Vol 461|17 September 2009|doi:10.1038/nature08292 nature

LETTERS

New particle formation in forests inhibited by isoprene emissions

Astrid Kiendler-Scharr[1], Jürgen Wildt[2], Miikka Dal Maso[1,3], Thorsten Hohaus[1], Einhard Kleist[2], Thomas F. Mentel[1], Ralf Tillmann[1], Ricarda Uerlings[2], Uli Schurr[2] & Andreas Wahner[1]

It has been suggested that volatile organic compounds (VOCs) are involved in organic aerosol formation, which in turn affects radiative forcing and climate[1]. The most abundant VOCs emitted by terrestrial vegetation are isoprene and its derivatives, such as monoterpenes and sesquiterpenes[2]. New particle formation in boreal regions is related to monoterpene emissions[3] and causes an estimated negative radiative forcing[4] of about -0.2 to $-0.9\,\mathrm{W\,m^{-2}}$. The annual variation in aerosol growth rates during particle nucleation events correlates with the seasonality of monoterpene emissions of the local vegetation, with a maximum during summer[5]. The frequency of nucleation events peaks, however, in spring and autumn[5]. Here we present evidence from simulation experiments conducted in a plant chamber that isoprene can significantly inhibit new particle formation. The process leading to the observed decrease in particle number concentration is linked to the high reactivity of isoprene with the hydroxyl radical (OH). The suppression is stronger with higher concentrations of isoprene, but with little dependence on the specific VOC mixture emitted by trees. A parameterization of the observed suppression factor as a function of isoprene concentration suggests that the number of new particles produced depends on the OH concentration and VOCs involved in the production of new particles undergo three to four steps of oxidation by OH. Our measurements simulate conditions that are typical for forested regions and may explain the observed seasonality in the frequency of aerosol nucleation events, with a lower number of nucleation events during summer compared to autumn and spring[5]. Biogenic emissions of isoprene are controlled by temperature and light[2], and if the relative isoprene abundance of biogenic VOC emissions increases in response to climate change or land use change, the new particle formation potential may decrease, thus damping the aerosol negative radiative forcing effect.

Land vegetation contributes 90% of the global VOC emissions[2]. The main compound classes emitted by terrestrial vegetation are isoprene and its derivatives, such as monoterpenes and sesquiterpenes. Isoprene comprises one-third of the annual global VOC emission from all natural and anthropogenic sources. Annual global isoprene emissions are estimated to be in the range 440–660 teragrams of carbon (Tg C)[6]. While the detailed biological functionality of isoprene and monoterpene emissions is not fully understood[7], the dependence of emissions on light intensity and temperature has been investigated in detail[2,7].

In addition to their importance for gas phase chemistry, the involvement of biogenic VOCs in tropospheric aerosol formation, first suggested in ref. 8, underlines the importance of taking into account biogenic VOCs in particle formation. Globally, the amount of secondary organic aerosols (SOA) produced from biogenic sources is still unclear. A source strength of 61–79 $\mathrm{Tg\,yr^{-1}}$ at present day conditions has been estimated[9] . Bottom-up approaches, based on SOA yields for single compounds derived in laboratory experiments, estimate a global SOA production of 12–70 $\mathrm{Tg\,yr^{-1}}$ (ref. 10). Recent estimates suggest that SOA production may be even higher, of the order of 223–615 $\mathrm{Tg\,yr^{-1}}$ (ref. 11).

In regions with low primary aerosol concentrations, biogenic SOA production proceeds via nucleation of gas phase species. Investigations of the mechanism underlying the frequently observed nucleation events in the European boreal forest demonstrate a straightforward relation between monoterpene emissions and gas-to-particle formation[3]. This is important, because nucleation can provide substantial numbers of aerosols.

Number density and size distribution of aerosols are key quantities that determine direct and indirect climate effects of aerosols. Current radiative forcing by new particle formation in boreal regions has been estimated[4] as -0.2 to $-0.9\,\mathrm{W\,m^{-2}}$. Extrapolating current monoterpene emission rates into the year 2100 has led to a prediction[12] of a 40% increase of cloud condensation nuclei over boreal forests caused by a temperature increase of 5.8 °C.

