Author reply to review by anonymous referee #2:

We would like to thank referee #2 for his useful comments, which helped clarifying and improving this paper. The review comments are repeated in black font and the author replies are highlighted in blue font ("*italic style is used for modifications to the manuscript*").

This paper furthers current understanding relating to the detection efficiency of the single particle soot photometer, which previously appeared to be well understood (Schwarz et al., 2010). The paper describes the interesting result that spark-generated soot particles are poorly detected by the SP2.

This is clearly important for studies using spark soot as a surrogate for atmospheric BC and although, as the authors note, there is no evidence yet of a similar effect in ambient or other chamber data, it is certainly useful to bear this in mind.

While their conclusions of precisely why they have found this result require some further justification, the poor detection efficiency is still a worthwhile result to publish. The details of the experiments are very clear and the written English is generally very good.

I recommend this paper is published after addressing the following points.

Specific comments

There are 3 explanations for the apparent lack of incandescence by spark soot particles in the SP2:
1) Differences in the chemical structure of spark soot prevent it from incandescing efficiently in the SP2 (this is addressed more fully by the other reviewer)
2) Fractal spark soot particles disperse towards the edges of the laser beam, thereby experiencing a lower laser power and scatter but do not incandesce
3) The spherules in spark soot do not conduct heat efficiently between one another, and vaporise before they reach incandescence temperatures

The first explanation is possible and could be ruled out by collapsing the fractal structure of the soot, for example by condensation of sulphuric acid, then thermodenuding to leave just the collapsed core, then selecting the same mass of particle.
We would indeed expect that collapsing the PALAS soot, achieved by e.g. exposure of the PALAS soot sample to high RH before measurement with the SP2, would make it detectable by the SP2, or at least decrease the threshold laser power required for proper detection. Unfortunately we were not able to add such follow-up experiments to the original schedule of the BC-Act measurement campaign.

The following paragraph has been added to the revised manuscript in response to the review by R. Niessner to rule out chemical reactivity as a reason for missing incandescence:

"The nanocrystalline structure differs between different BC types and with that also their chemical reactivity. PALAS soot has been shown to be the most reactive BC material among several BC types, and this results in a lower combustion temperature during thermal(-optical) analysis (e.g. Schmid et al., 2011; Schuster et al., 2011). The question to be answered here is whether the PALAS soot particles lose a substantial fraction of their mass through combustion before they reach their vaporisation temperature in the SP2. The heating rate of BC particles in the SP2 is around nine orders of magnitude faster than that applied in thermal(-optical) analysis, which leaves very little time for combustion. Analysis of the time-resolved scattering signal of the non-incandescent PALAS soot particles revealed that the BC does neither evaporate nor react away in substantial amounts, while the particles cross the laser beam. Consequently, the high chemical reactivity can be excluded as a reason for the missing incandescence signals."

The second explanation has been identified and the authors have attempted to rule it out, however their conclusion does not appear fully justified- it is possible that the larger spark soot particles scatter enough light to be detected efficiently with the PSD but do not incandesce efficiently, whilst the smaller particles, with their smaller scattering cross section, do not scatter enough light to be detected efficiently even with the PSD.

Different types of instruments apply different methods to collimate particles to a narrow beam. Aerosol mass spectrometers typically use aerodynamic lenses to focus the particles into a narrow beam upon expansion of the sample into the vacuum, at the same time separating the particles from the air. With this approach the width/divergence of the particle beam depends on particle size and morphology. The SP2, where no separation of the particles from the air is needed, uses a concentric-nozzle jet system with a small pressure drop. The particles exit through the centre nozzle, while an eight times higher flow exiting through the outer nozzle forms a sheath flow that focuses the particles. No substantial differences in the particle beam width/divergence as a function of particle size and/or morphology are expected for this focussing method, though one never really knows. The fact that unit detection efficiency is achieved with the position sensitive detector (light scattering), shows that the particle beam is narrower than the laser beam. Furthermore, a large divergence of the particle beam would affect the scattering signals and incandescence signals in different ways. The random noise of the scattering cross section measured for multiple particles of equal size would increase, as individual particles would be exposed to substantially different laser intensities. In contrast, the incandescence signal is independent of laser intensity, except for the fact that it completely disappears, if the laser power falls below the incandescence threshold. A comparison of the ratio between the scattering and incandescence signals for the larger PALAS soot particles does not show increased random noise compared to other BC samples, which indicates a well-confined particle beam.

The discussion of the particle beam divergence has been adapted in the revised manuscript:

"The divergence of the particle beam could possibly be larger for the PALAS soot particles with a very low effective density than for the other BC samples with a higher effective density, thereby causing a similar effect as a misalignment. However, no substantial influence of particle size/morphology is expected for the concentric-nozzle jet system applied in the SP2. Furthermore, the bigger sizes of the PALAS soot particles (D_{mob} = 305 and 500 nm) are properly counted by the SP2's position sensitive detector (open green symbols in Fig. 2a), which detects elastically scattered light (while the smallest investigated PALAS soot particles fall below the normal lower detection limit of the position sensitive detector, such that only the multiply charged particles, ~20 % of the total number, are counted at the nominal size of D_{mob} = 200 nm). This shows that the particle beam has a smaller width than the laser beam also for PALAS soot particles. Thus, the hypothesis of larger particle beam divergence can be discarded."

