Supplementary Material for "Barriers, Pathways and Processes for Uptake, Translocation, and Accumulation of Nanomaterials in Plants—Critical Review"

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Content:

Supplementary **Table S1**, **Figure S1**, and **Figure S2**, sections **Uptake/Elimination Rate Equations**, **Root Cap Mucilage and Exudates**.

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19 **Table S 1:** Studies that proposed a nanoparticle (NP) pathway from cell to cell through plasmodesmata. Insoluble NPs are highlighted in **bold**. Observations
 20 were termed direct if NPs were directly visualized within the plasmodesmata, and indirect if NPs were detected in the vasculature, or if chemical analysis showed
 21 root–shoot translocation. EDS: Energy dispersive X-ray spectroscopy. SPIONs: super paramagnetic iron oxide NPs. ^aPrimary NP size as determined by transmis-
 22 sion electron microscopy (TEM). ^bHydrodynamic diameter.

Nanoparticle	Size ^a	Plant	Observation	Ref.
Fullerenes (C₇₀)	1.19 nm^b	Rice	Indirect	(Lin <i>et al.</i>, 2009)
SPIONs	9 nm	Soybean	Indirect	(Ghafariyan <i>et al.</i>, 2013)
C-coated Fe_xO_y	46 nm	Pumpkin (<i>Cucurbita pepo</i>)	Indirect	(Corredor <i>et al.</i>, 2009)
Iron oxide (Fe ₂ O ₃)	19 nm	<i>Nicotiana benthamiana</i>	Indirect	(Huang <i>et al.</i> , 2011)
Iron oxide (Fe ₂ O ₃)	9 nm	Soybean	Indirect	(Ghafariyan <i>et al.</i> , 2013)
Mesoporous SiO ₂ NPs	~20 nm	Lupin, wheat and corn	Indirect	(Sun <i>et al.</i> , 2014)
Zinc Oxide (ZnO)	20 nm	Ryegrass	Indirect	(Lin & Xing, 2008)
Silver	20, 40 nm	<i>Arabidopsis thaliana</i>	Direct, TEM-EDS	(Geisler-Lee <i>et al.</i> , 2013)
Silver	20 nm	<i>Arabidopsis thaliana</i>	NP in apoplast	(Ma <i>et al.</i> , 2010)
Silver	10 nm	Wheat	No uptake	(Vannini <i>et al.</i> , 2014)
Copper oxide (CuO)	30 nm	<i>Egeria densa</i>	Indirect	(Nekrasova <i>et al.</i> , 2011)
¹⁴¹Ceria (¹⁴¹CeO₂)	7, 25 nm	Cucumber	Indirect	(Zhang <i>et al.</i>, 2011)
Ceria (CeO₂)	10-30 nm	Tomato	Indirect	(Wang <i>et al.</i>, 2012)
Ceria (CeO₂)	37 nm	Maize (<i>Zea mays</i>)	No uptake	(Birbaum <i>et al.</i>, 2010)
Titanium dioxide	14-655 nm	Wheat	Indirect	(Larue <i>et al.</i> , 2012)
Gold	15 nm	Poplar	Direct, TEM	(Zhai <i>et al.</i>, 2014)

Figure S1: Example for linear relationship of insoluble nanoparticle exposure concentration and uptake rates at low exposure concentrations. Uptake rates in rice (*Oryza sativa*) calculated from Rico and co-workers (Rico *et al.*, 2013) by dividing nano-CeO₂ concentrations in shoots by exposure time (10 d). The primary particle size was 8±1 nm (rods). The authors found no visible signs of toxicity in the seedlings for all treatments, but subtle effects in biochemical assays at low concentrations and severe effects at 500 mg L⁻¹.

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43 **Figure S2:** Cell types and pores of the vascular system in gymnosperms and angiosperms. Adapted from Fahn
44 and co-workers (Fahn, 1982), additional pore size information from Liese and co-workers (Liese & Johann, 1954),
45 Jansen and co-workers (Jansen *et al.*, 2009), and Choat and co-workers (Choat *et al.*, 2008).

Details on Uptake/Elimination Rate Equations

First-order kinetics uptake and excretion rate constants are proportional to the bioavailable NP concentration in any medium (*e.g.* in soil pore water) C_{medium} (mg L⁻¹), or the NP concentration in the plant tissue C_{plant} (mg kg⁻¹), respectively (Wang *et al.*, 2013; Burken & Schnoor, 1997). In case of first-order kinetics, the uptake rate of NPs by plants dC_{plant}/dt (mg kg⁻¹d⁻¹) is therefore given by the rate law

$$dC_{plant}/dt = k_{uptake} \times C_{medium}, \quad \text{Equation S1}$$

whereas k_{uptake} (L kg⁻¹d⁻¹) is the uptake rate constant, and t (d) is the exposure time. The units may vary depending on the experimental setup.

Analogously, the excretion/elimination rate constant $-dC_{plant}/dt$ (mg kg⁻¹d⁻¹) in case of first-order kinetics is given by the rate law

$$-dC_{plant}/dt = k_{excretion} \times C_{plant}, \quad \text{Equation S2}$$

whereas $k_{excretion}$ (d⁻¹) is the excretion/elimination rate constant (Wang *et al.*, 2013).

If NP uptake is dominated by adsorption on the plant surface, the sorption process is limited by the total plant surface and can be expected to follow classical sorption isotherms under equilibrium conditions. A summary of classical sorption model equations such as the Freundlich or Langmuir equations are provided in the supporting information of (Schwab *et al.*, 2014).

Second order, or *pseudo*–second order sorption kinetics, analogous to classical sorption kinetics (Ho & McKay, 1999), results in rate laws such as

$$dC_{plant, sorbed}/dt = k_{sorption} \times (C_{plant, sorbed}(t=\infty) - C_{plant, adsorbed})^2 \quad \text{Equation S3}$$

whereas $C_{plant, sorbed}$ (mg kg⁻¹) is the NP concentration adsorbed to the plant surface, $k_{sorption}$ (kg mg⁻¹d⁻¹) is the rate constant of sorption, and $C_{plant, sorbed}(t=\infty)$ (mg kg⁻¹) is the NP concentration adsorbed to the plant surface at equilibrium.

Root Cap Mucilage and Exudates

Root caps primarily secrete mucilage by (partially sloughed off) root cap border cells or by lysis of cells in the epidermis and cortex (McNear Jr., 2013; Driouich *et al.*, 2013; Hawes *et al.*, 2000). Mucilage largely consists of sticky insoluble high molecular weight polysaccharides, antimicrobial proteins, and extracellular DNA, and secondary metabolites (McNear Jr., 2013; Driouich *et al.*, 2013; Walker *et al.*, 2003). The smaller fraction of exudates consist of a very diverse range of soluble low molecular weight compounds such as amino acids, organic acids, sugars, proteins, phenolics, and secondary metabolites (Walker *et al.*, 2003; McNear Jr., 2013). Both M/E serve to respond to symbiotic or pathogenic soil microorganisms, and to produce an acidic root surface microenvironment, which alters the bioavailability of soil minerals (Hawes *et al.*, 2000), and heavy metals (Vervaeke *et al.*, 2004; Horst *et al.*, 1982). Another important function of border cells and associated mucilage is to protect the sensitive apical meristem from physical damage when the root makes its way through the soil (lubrication) (McNear Jr., 2013; Hawes *et al.*, 2000; McKenzie *et al.*, 2013). Further functions of the border cells and M/E interfering with NP exposure include aggregating soil particles (McNear Jr., 2013), and sensing of environmental signals such as gravitation, water, and nutrients (Hawes *et al.*, 2000).

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