With their potential impact on climate, aerosol particles generated from biogenic emissions constitute a possible link in a feedback loop between climate, atmosphere and biosphere[1]. Biogenic emissions of isoprene, for instance, are controlled by temperature and light[2]. It is therefore expected that future biogenic isoprene emissions will change as temperature and land cover change[13]. For example, the impact of European afforestation may be significant, with a 126% increase in isoprene and a 13% increase in monoterpenes[14,15] on the European scale.

Here we present laboratory evidence that isoprene can significantly inhibit new particle formation. Experiments were conducted in a plant chamber over a period of 21 days for a small mixed stand consisting of birch (*Betula pendula* L.), beech (*Fagus sylvatica* L.) and spruce (*Picea abies* L.), and over a period of 10 days for pines (*Pinus sylvestris* L.). These species emit only low amounts of isoprene, allowing the study of the influence of isoprene on particle formation by adding it to the natural emissions. The isoprene concentration was varied between 2 and 30 parts per billion (p.p.b.), which is within the range of atmospheric observations[16,17]. In order to minimize effects of changes in the amount and composition of the plant VOC emissions, experiments with and without isoprene addition were conducted alternately on a daily basis.

Figure 1 presents the observed number concentration and volume concentration for particle formation from the VOCs emitted from the plants, and from the plant-emitted VOCs with the addition of isoprene. The presence of isoprene in plant-emitted VOCs decreases both the number and volume concentration compared to the case of particle formation from the VOC mixture from the plants alone. As indicated in Fig. 1, isoprene was switched off 3 hours after new

---

[1]Institut ICG-2, Troposphäre, [2]Institut ICG-3, Phytosphäre, Forschungszentrum Jülich, Jülich 52425, Germany. [3]Department of Physics, University of Helsinki, 00014 Helsinki, Finland.

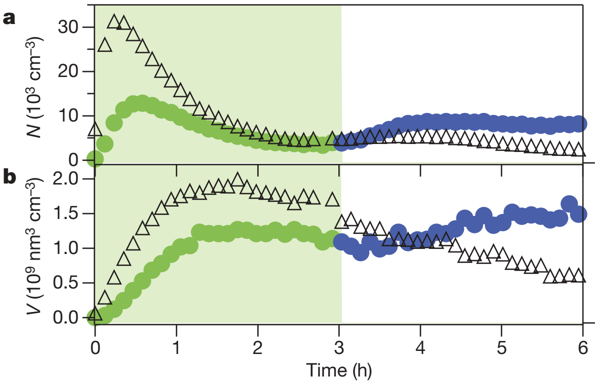

Figure 1 | Time series of particle properties for two experiments. a, Particle number concentration; **b**, particle volume concentration. The influence of isoprene on particle number concentration is clearly seen when comparing plant emissions plus isoprene (green filled circles) with plant emissions only (open triangles). The addition of isoprene reduces both particle number and volume concentration. Stopping the isoprene addition after 3 h (blue filled circles) results in an increase of both aerosol number and volume concentration.

particle formation had started. Total number and volume concentrations are increasing after the removal of isoprene. This clearly indicates that the presence of isoprene suppresses the formation of new particles with diameters larger than 5 nm.

The observation of a reduction of the total particle number and volume concentration indicates that isoprene affects the particle formation at an early stage. Our measurements (see Supplementary Information for details) show a significant reduction of OH concentrations in the presence of isoprene. Figure 2 shows the dependence of the nucleation rate on the OH concentration. The nearly linear power-law dependence of the nucleation rate on the OH concentration is indicative of the nucleation mechanism, where OH oxidation is the rate-limiting step determining the production rate of the nucleating vapours. Henceforth we regard the formation rate of particles with threshold diameters of 5 nm as the nucleation rate.

Thus the concentrations of nucleating vapours depend on the OH concentration. The identity of the nucleating vapour is unknown in our experiments. The nucleation rate is clearly dependent on the precursor VOC concentration[18], showing that the VOC oxidation products are controlling the particle formation process.

