crystal
Oil soil	Radiochemical model soil containing labelled triolein
Organic particle soil	Radiochemical model soil containing labelled chromium acetyl acetonate
PUR	Polyurethane
PVC	Vinyl, poly(vinyl chloride)
R_a	Roughness, arithmetical mean deviation of the profile
RH	Relative humidity
RLU	Relative light unit
SEM	Scanning electron microscopy
TiO_2	Coating of ceramic surface, titanium dioxide
UHV	Ultra high vacuum
UV	Ultra violet
wt%	Weight percent
α-decay	Alfa-decay, the emission of helium nuclei, ${}^{4}_{2}He^{++}$
β-decay	Beta-decay, the creation and emission of either electrons or positrons
γ-decay	Gamma-decay, the emission of electromagnetic radiation where the transition occurs between energy levels of the same nucleus
θ	Contact angle
ΔE	Total change of colour value

LIST OF ORIGINAL PUBLICATIONS

I **Määttä, J.,** Koponen, H.-K., Kuisma, R., Kymäläinen, H.-R., Pesonen-Leinonen, E., Uusi-Rauva, A., Hurme, K.-R., Sjöberg, A.-M., Suvanto, M. and Pakkanen, T.A. 2007. Effect of plasticizer and surface topography on cleanability of plasticized PVC materials. Applied Surface Science 253, 5003-5010.

II **Määttä, J.,** Piispanen, M., Kuisma, R. Kymäläinen, H.-R., Uusi-Rauva, A., Hurme, K.-R., Areva, S., Sjöberg, A.-M. and Hupa, L. 2007. Effect of coating on cleanability of glazed materials. Journal of the European Ceramic Society 27, 4555-4560.

III **Määttä, J.,** Piispanen, M., Kymäläinen, H.-R., Uusi-Rauva, A., Hurme, K.-R., Areva, S., Sjöberg, A.-M. and Hupa, L. 2007. Effects of UV-radiation on the cleanability of titanium dioxide-coated glazed ceramic tiles. Journal of the European Ceramic Society 27, 4569-4574.

IV Kymäläinen, H.-R., **Määttä, J.,** Puumala, M., Kaustell, K.O., Mattila, T., Joutsen, B.-L., Kuisma, R., Hurme, K.-R., Uusi-Rauva, A. and Sjöberg, A.-M. A laboratory study of the effect of coating on cleanability of concrete flooring for use in piggeries. Biosystems Engineering (In press).

V **Määttä, J.,** Kymäläinen, H.-R., Puumala, M., Mahlberg, R., Kuisma, R., Salparanta, L., Löija, M., Talibachew, A., Hurme, K.-R., Uusi-Rauva, A., Ritschkoff, A.-C., Sjöberg, A.-M. Properties and cleanability of new and traditional agricultural surface materials. Agricultural and Food Science (Accepted).

In this dissertation the Roman numerals I-V are used to refer to these original publications.

THE AUTHOR'S CONTRIBUTION IN THE ORIGINAL PUBLICATIONS

I Jenni Määttä designed and performed the radiochemical measurements, analysed part of the data, interpreted the results and wrote part of the publication. She commented and revised the whole publication.

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V Jenni Määttä designed and performed the radiochemical measurements, analysed the data, interpreted the results and wrote the main part of the publication.

1 INTRODUCTION

Building materials must withstand chemical and mechanical hazards such as moisture, soils, air pollutants and wearing. Soiling of surfaces incurs considerable expense to building operations and maintenance. The development of new easy-to-clean or even self-cleaning surfaces has recently been under the focus of nanotechnology, e.g. by investigating different surface structures. Some models of self-cleaning surfaces are available in nature, such as lotus plant leaves (Neinhuis and Barthlott 1997) and the wings of insects (Watson and Watson 2004). They have special nano- and microstructures which affect the cleanability properties of surfaces. Chemical effects, such as UV-radiation of TiO_2-surfaces, can also be used to improve surface cleanability properties (Wang et al. 1997, Fujishima et al. 2000a, Fujishima et al. 2000b). Surface properties, e.g. hydrophobicity, porosity, topography and surface forces affect the soiling and cleanability phenomena. In addition the different soil types and components of surfaces have an effect on cleanability.

The present study concerns parts of three projects, which were coordinated by or participated in by the Department of Agrotechnology, University of Helsinki. The PVC (poly(vinyl chloride)) materials and the ceramic studies were part of the ELPI (Control of surfaces in everyday life) project in the Clean Surfaces programme of Tekes (the Finnish Funding Agency for Technology and Innovation) (Technology Programme Report 17/2006). The study concerning concrete materials of piggeries was a part of the “Floor surface quality of farm buildings” project financed by MMM (Finnish Ministry of Agriculture and forestry) (Puumala et al. 2006). The flooring materials of cattle barns were evaluated in the project “Easy-to-clean surfaces in farm buildings”, also financed by MMM.

The main focus of the ELPI project was in understanding the chemistry and physics of soil-resistant surfaces of everyday life and developing research methods to fit the specific features of the surface materials in question. The soiling and cleaning processes of plastics and ceramics were studied. Two earlier dissertations of our group have discussed determination of cleanability of plastic surfaces (Pesonen-Leinonen 2005) and physical characterization of plastic surfaces in wearing and cleanability research (Kuisma 2006). The focus of the agricultural projects was on evaluating the effects of quality of floor surface and especially coatings on animal well-being, food safety, safety at work, durability and cleanability. The effects of different compositions and coatings of concrete on cleanability were examined in our studies.

The focus of this dissertation is on the development of radiochemical methods for evaluating cleanability of different surface materials and different soil types. The cleanabilities of plastic, ceramic and concrete materials and coatings were examined.

Four different radiochemical model soils and two labelled natural soils were used in the radiochemical studies. Unlabelled natural soils were used in the colorimetric study and the ATP bioluminescence study which were used as supporting methods. Different kinds of analytical methods are useful when developing new easy-to-clean or even self-cleaning surfaces for different environments.

2 REVIEW OF THE LITERATURE

2.1 Methods in cleanability research of materials

2.1.1 Radiochemical methods

Radioactive decay is a spontaneous process which is insensitive to pressure, temperature or chemical form. For this reason, radioactive nuclei can be characterized by their decay period and their mode and energy of decay. Radiation can arise from three different components: α- or β-particles or γ-rays (Choppin et al. 2002). The main advantage of the radiochemical methods is their ability to provide quantitative information on the amount of soil both on the surface and soaked into the material.

The application of radiochemical methods in cleanability research has been used to determine soiling and cleaning of different kinds of surface materials (Table 1) and textile floor coverings (Jokelainen and Uusi-Rauva 1976b, Jokelainen and Uusi-Rauva 1979, Jokelainen et al. 1982). Radiochemical methods have also been used to compare the efficiencies of detergents on PVC, chromium and steel surfaces (Table 1) and cleaning methods for removing metallic impurities (Wang et al. 1999, Lu et al. 2000, Wang et al. 2001). In addition, radiochemical methods have been used in laundering studies (Morris and Prato 1985, Shebs 1987).

Table 1. Examples of radioactive tracer techniques used in cleanability studies of different kinds of surface materials.

Materials	**Radio-isotope**	**Determination method**	**Soil**	**Conclusion**	**Reference**
Linoleum, rubber sheet, asphalt-tile, vinyl asbestos tile, quartz filled vinyl tile, vinyl sheet	^{14}C, ^{51}Cr, ^{56}Mn	a NaI(Tl)-crystal, a GM-detector	Olive oil, ferric oxide, ferric oxide+olive oil, chromium oxide	Differences in soiling of different flooring materials	Ohlson and Wäänänen 1971
Linoleum, PVC	^{51}Cr	a NaI(Tl)-crystal	Chromium oxide, chromium oxide+oil, chromium oxide+water	Accumulation on the linoleum flooring. No accumulation was found on the PVC flooring	Jokelainen and Uusi-Rauva 1976a
PVC, chromium on glass	^{14}C	a GM-detector	Tripalmitin and triolein	Ellipsometer can be used to study the efficiency of detergents	Engström and Bäckström 1987
Stainless steel tubes	^{14}C	a proportional counter	Palmitic acid	Detergents were preferable to solvents for cleaning UHV components	Benvenuti et al. 1999
PVC model materials, quartz vinyl, linoleum	^{51}Cr	a NaI(Tl)-crystal	Chromium oxide, chromium oxide+triolein, chromium acetyl acetonate+triolein	The type and amount of plasticizer affected soil adhesion on PVC materials. Chromium acetyl acetonate+triolein accumulated	Pesonen-Leinonen et al. 2006a

In general, β- and γ-decays are used in surface cleanability research (Table 2). The determination method is chosen according to the type of measured radiation. In cleanability research the radiation can be measured directly from the surface as in gammaspectrometry, or radioactive material can be dissolved in a scintillation liquid as in liquid scintillation counting. The advantages and disadvantages of radiochemical determination methods in cleanability research are presented in Table 2.

Typically, liquid scintillation counting is used to measure the activity of α- and β-decay. It is not recommend for use in direct measuring methods (such as the Geiger Müller-counter) to measure low energy β-decay because the absorption in soil is not constant. Therefore the β-decay must be measured with methods in which the soil is separated from the surface. When using liquid scintillation counting, the β emitter is dissolved homogenous by in the scintillation liquid. The counting efficiency for ^{14}C is very high (Knoll 1989). Gammaspectrometry is used to measure γ-radiation. The absorption of γ-decay in the soil is so low that the method can be used in for direct measurements.

Table 2. Examples of the radiochemical determination methods used in material and cleanability research.

Device	Observed radiation	Site of radiation	Advantage	Disadvantage	Study where used
Geiger-Müller-detector	β	Surface	Sample is not destroyed	Adhered activity cannot be observed (low energy of β), long dead time	Ohlson and Wäänänen 1971, Engström and Bäckström 1987, Benkovich and Anderson 2003
Liquid scintillation counter	β	Scintillation liquid	High detection efficiency, sample geometry has no effect	Sample is destroyed, sample colour and composition can have an effect	Jokelainen et al. 1982
Proportional counter	β	Surface	Sample is not destroyed, sample's colour and composition have no effect	Adhered activity cannot be observed (low energy of β)	Benvenuti et al. 1999
NaI(Tl)-crystal	γ	Surface	Sample is not destroyed, also detects adhered activity, sample's colour and composition have no effect	Sensitive to humidity and temperature, lower energy resolution	Ohlson and Wäänänen 1971, Jokelainen and Uusi-Rauva 1976a, 1976b, 1979, Jokelainen et al. 1982, Pesonen-Leinonen et al. 2006a
HPGe-detector	γ	Surface	High energy resolution	Low detection efficiency	Wang et al. 1999, 2001, Lu et al. 2000

Radiochemical model soils consist of bulk soil matter, labelled radioisotope and solvent. The model soils used should contain typical components of the environment of the evaluated materials. The natural soils of buildings may contain inorganic particles, organic particles and oil components (Pesonen-Leinonen 2003). Manure and feed are typical soils in agricultural buildings. The prerequisite for selection of the isotope is that it is chemically bound to the bulk soiling agent. The initial radioactivity of the surface is compared to the amount of the labelled component of soil on the surface. By using different radio-isotopes, cleanabilities of different components of model soils can be examined. Different particle components, ^{51}Cr and ^{56}Mn, are used to label particle model soils, whereas ^{14}C and ^{3}H are normally used to label oil model soils (Table 1, Jokelainen et al. 1982). In addition ^{22}Na, ^{54}Mn, ^{59}Fe, ^{60}Co, ^{64}Cu, ^{65}Zn and ^{137}Cs are used as radio tracers to compare cleaning methods (Wang et al. 1999, Lu et al. 2000, Wang et al. 2001). The selected isotope should have a half-life long enough to be suitable for measurements. In addition the energy of emitted decay must be high enough to be observed.

