# Release of engineered $TiO_2$ particles from landfills

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## Introduction

Recent mass flow models suggest that the majority of engineered nanoparticles (ENP) are collected in managed waste streams and either eliminated during waste treatment processes (namely wastewater treatment and waste incineration), recycled or transferred to landfills, either directly or after passing managed waste facilities (Keller et al., 2013; Sun et al., 2014). The largest share of waste originates from the construction industry and is classified as inert construction waste in Switzerland and the leachate from respective landfills can be directly discharged into surface waters.

## Objectives

In mass flow models landfills are treated as ultimate sinks for ENP, however, there is no experimental evidence supporting this assumption. Therefore, we have initiated a monitoring study covering more than 20 different landfills in the Northern part of Switzerland to evaluate whether ENP can be detected in the leachates.

## Experimental setup

The settings of several landfills (age, type of waste) were evaluated and leachate samples were collected from selected landfills (Figure 1) under dry weather conditions. Bulk parameters, including temperature, oxygen content, redox-potential, and electrical conductivity were measured in the field. Furthermore, total suspended solids (TSS), total and dissolved organic carbon (TOC/DOC), and the concentrations of selected elements were determined in the lab. Elemental concentrations were determined by inductively-coupled plasma optical emission spectroscopy (ICP-OES) measurements. Particles smaller than a few microns were investigated using scanning electron microscopy (SEM) coupled to an energy dispersive X-ray (EDX) analysis system. For that purpose, samples were first sonicated for 15 minutes to disperse the particles and then sedimented for 1 h to remove the larger particles. The supernatant was filtered using 0.2 µm Nuclepore membrane filters and analysed in the SEM under low vacuum conditions. The morphometric parameters and the elemental composition of all individual particles were determined using an automated particle analysis system.

***Figure 1:*** *Selected landfills and sampling sites*

***Figure 2:*** *Leachats collected from different sampling sites.*

## Bulk parameters

The temperature of the leachates varied between 12 and 37 °C and the pH values were between 7 and 12. The TSS content ranged from a few to a few hundred of mg $L^{-1}$, which was also reflected in the different turbidity and colour of the leachates (Fig. 1). ICP-OES revealed Ti concentrations in the order of a few mg $L^{-1}$.

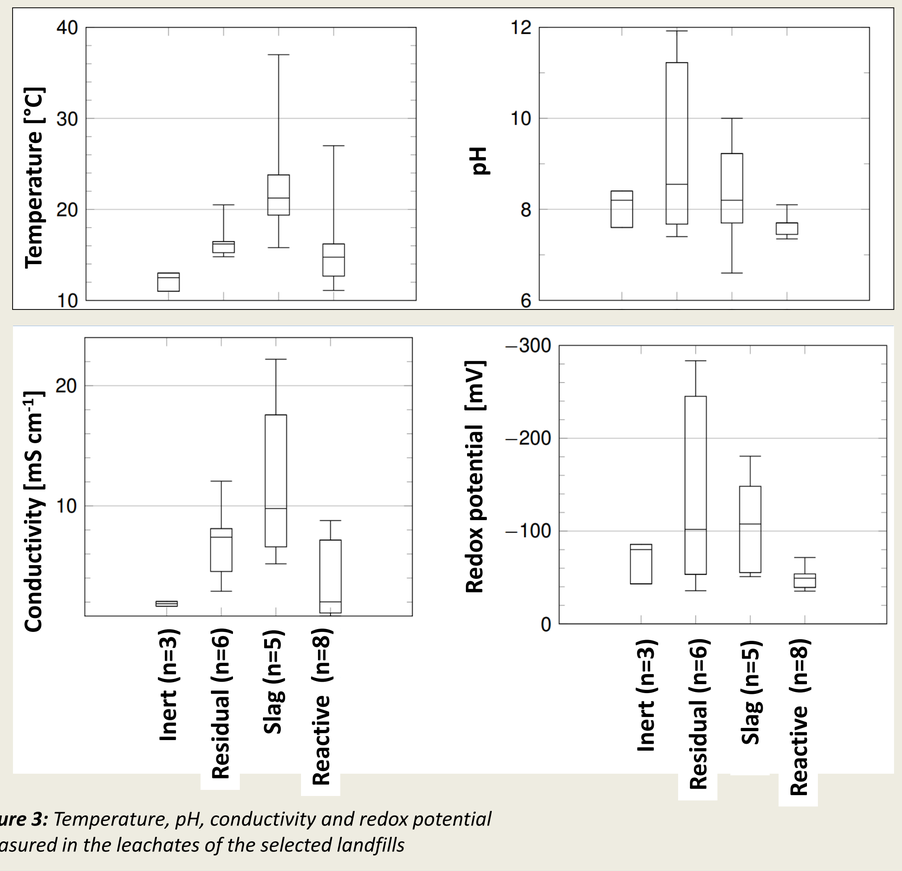


***Figure 3:*** *Temperature, pH, conductivity and redox potential measured in the leachates of the selected landfills*

## Computer controlled SEM (CC-SEM)

To screen the samples for the presence of $TiO_2$ particles, we conducted an automated particle analysis using an scanning electron microscope (NanoSEM230, FEI, USA). In total, 2707 particles were detected and the particle size distribution an exponential increase of the particle numbers with decreasing diameter (Figure 4A), typically observed for particles in surface waters (Gregory, 2005). Energy dispersive X-ray analysis of the individual particles reveal that 48 particles contained substantial amounts of Ti (Figure 4B) and particles containing more that 20 wt% of Ti were defined as pure $TiO_2$ particles. The histogram of these 48 $TiO_2$ particles again shown an exponential increase with decreasing particle diameter (Figure 4C).