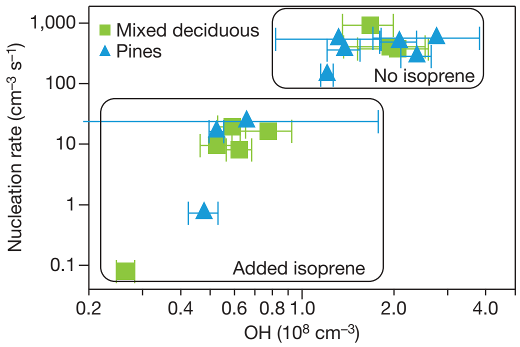

Figure 2 | Experimentally observed particle number as function of OH concentration. The OH concentration, [OH], was calculated from the decrease of camphene and 1,8-cineole in the chamber. Data for [OH] are the mean obtained from the calculations using both VOCs, and the error limits show minimum and maximum [OH] as calculated from either camphene or 1,8 cineole. The emissions were generated from a mixed deciduous stand (one birch, two beech, and one spruce; squares), and from two pines (triangles). Lower OH concentrations result in decreased particle number concentrations.

According to the nucleation theorem, the slope of the logarithm of nucleation rate versus the logarithm of concentration of the nucleating vapour determines the number of molecules in the critical cluster[19]. By analogy, we can read from the slope in Fig. 2 that the number of OH oxidation steps leading to observable particles is 3 to 4. This can involve parallel or consecutive OH oxidations or a combination of both.

This power-law exponent of 3–4 is approximately a factor 2 above the exponents observed in atmospheric nucleation. For atmospheric conditions, data are only available for the relation of new particle formation rates and the OH-dependent sulphuric acid concentration (see, for example, ref. 20). Under such conditions, the dependence shows an exponent of 1–2 (see, for example, refs 20, 21). In laboratory experiments (see, for example, ref. 22), this dependence has exponents of the order of 4–10. In the very recent literature, evidence is mounting that VOC oxidation products may play a key role in atmospheric nucleation events[23]. So far no systematic information on the dependence of nucleation rates on VOC oxidation products is available, impeding the direct comparison of our results with ambient observations.

According to our measurements, isoprene OH oxidation products do not contribute to the nucleation process. Therefore, the main factor controlling the nucleation rate should be the concentration of OH radicals reacting with non-isoprene VOCs to form particles.

In order to allow a straightforward modelling approach to the observations, a set of experiments was conducted replacing the plant emissions by α-pinene only. If we consider the reactions:

$$\begin{aligned}\alpha\mathrm{P}+\mathrm{OH} &\xrightarrow{k_\mathrm{A}} \mathrm{P}_1\\ \mathrm{Is}+\mathrm{OH} &\xrightarrow{k_\mathrm{I}} \mathrm{P}_2\end{aligned}\tag{1}$$

we obtain simple expressions for the steady state concentrations of α-pinene ([αP]), isoprene ([Is]) and OH (Supplementary Information). Here P_1 denotes the first-generation oxidation product of α-pinene, and P_2 is the first-generation oxidation product of isoprene. We used the Master Chemical Mechanism (version 3.1; ref. 24) applied to the oxidation of α-pinene and isoprene to model a range of isoprene (Q_Is) versus α-pinene ($Q_{\alpha\mathrm{P}}$) source rates. The resulting normalized source term of product P_1 ($Q_{\mathrm{P}1}$) is given by a fitted function of the form

$$\frac{Q_{\mathrm{P}1}}{Q_{\mathrm{P}1,0}}=\frac{1}{1+\beta\dfrac{Q_\mathrm{Is}}{Q_{\alpha\mathrm{P}}}}\tag{2}$$

Here $Q_{\mathrm{P}1,0}$ is the source rate of P_1 in the absence of isoprene, and β ($=1.5\pm0.1$) is a fitting parameter derived from log-least squares fitting of the experimental data (see Supplementary Information).

Assuming that the nucleating vapour concentration C is proportional to $Q_{\mathrm{P}1}$ and the rate of particle production (J) is proportional to C^n (see, for example, ref. 21), we obtain the following expression for the inhibition of particle production:

$$\frac{J}{J_0}=\left(\frac{1}{1+\beta\dfrac{Q_\mathrm{Is}}{Q_{\alpha\mathrm{P}}}}\right)^n\tag{3}$$

where J_0 is the particle production rate in the absence of isoprene.