2.1.2 Other methods

When the purpose of the investigations is wider than material research, examination of surface cleanability has included other kinds of methods in addition to radiochemical determination. In earlier studies different chemical and physical methods have been used, for example colorimetry, bioluminescence of ATP, FTIR (Fourier Transform Infrared), Auger spectrometry and optical methods (Table 3). These determination methods give qualitative or semi-quantitative information about the amount of soil on the surface, in contrast to the radiochemical methods which provide quantitative information about both on and beneath the surface.

Table 3. Examples of chemical and physical methods in cleanability research.

Determination method	**Evaluation of the method**	**Study where used**
ATP (Adenosine triphospate) bioluminescence	Semi-quantitative. Suitable for field and laboratory studies	Poulis et al. 1993, Kuisma et al. 2003, Larson et al. 2003, Kuisma et al. 2005a, Aycicek et al. 2006, Redsven et al. 2007
Colorimetric	Semi-quantitative. Suitable for field and laboratory studies	Pitts et al. 1998, Williamsson 1999, Pesonen-Leinonen et al. 2003, Redsven et al. 2003, Tenorio Cavalcante et al. 2004, Dondi et al. 2005, Kuisma et al. 2005a, Kuisma et al. 2005b, Pesonen-Leinonen et al. 2005
Optical methods (near infrared optical range)	Semi-quantitative. Suitable for laboratory studies	Benvenuti et al. 1999, Minabe et al. 2000, Fretwall and Douglas 2001, Tikka et al. 2004, Braithwaite et al. 2005, Zhang et al. 2006, Kronberg et al. 2007
Atomic Force Microscopy	High resolution pictures. Unsuitable for rough surfaces	Myshkin et al. 1999, Verran et al. 2000, Myshkin et al. 2003, Verran et al. 2003, Peltonen et al. 2004, Shulha et al. 2004, Whitehead et al. 2004, Kuisma et al. 2005a, Kuisma 2006, Koponen et al. 2007a
Confocal Microscopy	Minimal sample preparation. Background texture often confuses the detectors. Suitable for various surface materials	Hupa et al. 2005, Kuisma 2006, Al-Shammery et al. 2007, Jones et al. 2007, Kronberg et al. 2007, Sundberg et al. 2007
Profilometry	No sample preparation. Suitable for various surface materials	Verran et al. 2003, Kuisma et al. 2005a, Kuisma et al. 2005b, Kuisma et al. 2005c, Pesonen-Leinonen et al. 2005, Kuisma 2006, Koponen et al. 2007a
Scanning Electron Microscopy	High magnification imaging. Samples must be vacuum compatible. Requires a conducting surface. Suitable for various surface materials	Verran et al. 2000, Adl and Rahman, 2001, Jullien et al. 2002, Dondi et al. 2005, Hupa et al. 2005, Kuisma et al. 2005a, Kuisma et al. 2005b, Kuisma 2006, Arstila et al. 2007, Fröberg et al. 2007a, Fröberg et al. 2007b

The cleanability of a surface is related to its properties, for example topography and surface chemistry. Kuisma (2006) presented methods for measuring surface topography. Different roughness parameters were presented by Gadelmawla et al. (2002) and Peltonen et al. (2004). Kuisma (2006) also studied the wearing mechanisms and the effect of wearing on cleanability of plastic surfaces.

Surface properties can be described for example by the chemical composition of a surface, or by its porosity, hydrophobicity or hydrophilicity of surface. The terms hydrophilic and hydrophobic are used to describe the tendency of a surface to become wetted by aqueous liquid (Shaw 1994). Contact angle characterizes the hydrophobic properties of surfaces and it can be used to define surface energies, surface heterogeneity and surface roughness (Lam et al. 2001). The most commonly used technique is the sessile drop method (Adamson and Gast 1997). The Young-Laplace equation is used for fitting angle curves using a calculation based on the contact angles on either side of the droplet and their mean values (Pesonen-Leinonen et al. 2005). In one study by Pesonen-Leinonen et al. (2006b), contact angles provided tentative relationships between the surface characteristics, such as wettability and surface free energy, and the cleanability of plastic surfaces.

2.2 Development of new model materials and coatings

Soil-resistant surface properties of materials are important for example in the food industry and in agricultural buildings. During recent years increasing effort has been made towards on modification of surface properties to develop more easy-to-clean or self-cleaning surface materials (Wang et al. 1997, Fujishima et al. 2000a, Fujishima et al. 2000b, Fretwell and Douglas 2001). Nano- and microscale surface structures are common in nature, improving surface properties e.g. by increasing soil resistance. The self-cleaning effect of lotus plant leaves (lotus effect) is due to the superhydrophobic properties and the surface structure, which decreases the water sliding angle of the leaves (Neinhuis and Barthlott 1997, Gould 2003). On the other hand superhydrophilicity can also affect self-cleaning, when water spreads out to superhydrophilic surface (Gould 2003). Koponen (2007) recently examined the lotus effect, i.e. superhydrophobic properties of surfaces and micropatterning of surfaces.

2.2.1 Plastic materials

The soil resistance of commercial PVC products is affected by each component of the product formulation, including plasticizers, stabilizers, fillers, extenders, lubricants, antioxidants and dyes (Colletti et al. 1998). Pesonen-Leinonen (2005) presented the components of plastic materials in more detail. Puukilainen (2007) discussed chemical modification and surface structuring of hydrophobic polyolefins. In his study, the hydrophobicity of polyethylenes improved after perfluoropolyether treatment. The lubricant treatment improved the friction properties and surface structuring had a great effect on the water contact angle. The common targets of modification of plastic surfaces were to develop new plasticizers and mixtures (Bohnert et al. 1998, Puukilainen and Pakkanen 2005, Koponen et al. 2007a), and to modify hydrophobic properties (Fresnais et al. 2006, Li et al. 2006, Puukilainen et al. 2006, Koponen et al. 2007b) and surface structures (Li et al. 2006, Puukilainen et al. 2006, Koponen et al. 2007b). Surface structure was reported to affect the hydrophobic properties (Fresnais et al. 2006, Li et al. 2006, Koponen et al. 2007b).

2.2.2 Ceramic materials and coatings

During recent years, the properties of glazed ceramic tiles have been improved by using different compositions and coatings. In general the studied properties have been surface structure (Liu et al. 1996, Bolelli et al. 2005, Mateus et al. 2005), hydrophilic properties (Watanabe et al. 1999, Fujishima et al. 2000a, Wu et al. 2005, Fujishima and Zhang 2006, Pore et al. 2006, Kronberg et al. 2007) and crystallization (Llusar et al. 2002, Romero et al. 2003, Hsiang and Lin 2004, Jung and Park 2004, Bolelli et al. 2006, Fröberg et al. 2007a, Fröberg et al. 2007b). In some studies it was reported that the manufacturing process affected crystallization and surface properties (Llusar et al. 2002, Romero et al. 2003, Hsiang and Lin 2004, Pore et al. 2006, Fröberg et al. 2007b). A new function of the coating is to make the surface easy-to-clean or self-cleaning. One of the most used of these coating materials is titanium dioxide, TiO_2. It generates two separate photo-induced phenomena: a photocatalytic phenomenon and a superhydrophilic phenomenon. In many studies, the contact angles of TiO_2 coated surfaces decreased with the illumination time of UV-light (Watanabe et al. 1999, Nakajima et al. 2000, Fujishima et al. 2000b, Sakai et al. 2003). Increasing crystallite size was reported to increase photoactivity (Jung and Park 2004).

2.2.3 Concrete materials and coatings

In agricultural buildings concrete is a very generally used floor material. The floorings should withstand strong chemical and mechanical stresses and in other hand they should provide comfortable areas for animals. The mechanical stresses on surfaces of in animal buildings come especially from animals and machines. The chemical stresses especially are due to milk, silage and manure (ACI 515.1R-79 1985, Bertron et al. 2005, Nilsson 2005). Because concrete is a very porous material, in many cases the improvement of concrete is based on limiting its absorption of liquids (Barbucci et al. 1997, Almusallam et al. 2003, Moon et al. 2007). Durability of concrete can also be improved by using different cement types and pozzolanic additions, changing the aggregate type, addition of polymers to the concrete mix, application of cement-bound surface layers and impregnation with water repellents, pore blockers or coatings (Barbucci et al. 1997, De Belie et al. 1997, De Belie et al. 1998, De Belie et al. 2000, Almusallam et al. 2003, Moon et al. 2007). The other targets of modification studies of concrete materials were improved durability (De Belie et al. 1997, De Belie et al. 1998, Moon et al. 2007) and anti-bacterial and anti-fungal properties (Navas Martin and Borralleras Mas 2005).

2.3 Cleanability studies of new materials

Pesonen-Leinonen (2005) discussed different soiling and cleaning apparatus which are generally used in laboratory studies to simulate and control soiling and cleaning of plastic and ceramic surfaces. The different types of apparatus differ in their soiling and cleaning mechanisms and are used for different types of soils or surface materials. In addition Pesonen-Leinonen (2003 and 2005) has presented different types of artificial model or standard soils.

2.3.1 Cleanability of plastic materials

There are only a few studies focusing on the components of plastic materials and their effects on cleanability, and these are summarised in Table 4. Structure, volatility, concentration, extraction resistance and solubility parameters of the plasticizer, the abrasion resistance of the wearing surface and the thermoplastic nature of plasticized PVC affect soiling (Colletti et al. 1998). In studies by Colletti et al. (1998) and Pesonen-Leinonen et al. (2006a), increasing the amount of plasticizer decreased the soil resistance of samples. However, a minimum level of plasticizer is needed in the uppermost surface in order to give the surface suitable mechanical properties (Colletti et al. 1998). The type of soil affected both soiling and cleaning (Kuisma et al. 2003, Tikka et al. 2004, Kuisma et al. 2005b).