The results from the microscopy analysis suggested that about 1 – 2 % of the detected particles were $TiO_2$ particles. A closer inspection of the automatically detected $TiO_2$ particles (Figure 5) revealed that these particles show rather spherical morphologies and consisted of aggregates of several smaller particles (Figure 6A, B). Such characteristic particle morphologies have been described from façade runoff (Kaegi et al., 2008) and represent white pigments which are essential components in paints.

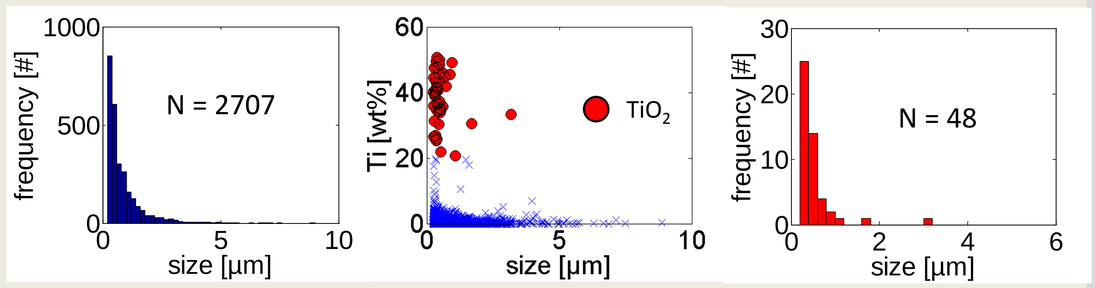


***Figure 4:*** *A: Particle size distribution of all particles detected using computer controlled scanning electron microscopy. Larger particles were removed previously by sedimentation. B: Size vs. Ti content of all particles. The $TiO_2$ particles are marked in red. C: Size distribution of $TiO_2$ particles.*

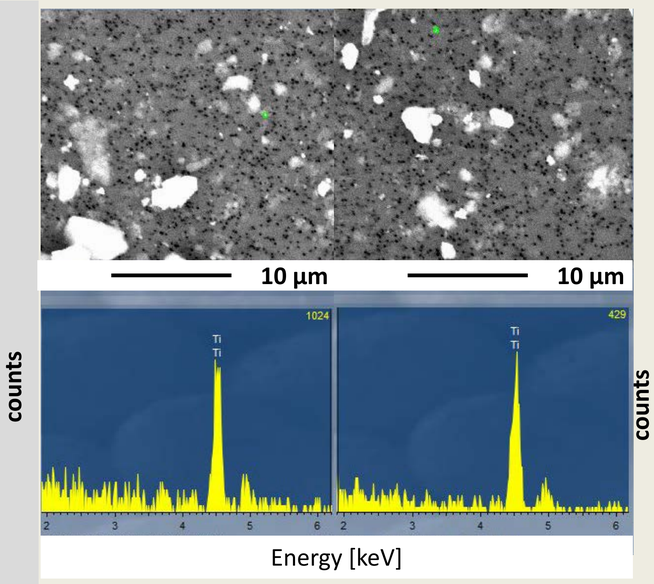


***Figure 5:*** *top: Backscattered electron (BSE) image resulting from CC-SEM. Bottom: EDX spectra of TiO2 particles detected by CC-SEM:*

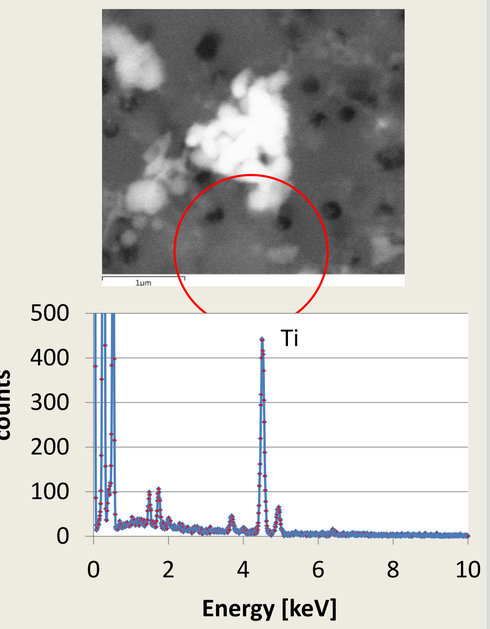


***Figure 6:*** *top: Backscattered electron (BSE) image of a $TiO_2$ particle recorded at higher magnification. Bottom: Respective EDX spectrum.*

## Conclusions and outlook

The first results from this study clearly indicate that colloidal particles (and possibly also ENP) are present in the leachates of landfills. Thus, contrary to the general assumption that landfills represent ultimate sinks for the ENP, landfills may serve as continuous sources for ENP, which, depending on the type of landfill, will be directly discharged into the surface waters.

## References

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