Figure 3 presents data of the observed suppression of particle formation as a function of the concentration ratio of isoprene to all other VOCs for the α-pinene and plant experiments. With increasing isoprene to monoterpene ratio, the number of particles decreases. Both data sets can be represented with equation (3), with n equal to 6.8 ± 0.5 for the α-pinene experiments and 3.7 ± 0.4 for the tree

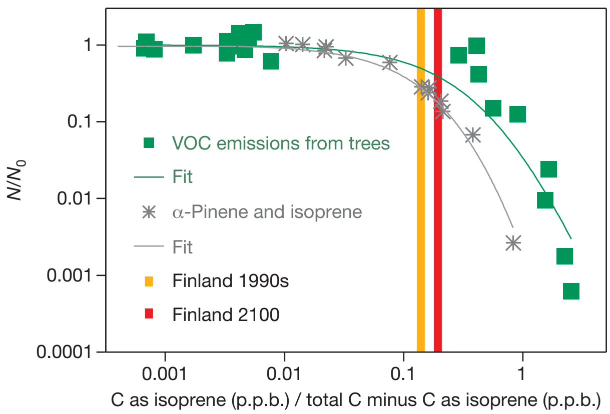

Figure 3 | Inhibition of particle number concentration as a function of the carbon based ratio of isoprene to other VOC concentrations. Data are shown for all plant emissions studied (filled squares) and α-pinene (asterisks). The fit functionality is derived from MCM modelling of the first generation of OH oxidation products of non-isoprene emissions: $N/N_0 = [1/(1 + 1.5R)]^n$, where $n = 3.7 \pm 0.4$ (green line) and $n = 6.8 \pm 0.5$ (grey line). Vertical bars indicate modelled concentration ratios of isoprene and monoterpenes for Finland[28] in the 1990s (orange) and in 2100 (red).

emissions. Note that our experiments were performed in the absence of seed aerosols. The experimental results are comparable to atmospheric conditions with negligible condensational sink only, and the expression for inhibition will only be applicable for such conditions. In comparison with the α-pinene experiments, we find that for tree-emitted VOCs a larger relative isoprene concentration is needed for the same suppression. This is consistent with the finding that the mixture of the VOCs emitted from trees forms more efficiently nucleating vapours than α-pinene[18]. The observed exponent of 3.7 ± 0.4 for the tree emissions is the same as the exponent of 3–4 derived from the dependence of the nucleation rate on OH (Fig. 2).

Comparing different ecosystems, the maximum ratio R of emitted isoprene carbon to monoterpene carbon is observed for temperate broadleaf summer green trees ($R = 56$; ref. 15), and the minimum R is reported for Finland country means ($R = 0.16$; ref. 25) and the south boreal forest ($R = 0.15$; ref. 26). The ratios used in our study range from 0 to 2.5 (see Fig. 3), and are thus representative for boreal and temperate forests.

The boreal forests are strong monoterpene emitters but have a maximum of R during summer[27]. The observed inhibition of new particle formation by the presence of isoprene in a biogenic VOC mixture may thus explain observations from the boreal forest in which the number of nucleation events is lower during the summer period than in spring and autumn[5].

Our research points to an efficient suppression of new particle formation by isoprene. This efficient suppression could be verified when an oak tree (*Quercus robur*) was added to the mixed stand. *Quercus robur* is a high isoprene emitter, resulting in an R of 19.5 in this experiment. No significant particle formation event was detectable under these conditions. The observed reduction in nucleation rate is highly correlated with the reduction of OH concentrations. The reaction with OH is the rate limiting step in the formation of new particles from plant-emitted VOCs.

We therefore conclude that through its effect on OH concentration isoprene plays an important role in atmospheric new particle formation. It is expected that future isoprene emissions from land vegetation will change as climate and land cover change. Our results show that besides the magnitude of VOC input into the atmosphere, the specific pattern of the emitted VOC affects SOA formation. It is to be expected that this effect will be most pronounced for regions already susceptible to nucleation, that is, regions with low pre-existing aerosol concentration. Certainly this includes the boreal forests. Owing to the local to regional dimensions of nucleation events, isoprene emissions from, for example, monocultures adjacent to areas with large terpene emissions, are expected to regionally suppress new particle formation.

Future particle formation potential may thus critically depend on the relative increase of isoprene and other VOCs in response to climate change. In particular, an increase of the isoprene/monoterpene emission ratio R can lead to a suppression of nucleation events. If rising temperatures cause an increase in R, which in turn causes a decrease in particle formation rates, the observed suppression of particle formation by isoprene constitutes a positive feedback in the climate–biosphere–atmosphere interactions. Current estimates predict an increase of R from 0.14 in the 1990s to 0.19 in 2100[28] for boreal forests in Finland. From our results, we conclude that this implies a decrease of nucleation mode particles by 20% compared to present day values. If isoprene emissions were completely stopped in Finland, nucleation mode particles would be doubled. Following the approach used in ref. 4, a 20% decrease in nucleation mode particles translates into a 12% change in radiative forcing, decreasing the aerosol cooling effect. By changing R, land vegetation thus influences new particle formation and subsequent radiative forcing.