Table 4. Cleanability studies of plastic surfaces.

Materials	**Soil**	**Methods**	**Results**	**Reference**
Unplasticized PVC	Triglycerides: triolein, tripalmitin, palmitic acid	Ellipsometry	The performance of a surfactant was sensitive to other components in the solution and depended on the type of surfactant	Bäckström et al. 1988
PVC plastics; plasticizers BBP, DIHP, DOP, DINP and DHP	Asphalt coal tar, shoe polish, oil-soluble yellow dye	Spectrophotometry	Increasing amount of plasticizer decreased soil resistance, alkyl phthalates were soiled more than alkyl benzyl phthalates	Colletti et al. 1998
PUR-coated PVC platics	Blood soil, food soil	ATP bioluminescence, protein residue test	Food soil was easier to remove from the polished floorings than blood soil	Kuisma et al. 2003
Commercial plastics	Inorganic particle soil (EN 14565)	Colorimetry	PUR-coated polyolefin was cleaned the most efficiently	Redsven et al. 2003
Unplasticized PVC	Tripalmitin, palmitic acid, triolein	FTIR, optical microscopy, AFM	Differences in soiling; clear differences were oberved between clean and soiled samples	Tikka et al. 2004
Commercial plastics	Inorganic particle soil (EN 14565), oil soil, biological soil	ATP bioluminescence, colorimetry, contact angle	A weak correlation between roughness and soilability was observed but no other correlations were reported	Kuisma et al. 2005a
Commercial plastics	Inorganic particle soil (EN 14565), oil soil	Colorimetry	More soils were removed from new than from worn surfaces; oil soil was more difficult to remove than particle soil	Kuisma et al. 2005b
Commercial plastics	Inorganic particle soil (EN 14565), oil soil	Colorimetry, contact angles	The contact angles related to the soil residues; materials with high surface energy were cleaned better	Pesonen-Leinonen et al. 2005
PVC model materials; plasticizers DOP and Hexamoll	Inorganic soil, inorganic soil in organic matrix, organic soil in organic matrix	Radiochemistry	The type and amount of plasticizer affected soil adhesion	Pesonen-Leinonen et al. 2006a
Commercial plastics	Blood soil	ATP bioluminescence	More soil was removed from worn than from new surfaces when cleaned with water; no such differenece when cleaned with detergents	Redsven et al. 2007

2.3.2 Cleanability of ceramic materials and coatings

In earlier studies the effects of compositions and coatings of glazed ceramic tiles on their cleanability have been examined. The cleanability studies are summarised in Table 5. It has generally been concluded that smooth surfaces are easier to keep clean than rougher surfaces (Tenorio Cavalcante et al. 2004, Dondi et al. 2005, Hupa et al. 2005, Kuisma et al. 2007). In a study by Kronberg et al. (2007) the soil resistance was improved by applying functional thin fluoropolymers and silane-based coatings.

In TiO_2-coated materials, such as ceramic wall tiles, organic oil soil on surfaces is decomposed by the photocatalytic property (Fujishima et al. 2000b, Minabe et al. 2000), whereas organic particle soil and dust can be cleaned by its superhydrophilic property (Guan 2005, Fujishima and Zhang 2006). It has been estimated that the surface hydrophilicity is probably more important than photocatalysis for the self-cleaning effect (Guan 2005). Photocatalysts are not very effective for decomposing large volumes of soil, but they are capable of preventing accumulation of soil layers (Fujishima and Zhang 2006, Yoshida et al. 2006). A small amount of water can be spread over the surface due to photo-induced superhydrophilicity, and soil can easily be swept away from the surface (Fujishima and Zhang 2006, Yoshida et al. 2006). Surface roughness increased the photocatalytic effect in the study by Mellott et al. 2006.

Table 5. Studies concerning cleanability properties of glazed ceramic and titanium dioxide coated surfaces.

Materials	Soil	Methods	Results	Reference
TiO_2-thin films	Glycerol trioleate, octadecane, stearic acid	FTIR spectroscopy	Octadecane and glycerol trioleate were decomposed better than stearic acid	Minabe et al. 2000
Thin films of anatase TiO_2	Stearic acid	FTIR spectroscopy	The films have relatively high quantum efficiency for the photo-oxidation of stearic acid depositions	Fretwall and Douglas 2001
Polished and unglazed white porcelain stoneware tiles	Standard red soil (ferric oxide in light oil)	Colorimetry	The soil resistance and cleanability depended on the polishing process and the surface microstructure	Tenorio Cavalcante et al. 2004
Commercial porcelain stoneware tiles	Standard red soil (ferric oxide in light oil)	Colorimetry	Soiling of surfaces depended on microstructure	Dondi et al. 2005
TiO_2/SiO_2 composite films on silicate glass plates	Acetic acid	Gas chromatography, X-ray photoelectron spectroscopy	Amount of adsorbed organic substances decreased with the increased SiO_2 in TiO_2 films.	Guan 2005
Experimental glossy and matt glazes	Sebum soil (ethanol, sebum, soot)	Spectrophotometry	Cleanability depended rather on surface micro- and macrostructure than on chemical comosition	Hupa et al. 2005
TiO_2-thin films	Stearic acid	FTIR spectroscopy	The photocatalytic effect increased with increasing roughness and with increasing crystal size	Mellott et al. 2006
Sanitary glaze, coated with fluoropolymers and silane-based sol gels	Oleic acid	FTIR spectroscopy	The soil resistance can be improved by functional thin coatings	Kronberg et al. 2007
Experimental and commercial glazes, coated with fluoropolymer, zirkonia and titania	Sebum soil (ethanol, sebum, soot)	Colorimetry	Smoother surfaces were cleaned more efficiently than rougher ones	Kuisma et al. 2007

2.3.3 Cleanability of concrete materials and coatings

In this study concrete is examined in the framework of agricultural buildings. It is a very generally used material in these buildings, but plastics, metals and wooden materials are also used. Previous studies of cleanability of animal houses have focused on evaluating the cleanability from manure using mainly visual or microbiological determination. The studies concerning cleanability of different kinds of agricultural surfaces are presented in Table 6. In general, coated and smoother surfaces were cleaned most efficiently (Puumala and Lehtiniemi 1993, Hörndahl 1995, Pelletier et al. 2002). The soiling and cleaning of surfaces depended on soil and floor type (Sundahl 1974, Hultgren and Bergsten 2001, Maw et al. 2001). Cleanability of concrete materials and coatings affects the well-being of animals and even food safety. Cleanness of body affects the animal´s well-being and health (Hultgren and Bergsten 2001, Nørgaard et al. 2003, Schreiner and Ruegg 2003). Diseases cause economic loss at a significant level on dairy farms (Somers et al. 2003, Spencer 2003).

Table 6. The cleanability studies concerning agricultural surfaces.

Materials	Soil	Methods	Results	Reference
Concrete, ceramic, steel, aluminium, wood, glass, plastics, asphalt, rubber	Manure (cow, pig)	Visual	Pig manure was removed more easily from surfaces than cow manure	Sundahl 1974
Concrete, plastic coatings	Artificial soil	Visual	Coatings improved cleanability	Puumala and Lehtiniemi 1993
Asphalt, concrete	Manure (cow)	Visual	Smooth surfaces were cleaned more easily than rough ones	Hörndahl 1995
Concrete, timber, rubber, aluminium	Organic wastes	Microbiological	The optimal temperature for liquids used in cleaning and disinfection was 40°C	Böhm 1998
Concrete, wood	Manure (pig)	Microbiological	Cleanliness was improved by cleaning and disinfection	Larsson 2000
Rubber solid floor, solid stall floor	Manure (cow)	Visual, scoring cleanliness and health of cows	Rubber-slatted floor cleaned better than solid floor	Hultgren and Bergsten 2001
Concrete, fully slatted pens, partly slatted pens	Manure (pig)	Visual, scoring cleanliness of pigs	Slatted floors were cleaned better than concrete floor	Maw et al. 2001
Concrete, epoxy-coated concrete	Manure (pig)	Microbiological	Epoxy-coating improved cleanability	Pelletier et al. 2002
Concrete, plastic, wood, metal	Manure (pig)	Visual sensor system, spectral characterisation	The determination method was able to locate dirty areas	Braithwaite et al. 2005
Concrete, plastic, wood, steel	Manure (pig)	Visual and optical	The determination method was able to locate dirty areas	Zhang et al. 2006

2.4 Summary of the literature review

Radiochemical methods utilize radioisotope labelling to model soiling and cleaning. These methods have earlier been used for plastic materials (Table 1) and textile floorings. In addition, labelling technique has been used to compare the efficiencies of detergents and cleaning methods and in laundering studies. The radiochemical methods (Table 2) also take into account soil soaked into the surface. This capacity is especially important when porous materials are evaluated.

This literature review focused on modifications of surface materials and cleanability research (Tables 4-6). The materials discussed were plastics, ceramics and concrete. In several studies found in the literature, surface properties were modified by different manufacturing processes, coatings and compositions of materials. In some studies surface structure was modified by different nano- and micro patterns. According to the literature, one of the most used coatings of ceramic materials was titanium dioxide, which generates two separate photo-induced phenomena: a photocatalytic phenomenon and a superhydrophilic phenomenon.

Probable use environments are different for the different materials. In the frame of this study, plastics and ceramics are used in various kinds of buildings whereas concrete materials are mainly intended for use in agricultural buildings. These different buildings represent environments with very different amounts and types of soils. In addition, the demands of cleanliness vary widely in these environments. In earlier studies the composition of materials, roughness and coatings were all reported to affect the cleanability of surfaces (Tables 4-6).

3 AIMS OF THE STUDY

The purpose of the present study was to examine the feasibility of radiochemical methods to investigate the cleanability of different surface materials and soil compounds. Several new surface materials were developed and investigated.

The specific aims were:

1. To develop radiochemical methods for evaluating cleanability of different surface materials and different soil types (I-V).

2. To examine the effects of composition and surface structure on the cleanability of plastics (I).

3. To examine the effects of coatings on cleanability of ceramic materials (II, III).

4. To examine the feasibility of radiochemical methods in examining cleanability of different kinds of compositions and coatings of concrete (IV, V).

4 MATERIALS AND METHODS

4.1 Study design

The study design consisting of the UV and wearing treatments, soiling and cleaning and measurements is presented in Figure 1. The cleanability of materials was studied using radiochemical, colorimetric and biochemical methods. In addition, contact angles and surface topography were used for the characterisation of the materials and evaluation of the cleanability methods. The focus of this study was on development of radiochemical methods.