METHODS SUMMARY

Experiments were conducted in the Jülich plant aerosol chamber (JPAC), which has been described in detail elsewhere[18,29]. In brief, the set-up consists of two borosilicate glass chambers. The chambers are housed in individual climate chambers. Each chamber can be temperature controlled individually between 10 and 50 °C with a stability of ±0.5 °C. The chambers are operated as continuously stirred tank reactors, with residence times of 20 min in the plant chamber and 65 min in the reaction chamber. Purified air with an added CO_2 concentration of 350 p.p.m. and humidified with Milli-Q water was passed through the plant chamber. The air stream leaving the plant chamber carried the VOCs emitted by the plants in representative mixing ratios. This air was fed into the reaction chamber. Ozone concentration and relative humidity in the reaction chamber were controlled by two additional air streams and held at 80 p.p.b. and 60%, respectively (reaction chamber temperature, 15 °C). For photochemical generation of OH radicals, the reaction chamber was equipped with an internal ultraviolet source (Philips, TUV 40 W, $\lambda_{max} = 254$ nm). Plants used for these experiments were birch, beech, spruce and pines. Isoprene (Aldrich, 99% purity) was added at different concentrations to the plant chamber air through a varied flow from a diffusion source. For the reference experiments, α-pinene (Fluka, 99% purity) and isoprene were added to the reaction chamber to give concentrations ranging from 7 to 12 p.p.b. and 0 to 20 p.p.b., respectively. Aerosol number concentrations were measured with a condensation particle counter (CPC) (TSI Model 3022A). The maximum number concentration measurable was 1×10^7 cm^{-3}. The size distribution of the particles was measured with a scanning mobility particle sizer (SMPS) system (TSI Model 3934), consisting of a TSI Model 3071 electrostatic classifier and a TSI Model 3025 CPC. The SMPS was operated to measure particles between 15 and 750 nm.

Received 11 December 2008; accepted 13 July 2009.

1. Kulmala, M. *et al.* A new feedback mechanism linking forests, aerosols, and climate. *Atmos. Chem. Phys.* **4**, 557–562 (2004).
2. Guenther, A. *et al.* A global model of natural volatile organic compound emissions. *J. Geophys. Res.* **100**, 8873–8892 (1995).
3. Tunved, P. *et al.* High natural aerosol loading over boreal forests. *Science* **312**, 261–263 (2006).
4. Kerminen, V. M., Lihavainen, H., Komppula, M., Viisanen, Y. & Kulmala, M. Direct observational evidence linking atmospheric aerosol formation and cloud droplet activation. *Geophys. Res. Lett.* **32**, L14803, doi:10.1029/2005GL023130 (2005).
5. Kulmala, M. *et al.* Formation and growth rates of ultrafine atmospheric particles: a review of observations. *J. Aerosol Sci.* **35**, 143–176 (2004).
6. Guenther, A. *et al.* Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature). *Atmos. Chem. Phys.* **6**, 3181–3210 (2006).
7. Sharkey, T. Isoprene emission from plants: why and how. *Ann. Bot. (Lond.)* **101**, 5–18 (2008).
8. Went, F. W. Blue hazes in the atmosphere. *Nature* **187**, 641–643 (1960).
9. Tsigaridis, K. & Kanakidou, M. Global modelling of secondary organic aerosol in the troposphere: a sensitivity analysis. *Atmos. Chem. Phys.* **3**, 1849–1869 (2003).
10. Kanakidou, M. *et al.* Organic aerosol and global climate modelling: a review. *Atmos. Chem. Phys.* **5**, 1053–1123 (2005).
11. Goldstein, A. H. & Galbally, I. E. Known and unexplored organic constituents in the Earth's atmosphere. *Environ. Sci. Technol.* **41**, 1515–1521 (2007).