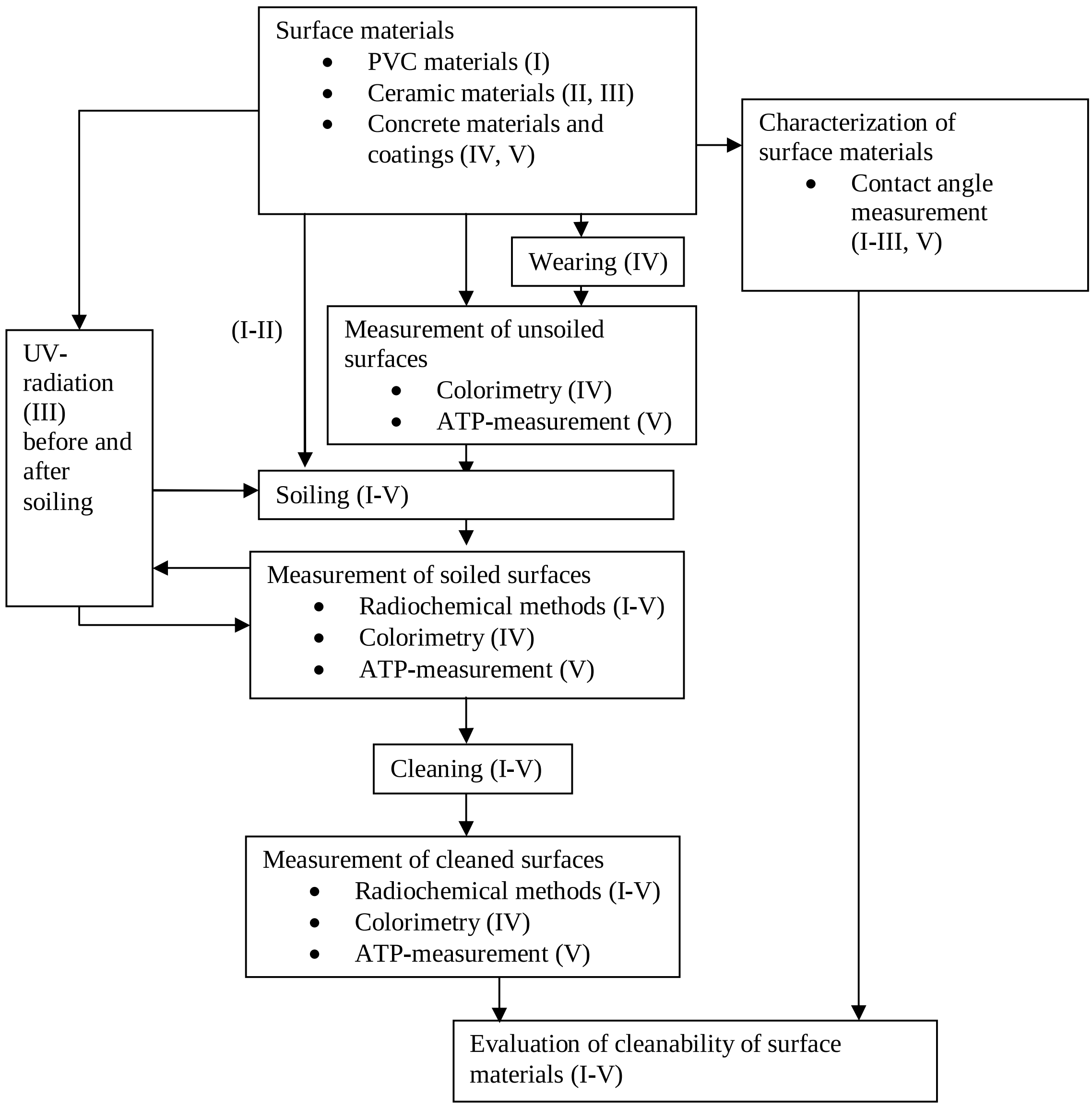

Figure 1. Experimental design of the study.

4.2 Surface materials

In this study a total of 18 PVC-materials, 14 glazed ceramic tiles and 22 concrete materials with different compositions and coatings were investigated. Detailed information of surface materials is given in the Publications. The effects of different surface treatments and topographies on cleanability were investigated.

4.2.1 Plastic materials

The effects of different plasticizers and surface topographies on the cleanability of eighteen different laboratory-made PVC materials were evaluated (Table 7 and Publication I). The manufacturing of the PVC materials is presented in Publication I.

Table 7. Plastic materials. The explanations of abbreviations and chemical compositions of the additives of plastics are presented in Tables 1 and 2 in Publication I.

Code	**Micro-structure (µm)**	**Plasticizer (wt-%)**	
DOP20	-	DOP	20
DOP20 25µm	25		
DOP20 40µm	40		
DOP30	-	DOP	30
DOP30 25µm	25		
DOP30 40µm	40		
Hexa20	-	Hexamoll® DINCH	20
Hexa20 25µm	25		
Hexa20 40µm	40		
Hexa30	-	Hexamoll® DINCH	30
Hexa30 25µm	25		
Hexa30 40µm	40		
Benzo20	-	Benzoflex® 2160	20
Benzo20 25µm	25		
Benzo20 40µm	40		
Benzo30	-	Benzoflex® 2160	30
Benzo30 25µm	25		
Benzo30 40µm	40		

- Smooth.

4.2.2 Ceramic materials and coatings

The effects of different substrate and coating materials were evaluated on the cleanability of fourteen different ceramic materials (Table 8 and Publications II-III). The manufacturing of ceramic materials is presented in Publication II.

Table 8. Ceramic materials. The crystal phase composition, firing temperature and firing time are presented in Table 1 of Publication II and in Table 1 of Publication III.

Code	**Substrate**	**Coating**		**Publication**
3A	Experimental	None		II
3AF		Fluoropolymer	Commercial	II
3AZr		Zirconia (sol-gel)	Experimental	II
3ATi		Titania (sol-gel)	Experimental	II, III
K	Commercial	None		II
KF		Fluoropolymer	Commercial	II
KZr		Zirconia (sol-gel)	Experimental	II
KTi		Titania (sol-gel)	Experimental	II, III
M	Commercial	None		II
MF		Fluoropolymer	Commercial	II
MZr		Zirconia (sol-gel)	Experimental	II
MTi		Titania (sol-gel)	Experimental	II, III
S	Commercial	None		II
SF		Fluoropolymer	Commercial	II

4.2.3 Concrete materials and coatings

The effects of different treatments and coating materials were evaluated on the cleanability of sixteen different concrete materials (Tables 9-10, Publications IV-V). Concrete and five plastic coatings were examined in Publication IV (Table 9). All coatings were spread onto ready-made concrete garden tiles. Manufacture of the evaluated samples is presented in Publication IV. All materials were examined as new and worn. Wearing was carried out by grinding the surface of the tiles for 30 s with a floor grinding machine.

Table 9. Concrete materials and coatings. All coatings were applied onto concrete tiles and were commercial products. The composition and manufacturing of surfaces is presented in Table 1 of Publication IV.

Code	**Type of coating**	**Components**		
		Substrate	**Sand**	**Surface treatment**
EP mass	Epoxy mass finished with rubbing	Epoxy resin	Epoxy coated sand Mixed in the mass	Epoxy
EP concrete mass	Epoxy and cement modified polymer coating	Cement modified polymer coating	Sand Scattered on the top	Epoxy
MDI PUR	MDI-based polyurethane	Polyurethane without filler	Sand Scattered on the top	Rolling Polyurethane elastomer
PUR concrete mass	Polyurethane concrete mass	PUR-concrete mass	Sand Scattered on the top	Rolling Polyurethane elastomer
Rubber PUR	Rubber-polyurethane	Polyurethane without filler	Rubber crush Scattered on the top	-
Concrete	Concrete	Plant mixed fast setting floor concrete		-

- none.
MDI 4,4' –diphenyl-methane-di-isocyanate.

The materials studied in Publication V are presented in Table 10. Epoxy, polyurethane, polyester and acrylic were used as surface coatings. The basic cement paste was in some cases treated with fluosilicate or an inorganic sealant. In addition, the cement paste without any coating or extra treatment was examined. In all experimental materials, the basic cement paste was laboratory-made, whereas commercial versions of the other materials were examined. Three different joint materials were also evaluated (Table 10). Two of them were cement-based clinker joint materials, one of which was treated by spraying with fluorochemical. The third joint material was a commercial clinker material containing epoxy.

Table 10. Concrete materials and coatings. Manufacturing and formulation of substrate and surface coatings or treatments are presented in Table 3 of Publication V.

Code	**Components**		**Experimental material (E) or material already in use (U)**	**Site where (could be) used**		
	Substrate	**Surface coating or treatment**		**Floor**	**Feeding table**	**Joint**
J1	Joint material, cement-based	None	E	-	-	X
J2	Joint material with additives, cement-based	Fluorochemical	E	-	-	X
J3	Joint material, containing epoxy	None	U	-	-	X
C1	Cement paste	Trowelled	U	X	X	-
C2	Cement paste	Fluosilicate	U	X	X	-
C3	Cement paste	Inorganic sealant	E	X	X	-
Co1	Minerite	Acrylic coating	U	X	X	-
Co2	Minerite	Polyurethane coating	U	X	X	-
Co3	Cement paste	Epoxy coating	U	X	X	-
Co4	Plastic concrete	Polyester coating	U	-	X	-

- Not suitable.

4.3 Soiling and cleaning methods

4.3.1 Soils

Compositions and amounts of soils used in this study are presented in Table 11. The cleanabilities of different components of radiochemical model soils were estimated by measuring the different radio-isotopes. The ^{51}Cr isotope labels particle components of soil and the ^{14}C isotope oil components. An inorganic compound chromium oxide was used as a model of natural inorganic soils. An organic compound (chromium acetyl acetonate) represented natural organic soils. Triglyceride (triolein) was used as a model of natural oils and sebum. Pesonen-Leinonen et al. (2006a) showed that the amounts of residues of chromium oxide and chromium oxide mixed with triolein on each PVC material remained almost at the same level when labelling soils with ^{51}Cr.

In colorimetric studies (Publication IV) pig manure soil, representing the natural soil in piggeries, and coloured paste model soil (Puumala and Lehtiniemi 1993) were used (Table 11). The cow manure and feed were used both in radiochemical and ATP bioluminescence studies (Publication V). In radiochemical studies the natural soils were labelled with ^{51}Cr.

Table 11. Compositions and amounts of soils. Soils A-E were used in the radiochemical studies, soils G and H in the colorimetric study and soils I and J in the ATP bioluminescence study.