12. Tunved, P. *et al.* The natural aerosol over Northern Europe and its relation to anthropogenic emissions—implications of important climate feedbacks. *Tellus B* **60,** 473–484 (2008).
13. Wiedinmyer, C., Tie, X. X., Guenther, A., Neilson, R. & Granier, C. Future changes in biogenic isoprene emissions: how might they affect regional and global atmospheric chemistry? *Earth Interact.* **10,** 1–16 (2006).
14. Lathiere, J., Hauglustaine, D. A., De Noblet-Ducoudre, N., Krinner, G. & Folberth, G. A. Past and future changes in biogenic volatile organic compound emissions simulated with a global dynamic vegetation model. *Geophys. Res. Lett.* **32,** L20818, doi:10.1029/2005GL024164 (2005).
15. Lathiere, J. *et al.* Impact of climate variability and land use changes on global biogenic volatile organic compound emissions. *Atmos. Chem. Phys.* **6,** 2129–2146 (2006).
16. Greenberg, J. P. *et al.* Tethered balloon measurements of biogenic VOCs in the atmospheric boundary layer. *Atmos. Environ.* **33,** 855–867 (1999).
17. Kesselmeier, J. *et al.* Concentrations and species composition of atmospheric volatile organic compounds (VOCs) as observed during the wet and dry season in Rondonia (Amazonia). *J. Geophys. Res.* **107,** doi:10.1029/2000JD000267 (2002).
18. Mentel, T. F. *et al.* Photochemical production of aerosols from real plant emissions. *Atmos. Chem. Phys.* **9,** 3041–3094 (2009).
19. Kashchiev, D. On the relation between nucleation work, nucleus size, and nucleation rate. *J. Chem. Phys.* **76,** 5098–5102 (1982).
20. Weber, R. J. *et al.* Measured atmospheric new particle formation rates: implications for nucleation mechanisms. *Chem. Eng. Commun.* **151,** 53–64 (1996).
21. Riipinen, I. *et al.* Connections between atmospheric sulphuric acid and new particle formation during QUEST III–IV campaigns in Heidelberg and Hyytiala. *Atmos. Chem. Phys.* **7,** 1899–1914 (2007).
22. Berndt, T., Boge, O., Stratmann, F., Heintzenberg, J. & Kulmala, M. Rapid formation of sulfuric acid particles at near-atmospheric conditions. *Science* **307,** 698–700 (2005).
23. Laaksonen, A. *et al.* The role of VOC oxidation products in continental new particle formation. *Atmos. Chem. Phys.* **8,** 2657–2665 (2008).
24. Bloss, C. *et al.* Development of a detailed chemical mechanism (MCMv3.1) for the atmospheric oxidation of aromatic hydrocarbons. *Atmos. Chem. Phys.* **5,** 641–664 (2005).
25. Lindfors, V. & Laurila, T. Biogenic volatile organic compound (VOC) emissions from forests in Finland. *Boreal Environ. Res.* **5,** 95–113 (2000).
26. Lindfors, V., Laurila, T., Hakola, H., Steinbrecher, R. & Rinne, J. Modeling speciated terpenoid emissions from the European boreal forest. *Atmos. Environ.* **34,** 4983–4996 (2000).
27. Hakola, H. *et al.* Seasonal variation of VOC concentrations above a boreal coniferous forest. *Atmos. Environ.* **37,** 1623–1634 (2003).
28. Kellomaki, S. Impact of global warming on the tree species composition of boreal forests in Finland and effects on emissions of isoprenoids. *Glob. Change Biol.* **7,** 531–544 (2001).
29. Heiden, A. C., Kobel, K., Langebartels, C., Schuh-Thomas, G. & Wildt, J. Emissions of oxygenated volatile organic compounds from plants Part I: Emissions from lipoxygenase activity. *J. Atmos. Chem.* **45,** 143–172 (2003).

Supplementary Information is linked to the online version of the paper at www.nature.com/nature.

Acknowledgements We gratefully acknowledge support by the European Commission (IP-EUCAARI, contract number 036833-2).

Author Contributions A.K.-S., T.F.M. and J.W. developed the basic JPAC set-up and designed the study. All measurements were conducted by E.K., T.H., R.T. and R.U. Interpretation of the data was performed by A.K.-S., M.D.M. and J.W. A.K.-S. wrote the manuscript. A.K.-S., J.W., T.F.M., M.D.M. and A.W. discussed and commented on the manuscript. A.W. and U.S. provided the working environment and financial support.

Author Information Reprints and permissions information is available at www.nature.com/reprints. Correspondence and requests for materials should be addressed to A.K.-S. (a.kiendler-scharr@fz-juelich.de).