Code	**Publication**	**Method**	**Radio-isotope**	**Type of soil**	**Components of the soil**			
					Chromium component	**Solvent**	**Fatty acid**	**Other components**
A	I-II, IV-V	Radiochemical	^{51}Cr	Inorganic particle	Chromium(III)oxide	1-propanol	Triolein [d]	-
B	I-III, V	Radiochemical	^{51}Cr	Organic particle	Chromium acetyl acetonate	1-propanol	Triolein [d]	-
C	I-V	Radiochemical	^{14}C	Oil component	Chromium(III)oxide	1-propanol	Triolein [d]	-
D	I	Radiochemical	^{14}C	Oil component	-	1-propanol	Triolein [d]	-
E	V	Radiochemical	^{51}Cr	Manure [a]	Chromium(III)oxide	Water	-	Manure
F	V	Radiochemical	^{51}Cr	Feed [b]	Chromium(III)oxide	Water	-	Feed
G	IV	Colorimetrical	-	Manure [c]	-	-	-	-
H	IV	Colorimetrical	-	Paste	-	Water	-	Paste, Rye flour, Saw dust, Red caramel color
I	V	ATP bioluminescence	-	Manure [a]	-	Water	-	Manure
J	V	ATP bioluminescence	-	Feed [b]	-	Water	-	Feed

- Not included.
[a] Cow manure. Composition presented in Publication V.
[b] Cow feed. Composition presented in Publication V.
[c] Pig sludge manure containing sawdust. Composition was not measured in the present study (Publication IV).
[d] Triolein refers to glyceryl trioleate.

4.3.2 Soiling and cleaning procedures

The radiochemical model soils were applied as a liquid suspension on the middle of the sample. The soils were left to dry for 24 h ± 2 h at room temperature. The colorimetric soils (Publication IV) were spread manually over the whole area of the sample and allowed to dry. The amount and drying times of paste and manure soils were different because of their different viscosities. The paste model soil was left to dry for seven days after soiling and the manure soil for 14 days after soiling. In the case of ATP bioluminescence (Publication V) the liquid soil mixtures were applied in the middle of the sample and left to dry for 24 h ± 2 h at room temperature.

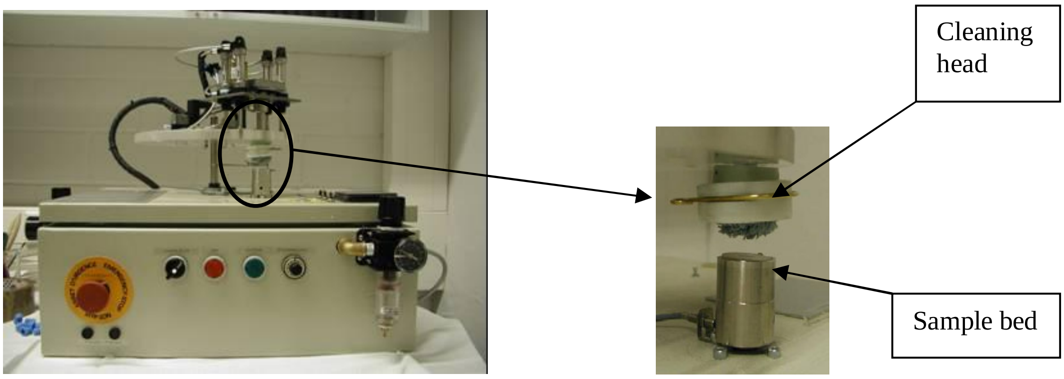

Figure 2. Mini Cleanability Tester used in radiochemical studies to clean samples.

Cleaning was carried out with the Mini Cleanability Tester (Figure 2, Table 12, Hupa et al. 2005, Pesonen-Leinonen et al. 2006a, Kuisma et al. 2007). In the studies, water and model detergents (Kuisma et al. 2005b, Pesonen-Leinonen et al. 2006a) were used as cleaning solutions, and a microfibre cloth (Pesonen-Leinonen et al. 2003, Pesonen-Leinonen et al. 2006a) was used as cleaning cloth. In the colorimetric study a high pressure cleaner (Puumala and Lehtiniemi 1993) was used in Publication IV. In the ATP bioluminescence study cleaning was carried out with the Erichsen Washability and Scrubbing Resistance Tester (Table 12) (Kuisma et al. 2005b, Pesonen-Leinonen et al. 2005, Pesonen-Leinonen et al. 2006b, Redsven et al. 2007).

Table 12. Cleaning methods using the Mini Cleanability Tester and Erichsen Washability and Scrubbing Resistance Tester.

Method/Parameter	Mini Cleanability Tester (I-V)	Erichsen Washability and Scrubbing Resistance Tester (V)
Cleanability determination method	Radiochemical	ATP bioluminescence
Pressure applied to the surface	25 kPa	1.4 kPa
Revolution/movements	3	5
Direction of movements	Asymmetrical, elliptical	Back and forth
Speed of revolution/movement	30 rounds per minute	37 movements* per minute
Material of mop cloths	Micro fibre mop (100 % polyester fibres)	Micro fibre mop (100 % polyester fibres)
Moisture regain of the mop cloth**	100 % (model soils in Publications I-V) 200 % (manure and feed soils in Publication V)	100 %
Detergent	Weakly alkaline	No detergent

* Movements back and forth together.
****** Moisture regain of the mop cloth means the moisture content of the mop cloth expressed as a percentage of the weight of the dry mop.

4.4 Determination of cleanability

4.4.1 Radiochemical determination

The radioactivity of the surface was comparable to the amount of the labelled component of soil on the sample. The cleaning result was presented as the proportion of the labelled component of soil after cleaning compared to that after soiling. Two different methods, a gammaspectrometric method and liquid scintillation counting, were used for evaluation of the cleanliness of the surfaces. The study design is described in Figure 3.

The cleanability of the soils labelled with the gamma-ray emitter ^{51}Cr (Table 11) was determined by a gammaspectrometric method using an NaI(Tl)-scintillation crystal. The counting geometry was constant. The results were calculated by subtracting the activity of the background and correcting the results for radioactive decay. The cleanabilities of soils labelled with the beta-ray emitter ^{14}C (Table 11) were measured using liquid scintillation counting. Calculation of the result included the quenching equalizer and subtraction of the background. Correction of radioactive decay was not needed because of the long half-life of carbon.

In Publication III samples were UV-radiated before and after soiling. The flow diagram of UV-radiation and determination of cleanability is described in Figure 3. Determination methods were the same as in all the other Publications.

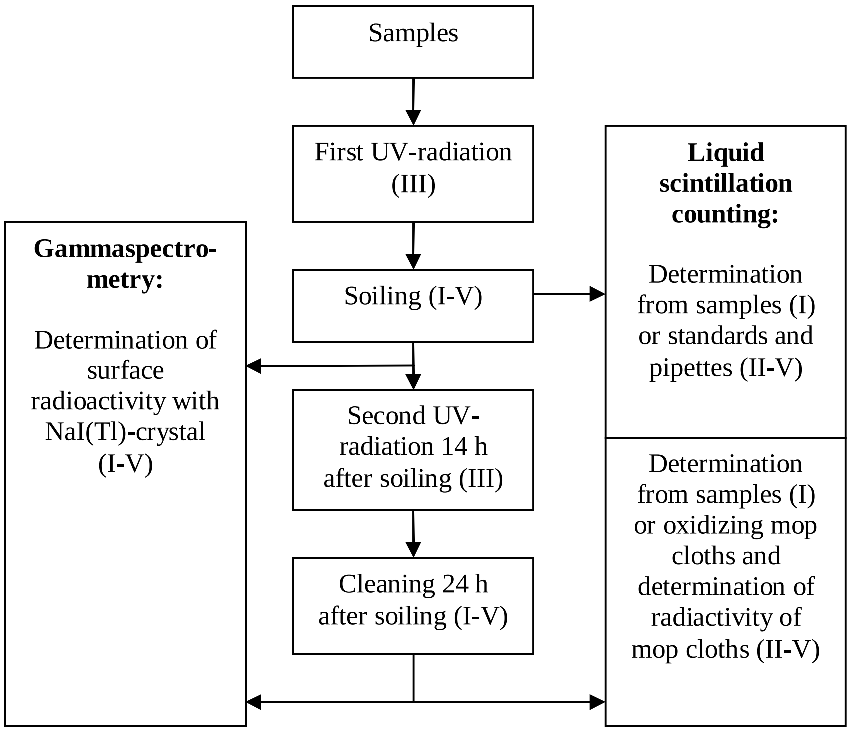

Figure 3. Flow diagram of determination of cleanability of radiochemical soils with NaI(Tl)-crystal and liquid scintillation counter. UV-radiations refer to Publication III.

4.4.2 Supporting methods

In addition the cleaning efficiency was determined with a colorimeter in Publication IV. Changes of colour of each sample were measured from six points before soiling, after soiling and after each cleaning cycle. The colorimetric parameters, method and calculation of ΔE (total change of colour value) are presented in Publication IV in more detail. The ATP (adenosine triphosphate) bioluminescence method is based on the hydrolysis of ATP by luciferase enzyme, detected by a luminometer. The method is presented in Publication V in more detail. RLU (relative light unit) is directly related to the amount of ATP and organic contamination on the surface. The samples were evaluated three times: before and after soiling and after cleaning.

Surface properties were evaluated by contact angles and surface topography in order to identify explanatory factors for cleanability. Static water contact angles on the experimental surfaces before soiling were measured (Publications I-III, V). UV-radiated TiO_2-coated ceramic tiles were also measured after two hours of radiation. A water drop (ultra pure water Milli-Q) was placed on the surface and imaged for 40 seconds. Determination of contact angle was based on the Young-Laplace equation. The measuring of contact angles is presented in more detail in Publications I-III and V. The data of surface topography are presented in Publications I-V. Roughness parameter (R_a) was used to describe surface roughness.

4.5 Statistical analyses

The cleaning result from the radiochemical method was presented as the proportion of the soil residue after cleaning compared to the amount of soil on the surface after soiling. Statistical analyses were performed using SPSS version 12.0 (SPSS Inc., Chicago IL, USA), based on the mean values of the results. In the all Publications the cleanability results for each of the soils were analysed separately. Analysis of variance was used to examine differences between the materials and treatments in all Publications. Bivariate correlation analysis (Pearson's correlation coefficients, two-tailed test of significance) was used to examine possible correlations between surface properties, roughness values, contact angles (except in IV) and soil residues in all the Publications. The significance used was 0.05 in analysis of variance and 0.01 in analysis of correlation.

5 RESULTS

5.1 Feasibility of radiochemical methods

Cleanability of surfaces was evaluated in all cases with radiochemical methods. The supportive methods, colorimetry and ATP bioluminescence determinations, were used for examining agricultural surfaces. Ten different soils were used to examine the cleanability of surfaces. Considering all the studies (I-V), the radiochemical inorganic soil (soil A) was in general removed more efficiently from all examined surfaces than the radiochemical organic particle or oil soils (soils B and C).

In Publications IV there were significant correlations between the cleanabilities of the surfaces from radiochemical soils and colorimetric manure soil: Pearson's correlation coefficient was $r = 0.656$ for inorganic particle soil A and manure soil G, and $r = 0.691$ for oil soil C and manure soil G. In the case of paste soil H there was a correlation only with soil A ($r = 0.611$). In Publication V the manure and feed soils were used both in radiochemical and ATP bioluminescence determination, except that the radiochemical soils included chromium oxide labelled with ^{51}Cr. No statistically significant correlations were observed between the cleanabilities of agricultural soils. In the case of the simplified radiochemical model soils, the cleanability of the oil soil C correlated significantly with the soil residue (ATP amount) of feed soil J after the first cleaning cycle (Pearson's correlation coefficient $r = -0.639$).

5.2 Plastic materials

As can be seen in Figure 4 the cleanability of materials containing 20 % plasticizer was better than that of materials containing 30 % plasticizer (soil A $p = 0.025$; soil B $p = 0.042$; soils C and D $p = 0.006$). The type of plasticizer affected the cleanability of the ^{14}C-labelled oil soils (soil C: $p = 0.002$ and soil D: $p = 0.008$). Considering particle soils A and B, the cleanability of microstructured surfaces containing 20 % plasticizer was better than that of the smooth materials containing 20 % plasticizer. However, in the case of oil soil C, the cleanability of the smooth surfaces containing 20 % plasticizer was better than that of the microstructured surfaces containing 20 % plasticizer.

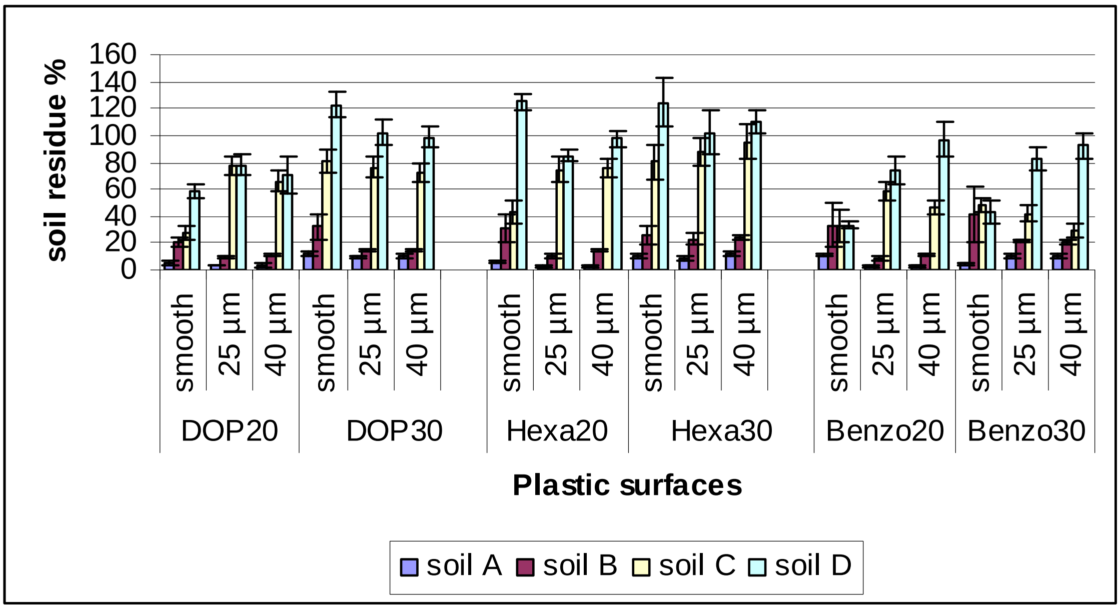

Figure 4. Radiochemical soil residues of PVC materials in Publication I. The lower the soil residue, the better is the cleanability result. Soils are presented in Table 11 and materials in Table 7. Columns are means of five replicates and bars are standard errors (±SE).

In the cases of soils C and D there were significant correlations between water contact angles and relative soil residues (Pearson's correlation coefficient $r = 0.894$ for soil C and $r = 0.517$ for soil D). The amount of plasticizer did not affect the water angles. Both 25 µm and 40 µm microstructures increased water contact angles compared to the corresponding smooth surfaces. However, the increase was only a few degrees. The water contact angles varied between 75^o and 91^o depending on the plasticizer, indicating that the examined plasticized PVC materials were slightly hydrophilic.

5.3 Ceramic materials and coatings

The cleanability of ceramic surfaces was studied in two parts. First the effects of different coatings and glaze materials were investigated. Secondly the effect of UV-radiation on cleanability of TiO_2-coated ceramic surfaces was studied.

The soil residues of ceramic surfaces are presented in Figure 5. The inorganic particle soil A was generally removed more efficiently from almost all surfaces than the two other soils (soils B and C). However, the additional coatings did not statistically significantly affect the cleanability of the inorganic particle soil ($p>0.05$). The morphology of the substrate glaze was found to affect the cleanability ($p = 0.003$). The inorganic particle soil (soil A) was removed most efficiently from the rough surfaces, i.e. glazes 3A and M.

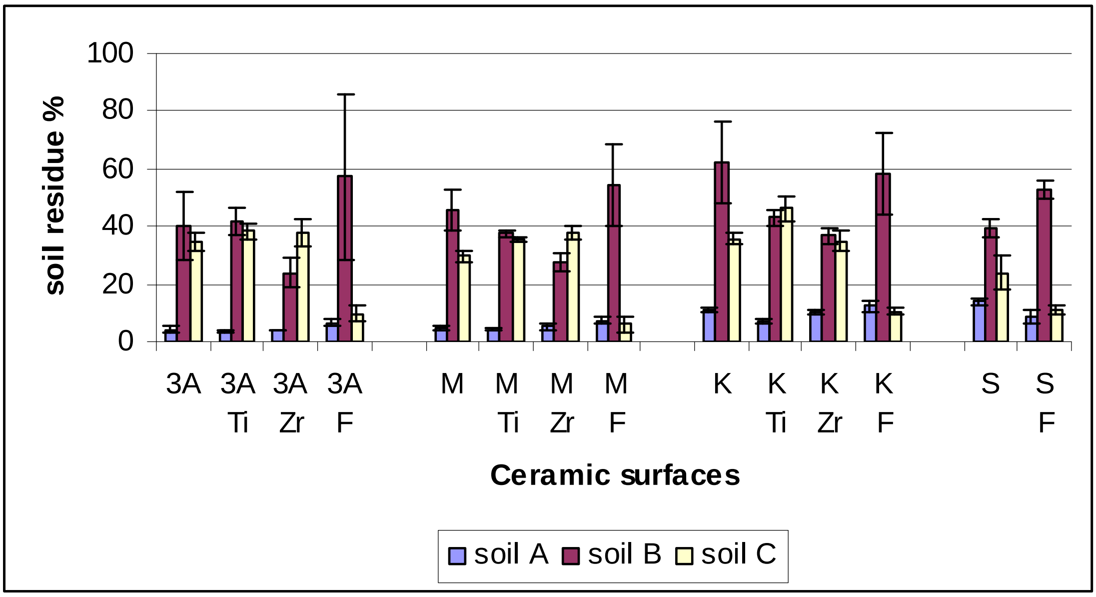

Figure 5. Radiochemical soil residues of ceramic materials in Publication II. The lower the soil residue, the better is the cleanability result. Soils are presented in Table 11 and materials in Table 8. Columns are means of five replicates and bars are standard errors (±SE).

In the case of organic particle soil (soil B) the coating affected the cleanability ($p=0.003$). Fluoropolymer coating increased soil attachment to the surface, whereas zirconia somewhat decreased the amount of soil left on the surfaces after cleaning. The glaze material was observed to affect surface topography, but did not statistically significantly affect the amount of the organic particle soil residue ($p = 0.675$).

The oil soil C was found to be removed from the surfaces very differently depending on the coating ($p = 0.000$). In contrast to the particle soils the soil residues of oil soil on the fluoropolymer surfaces were the lowest. As in the case of organic particle soil, the glaze material had no statistically significant effect on the cleanability ($p = 0.684$) of oil soil. However, the results indicate that residues of the oil soil were the lowest on M surfaces. There was a significant correlation between contact angles and soil residue of oil soil C (Pearson's correlation coefficients $r = -0.739$ for soil residues and contact angles).

As can be seen in Figure 6, UV-radiation improved the cleanability of all samples in the case of organic particle soil B. The difference between the untreated and UV-treated surfaces was statistically significant ($p = 0.029$). The soil was removed most efficiently from the 3A Ti-surface, which is a matt-glazed rough surface. The soil residue of the smooth K Ti-surface was the highest. However, no correlations were observed between roughness values, contact angles and soil residues. In the case of oil soil C no effect of UV-radiation was observed: the soil residues after irradiation of all samples were almost the same as before UV-radiation. This was confirmed by the statistical analysis ($p = 0.518$). Despite small differences between glazes, the glaze material did not statistically significantly affect cleanability from either of the soils ($p=0.740$ for soil B and $p=0.391$ for soil C).

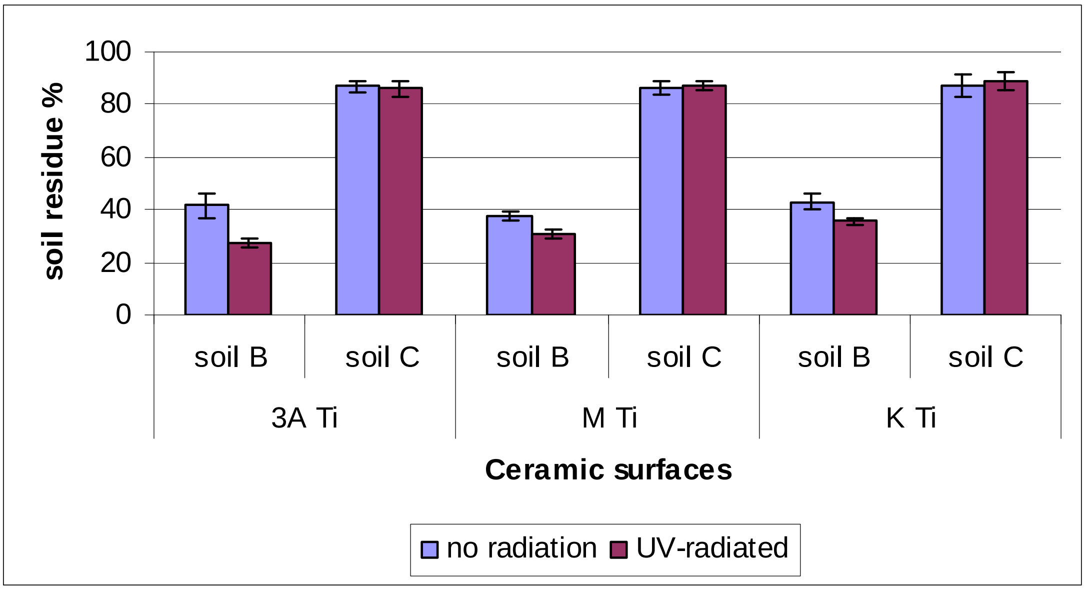

Figure 6. Radiochemical soil residues of UV-radiated ceramic materials in Publication III. The lower the soil residue, the better is the cleanability result. Soils are presented in Table 11 and materials in Table 8. Columns are means of five replicates and bars are standard errors (±SE).

The contact angle values examined varied between 28° and 82° (Publication II). The contact angles of the surface SF were the highest and of K the lowest. Slightly increased contact angles were measured for the zirconia coating. The contact angle for the titania coatings was of the same order as for the substrate glaze surface. Coating of glazes with fluoropolymer film generally increased the contact angle values. The TiO_2-coated ceramic surfaces were irradiated with UV-radiation for two hours (Publication III), after which the contact angles decreased significantly and were approximately 10 degrees. Significant correlations were observed between examined roughness parameters and contact angle values after UV radiation (Pearson's correlation coefficient $r = 0.997$).

5.4 Concrete materials and coatings

The radiochemical soil residues of evaluated surface materials of piggeries are presented in Figure 8. The particle soil A was removed more efficiently from surfaces than the oil soil C. Coating of concrete improved the cleanability of the surfaces (soil A: $p = 0.010$ and soil C: $p = 0.001$), cleanability of the uncoated concrete being the poorest. In the cases of both soils A and C the coatings did not differ statistically from each other. No differences between the new and worn surfaces were observed (soil A: $p = 0.384$ and soil C: $p = 0.983$).

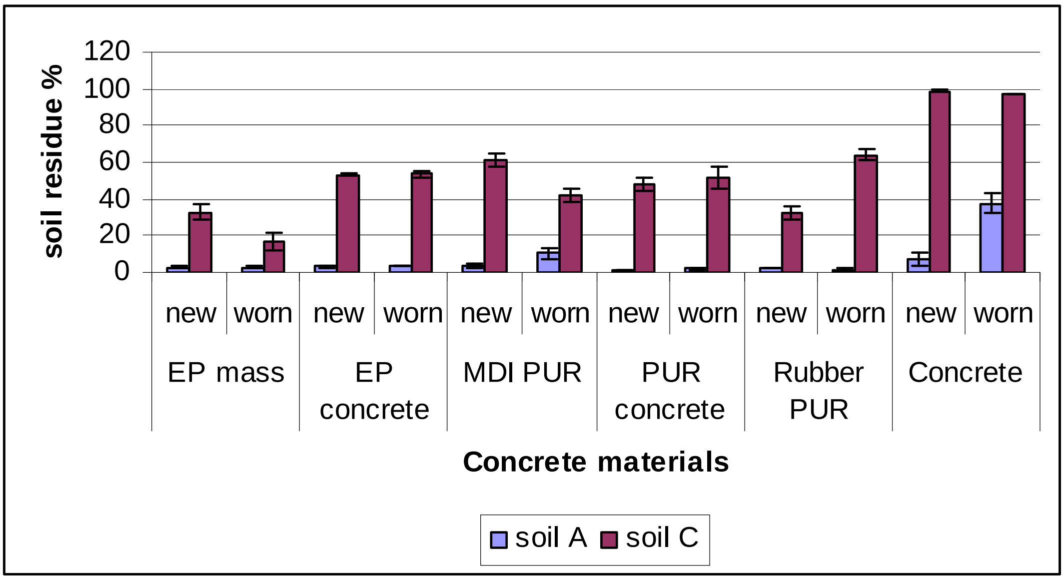

Figure 8. Radiochemical soil residues of concrete materials in Publication IV. The lower the soil residue, the better is the cleanability result. Soils are presented in Table 11 and materials in Table 9. Columns are means of five replicates and bars are standard errors (±SE).

The changes of colour of the samples before soiling and before and after cleaning are presented in Figures 3 and 4 in Publication IV. According to the colorimetric measurement the three different washing temperatures did not affect the cleanability of the surfaces from the paste soil. Therefore only the results of the warm wash (40 ºC) are presented. The effect of coating on cleanability from manure soil G was statistically significant ($p = 0.000$) but there was no significant difference between different coatings ($p = 0.050$). The coatings increased the cleanability of concrete ($p = 0.000$) from paste soil H. On the basis of experimental and theoretical E values, uncoated concrete had the poorest cleanability.

The soil residues of radiochemical model soils of all the cattle barn samples (Publication V) are presented in Figure 9. In the case of simplified model soils the soil residues of inorganic soil A were the lowest (except for J3) and in general the soil residues of oil soil C were the highest. According to the results for soil residues, the coating improved the cleanability of concrete surfaces from oil soil ($p = 0.001$). The coatings improved the cleanability of surfaces from labelled feed soil ($p = 0.021$) but not from labelled manure soil ($p = 0.412$). In general the soil residues of the organic soil B were at the same level as the soil residues of both labelled natural soils, but no statistically significant correlations were observed.

According to the cleanability results of the radiochemical study plastic, polyester (Co4), acrylic (Co1) and polyurethane (Co2) coatings improved cleanability most efficiently, whereas the cleanabilities of the non-coated concretes were the lowest (Figure 9). Interestingly, the cleanability of non-coated concrete including inorganic sealant (C3) from manure soil E was better than that of coated concretes. The epoxy-coated concrete (Co3) was cleaned most efficiently from the labelled natural soils in the radiochemical study. The cleanability of epoxy-based joint differed from that of the cement-based joint materials. The cement-based joint materials were cleaned better than the epoxy-based joint especially from the inorganic particle soil, but less efficiently from the oil model soil and labelled feed soil (Figure 8).

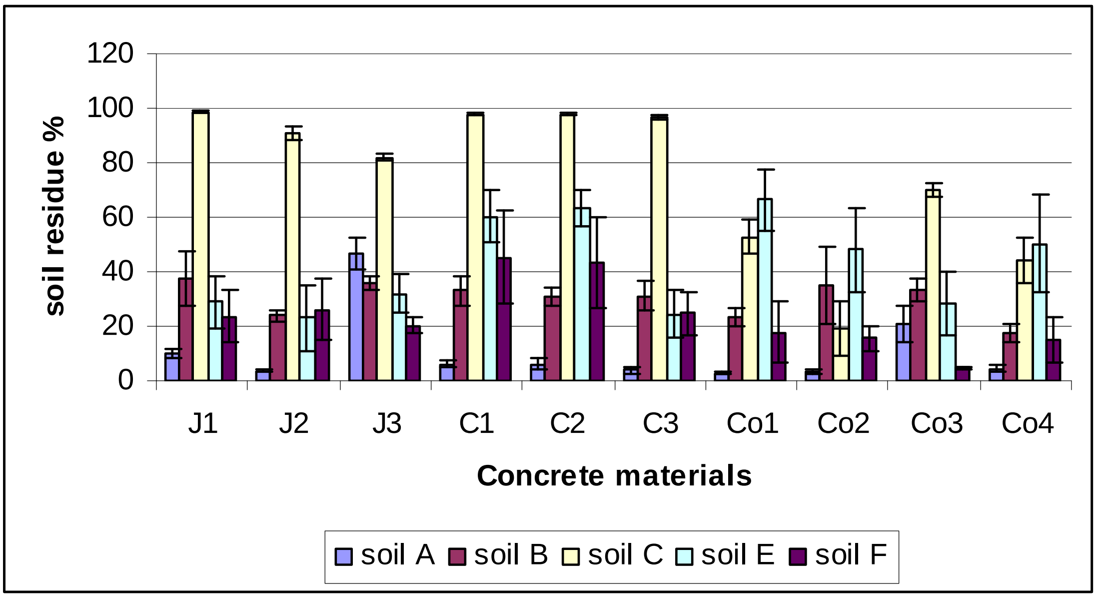

Figure 8. Radiochemical soil residues of concrete materials in Publication V. The lower the soil residue, the better is the cleanability result. Soils are presented in Table 11 and materials in Table 10. Columns are means of five replicates and bars are standard errors (±SE).

The ATP contents of the samples before soiling and before and after cleaning are presented in Figure 3 in Publication V. The ATP content of the manure soil was clearly greater on surfaces after soiling than that of the feed soil. The first cleaning cycle (method presented in detail in Publication V) removed a significant part of the manure soil from most surfaces. In the removal of the manure soil, the second cleaning cycle decreased the ATP content of the surfaces approximately to the same level as before soiling. The ATP content of the surfaces soiled with the feed soil decreased after the first cleaning cycle to the same level as before soiling or even lower. Material differences were negligible. In accordance with these results, there was a significant correlation between the ATP amounts of manure and feed soils after the second cleaning cycles ($r = 0.811$).

When surfaces were divided into three groups: non-coated concretes, coated concretes and joint materials, the surface type was found to affect the cleanability of radiochemical oil soil (soil C: $p = 0.004$), feed soil labelled with ^{51}Cr (soil F: $p = 0.010$) and the ATP amount of manure after the first cleaning (soil I: $p = 0.031$).

The contact angles of water in the surfaces varied between 19° and 84°. The variation in contact angle values was wide due to the different compositions of materials. Surface type affected the water contact angles ($p = 0.050$ in comparison between non-coated concretes, coated concretes and joint materials). The contact angles of C2 and J3 were the lowest and those of Co4 the highest. Materials C1 and C3 were such porous materials that contact angles could not be measured. Water was rapidly absorbed into these surfaces. No statistically significant correlations between contact angles and soil residues were observed.

5.5 Summary of the results

The presented results concerned different types of surface materials: plastics, glazed ceramic tiles, concretes and their coatings. The radiochemical study design was the same in all presented studies and the radiochemical model soils consisted of the same components. In addition the roughness parameters and contact angles were evaluated in all Publications, except for contact angles in Publication IV. The results presented in Publications I-V are summarized in Table 13. Generally, the cleanability from particle soils depended on surface topography and the cleanability from oil soil on contact angles.

In conclusion, the type of material affected cleanability in all material groups. The plasticizers affected cleanability in the case of plastics. The type of coating influenced the cleanability of ceramic materials. In the case of concrete materials, coatings improved cleanability from labelled feed soil, unlabelled manure and paste soils (soils F, G and H). Concrete with inorganic sealant was cleaned from manure soils (soils E and I) better than coated surfaces. In the case of unlabelled feed soil (soil J) material differences were negligible. The results of concrete and their coatings showed that coating improved cleanability.

The water contact angles of all materials varied between 10° and 97°. The UV-radiated TiO_2-coated ceramic tiles had the lowest contact angles and fluoropolymer-coated ceramic tiles the highest. The effect of UV-radiation of TiO_2-coated ceramic materials increased with increasing roughness. The plastics and plastic coatings had contact angles above 60°. Some concrete materials were so porous that contact angles could not be measured.

Table 13. A summary of the presented results concerning cleanability of plastics, glazed ceramic tiles, concretes and their coatings in Publications I-V. Radiochemical soils A-D are presented in Table 11.

Parameter	**I** **PVC materials**	**II** **Glazed ceramic tiles**	**III** **TiO_2-coated ceramic tiles**	**IV** **Concrete and coatings**	**V** **Concrete and coatings**
Material	The type and amount of plasticizers affected the cleanability	The type of coating affected the cleanability	UV-radiation affected rough surfaces most strongly	Coatings improved cleanability. Wearing had no effect	Coatings improved cleanability
Roughness, R_a	Depended on amount of plasticizer	Depended on the substrate glaze	Depended on the substrate glaze	Wearing had no effect	Joint materials were the roughest
Contact angle, CA	Depended on plasticizer, microstructured surfaces increased contact angles	Fluoropolymer coating increased most	UV-radiation decreased, smooth surface had the lowest	-	Coating sealed surfaces, concrete gave no result due to porosity
Soil A	Microstructured surfaces cleaned best (20 % plasticizer)	Morphology of the substrate glaze affected, rough surfaces cleaned best	-	Coatings improved cleanability	Coatings improved cleanability
Soil B	Microstructured surfaces cleaned best (20 % plasticizer)	TiO_2 and Zr coated surfaces cleaned best	UV-radiation improved cleanability	-	Coatings improved cleanability
Soil C	Soil residues correlated with CA, smooth surfaces cleaned best	Soil residues correlated with CA, fluoropolymer surface cleaned best	No effect of UV-radiation was observed	Coatings improved cleanability	Coatings improved cleanability
Soil D	Soil residues correlated with CA, spread onto the whole sample	-	-	-	-

- not included.

6 DISCUSSION

6.1 Evaluation of methods

In previous studies radiochemical methods have been used to evaluate cleanability of resilient flooring materials (Ohlson and Wäänänen 1971, Jokelainen and Uusi-Rauva 1976a, Jokelainen and Uusi-Rauva 1976b, Jokelainen & Uusi-Rauva 1979, Jokelainen et al. 1982, Pesonen-Leinonen et al. 2006a). Such determination methods have not earlier been used to evaluate ceramic or concrete materials. In a study by Pesonen-Leinonen et al. (2006a) gammaspectrometry was used to investigate soil adhesion on PVC materials and commercial plastic materials. Three different soils were labelled with ^{51}Cr isotope. The used soils were chromium oxide, chromium oxide with triolein and chromium acetyl acetonate with triolein. The amounts of soil residues of chromium oxide and chromium oxide with triolein were almost at the same level (Pesonen-Leinonen et al. 2006a). For this reason pure chromium oxide was not used as a model soil in this study. In addition to ^{51}Cr-labelled model soils, in this study ^{14}C isotope was used to label triolein. There is no previous published information concerning the use of isotope labelling with natural soils. In the case of radio labelled feed and manure soil, the results concern the labelled isotope in soil mixture, but indicate the behaviour of the whole soil mixture. From the practical point of view, addition of isotope to the bulk soil was the only way to label the feed and manure soil.

When using the radiochemical measuring methods it is evident that selection of the element to be labeled is critical for the final cleanability results. The use of simplified model soils provides detailed information about a single soil component. Due to the different radioactive emitters used to label the different soil types, the interaction of the surface with different soil types could be expressed. In this study a new collection of soils was presented. Although the compositions of soils A and C were chemically exactly the same there were significant differences in cleanability of the soils. This could be due to the different forms of the labelled component. The particle component was in solid form and may only have attached to peaks of the surface structure, whereas the oil component was spread over the surface and attached more heavily. In addition to simplified model soils natural agricultural soils were blended with labelled isotope as a new application. The use of a plate in the gammaspectrometry ensured that the measuring geometry was the same for each measurement. The gammaspectrometry technique can provide data at an accurate level. However, the measuring area is limited to the diameter of an NaI(Tl)-crystal, costs are relatively high and a high level of skill is needed. A limitation of liquid scintillation counting is that the radioactivity must be dissolved in scintillation liquid. The same sample could not be measured after soiling and after cleaning.

Supporting evaluation methods, colorimetric (Publication IV) and ATP bioluminescence determination (Publication V), were used to determine cleanability of surfaces from biological soils. Natural soils can be used as such when using these determination methods. However, a disadvantage of the present supporting methods is that they do not take into account the amount of absorbed soil. On the other hand, an advantage is that these methods are also suitable for field studies. Radiochemical methods are used only in material research in laboratory conditions. In this study the Mini Cleanability Tester was adapted to concrete materials. Surface properties were measured in order to identify explanatory factors of soiling and cleaning phenomena. The results showed that the cleanability from oil soils correlated with contact angles.

6.2 Surface materials

A wide selection of materials was examined. All samples were prepared in a laboratory. The chemical compositions of plastic and ceramic materials were well known. However, some concrete materials were commercials product and their exact compositions were not known.

The evaluated PVC surfaces contained different qualities and amounts of plasticizers and different kinds of microstructure (Publication I). According to the radiochemical studies, all these properties affected cleanability. The materials containing 20 % plasticizer were cleaned more efficiently than those materials containing 30 % plasticizer, which is in accordance with earlier studies (Colletti et al. 1998, Pesonen-Leinonen et al. 2006a). Surface microstructure improved the cleanability of materials when cleanability was determined by the chromium compounds of soils. Beach and Drelich (2002) reported that nanoscale roughness decreased the contact area between particle and solid surface and the resulting adhesion force, whereas micrometer roughness increased the adhesion due to increased contact area. The results of the cleanability studies with labelled triolen showed that smooth (unstructured) materials were cleaned better than structured materials. In general, according to the results the cleanability of the particle soils (labelled ^{51}Cr) was better than that of the oil soils (labelled ^{14}C), as was observed in the study by Kuisma et al. (2005b). The results showed that surface microstructuring increased contact angles, in accordance with the study by Li et al. (2006).

The effects of different glaze materials and coatings on cleanability of ceramic surfaces were determined (Publication II). The results of cleanability studies showed that the coatings had an effect on the cleanability of ceramic surfaces: particle soils (labelled ^{51}Cr) were removed most efficiently from glazes coated with TiO_2 and Zr. By contrast the fluoropolymer surface was cleaned most efficiently from oil soil (labelled ^{14}C). This could due to the increased water contact angle of fluoropolymer coatings. Generally, cleanability of the particle soils was found to be affected by roughness in this study. In earlier studies roughness affected the cleanability of ceramic tiles. In general rough surfaces were easier to soil and harder to clean than smooth surfaces (Tenorio Cavalcante et al. 2004, Dondi et al. 2005, Hupa et al. 2005, Kuisma et al. 2007).

In addition the influence of UV-radiation on the cleanability of titanium dioxide-coated ceramic surfaces was examined (Publication III). The observed effects of UV-radiation on cleanability of TiO_2-coated ceramic surfaces were greatest on rough surfaces, implying that increasing roughness increases the surface area available for photo-induced phenomena (Mellott et al. 2006). According to the results the contact angles of TiO_2-coated surfaces decreased under UV-radiation, in accordance with earlier studies (Watanabe et al. 1999, Fujishima et al. 2000b, Nakajima et al. 2000, Sakai et al. 2003). The results of cleanability studies showed that organic particle soil was removed more efficiently after UV-radiation than without UV treatment, whereas UV-radiation did not affect the removal of oil soil. Decomposition of organic soil to carbon dioxide was not observed, in contrast to earlier studies (Fujishima et al. 2000b, Minabe et al. 2000, Pore et al. 2006). Fujishima and Zhang (2006) concluded that depending on the composition and the processing, surfaces can be more photocatalytic and less superhydrophilic or vice versa.

According to the present results the coating improved the cleanability of concrete materials. This is in accordance with the results of Puumala and Lehtiniemi (1993). In the study by Sundahl (1974), cleanability of floated concrete from pig manure was poor but that of trowelled concrete was good. However, in these studies cleanabilities of surfaces were determined by visual observation. In agreement with the results of the present study (Publication IV), wearing did not affect the cleanability of concrete soiled with cattle slurry and cleaned with pressure cleaning in the study by Hörndahl (1995). However, in contrast to the present results, the cleanability of concrete was rated good in the earlier study. In Publication IV surfaces of the coatings were on average rougher than that of the reference surface, concrete. This is probably due to the sand particles added with the coating material. Roughness could have decreased the cleanability of some of the coatings. However, the general porosity of the concrete can affect cleanability compared to that of plastic coatings, because the absorptivity of concrete flooring can affect its soiling tendency (Pelletier et al. 2002). In a study by Kemppainen et al. (2002), epoxy as an additive improved the cleanability of joint materials from a sebum (fat)-based model soil. This is in accordance with our study (Publicaton V) although the cleanabilities of other model soils were poorer than those of other joint materials.

The aim was to develop different soil types to model different components of soils which could be labelled with different radioisotopes. In summary, the radiochemical methods were suitable for examining cleanability of plastic, ceramic and concrete materials. The effects of compositions, surface structures and coatings on cleanability and surface properties were studied. The results of this study can be used when developing new easy-to-clean or even self-cleaning surfaces. In future more information will be needed about optimized dimensions of micro- and nanosized surface structures and chemical compositions of coatings in order to improve self-cleaning properties of materials.

7 CONCLUSIONS

1. The radiochemical methods developed were suitable for evaluating cleanability of different surface materials and different soil types. Plastic, ceramic and concrete materials could all be examined. Due to the different labelled soil components, the interaction of the surface with different soil types could be expressed. In general, particle soils were cleaned more efficiently from surfaces than oil soil.

2. The quality and amount of plasticizers and the microstructure affected the cleanability of the plastics. Increasing the amount of plasticizer decreased the cleanability. Microstructuring improved the cleanability of PVC surfaces from particle soils, whereas for oil soil the microstructures reduced the cleanability of surfaces.

3. In the case of ceramic materials the coatings affected the cleanability. The roughness of the surfaces correlated with cleanability from particle soils. The cleanability from oil soil correlated with the contact angle of water on the surfaces. Organic particle soil was removed more efficiently after UV-radiation than without UV treatment, whereas UV-radiation did not affect the removal of oil soil.

4. Coatings improved the cleanability of the concrete materials. According to contact angle measurements and topographic data, the coatings sealed the concrete surfaces.

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ORIGINAL PUBLICATIONS I-V