The authors have concluded the third explanation is the correct one through process of elimination, but in light of the above this does not seem fully justified.

Our third hypothesis is that particle morphology has a substantial influence on the lower detection limit of the SP2, i.e. that agglomerates with a low fractal dimension and small primary particles require much high laser power for reaching incandescence than compact particles of equal BC mass. (By the way, heat conduction between the primary particles of an agglomerate is unimportant, as they all absorb the laser light themselves. Important is the fact that heat conduction to the surrounding air is approximately equal to the sum of the heat conduction of the isolated primary particles.)

Above we provide additional arguments to rule out the first and second hypotheses. Additional analysis of the data set, including a measurement performed at higher laser power, provides further supporting evidence for the third hypothesis. This is now included in the revised manuscript:

"…Consequently, for particles with a low fractal dimension and very small primary particles, the physical limit for reaching the vaporisation temperature at a certain laser power depends, for the most part, on the primary particle size, with a minor influence of the total BC mass in the agglomerate. This effect shifts the lower detection limit to much higher BC mass, or makes them completely undetectable. A more detailed analysis of the light scattering and incandescence signals shows that unit detection efficiency was actually achieved for the largest multiply charged PALAS soot particles with a BC mass of >4-6fg. This corresponds to an increase of the lower detection limit by a factor of ~5-10.

Varying the laser power provided further evidence that the unreliable detection of small PALAS soot particles is caused by the influence of particle morphology on the threshold laser intensity rather than chemical reactivity effects. An increase of the counting efficiency from ~12% to ~20% (dark green diamond in Figs. 2a and 3) was achieved for PALAS soot particles with a mobility diameter of D_{mob} = 305 nm by increasing the laser power as much as possible (~45% higher intensity)."

It is also surprising that discussion of detection efficiency has not made any reference to coincidence and the duty cycle of the SP2, both of which can greatly affect the detection efficiency of the instrument. It should be noted how much if at all these affected the results, or if the dilution involved in the sampling made them negligible.
These are indeed additional potential reasons for low counting efficiency. However, the samples were sufficiently dilute to avoid coincidence and the data acquisition was powerful enough to always maintain a duty cycle of >99%. This is now explicitly addressed with modifications made to the following paragraph:
"The SP2 records the signals from a particle only if at least one signal crosses the trigger threshold for data storage, which is set in the data acquisition software. The position sensitive detector's signal triggered storage of the signals from all detectors for all PALAS soot particles with D_{mob} =305 or 500 nm. The total number concentration of detected particles agreed within uncertainty with that measured by the CPC (Fig. 2a). This proves that neither coincidence nor duty cycle problems caused the low counting efficiency. On the contrary, the signal from the broadband incandescence detector was recorded for all particles but it contained only baseline noise without a true incandescence peak for most PALAS soot particles. Thus failure of signal triggering or any other issue with the data acquisition software can be excluded."

Their conclusion that the SP2 is "essentially unable to detect PALAS soot particles with the incandescence detector" is too strong, figures 2 and 3 show the larger particles are detectable by the incandescence detectors, just with low efficiency. The title of the paper is similarly too strongly worded, the SP2 does detect PALAS soot particles, but not well.
The statement in the conclusions reads now: *"This study reveals that the SP2 is unable to reliably detect PALAS soot particles with the incandescence detector, even if they contain substantially more BC mass than the typical lower detection limit of the SP2."*
The title reads now: *"Technical Note: The single particle soot photometer fails to reliably detect PALAS soot nanoparticles"*

Technical corrections

The authors make several references to the fact that their result is "surprising" or "unexpected". While this may be true, the way in which it is currently phrase make this sound like their opinion, rather than a logical conclusion based on previous literature. They should revise their use of these words to make the statements look more based on verifiable facts than opinions.
That is exactly what we tried to express. Previous literature (e.g. Bladh et al., 2011) on pulsed laser-induced incandescence shows that morphology effects must be expected for the lower detection limit of the SP2. However, this potential issue has not been addressed in previous literature on the continuous-wave laser-induced incandescence method applied in the SP2. Instead the lower detection limit at a certain laser power was simply considered to be determined by the total BC mass in a particle. Several sentences throughout the manuscript have been adapted. To give an example from the abstract: *"Previous knowledge from pulsed laser-induced incandescence indicated that particle morphology might have an effect on the SP2's lower detection limit, however, an*

increase of the lower detection limit by a factor of ~5–10, as reported here for PALAS soot, was not expected."

4906 line 6 several tenths of a femtogram
Done.

4907 line 2 climatic not climate
Adapted.

4907 line 5 not just organic carbon, organic aerosol. May be best to just use "nonrefractory aerosol"
Not changed. Dust is a refractory aerosol component which can interfere with light absorption measurements.

4907 line 7-8 Please rewrite these 2 sentences into 1, replace "few years ago" with "recently"
Done.

4907 line 20 Remove "to our knowledge" as this is unnecessary, and sounds like you are speaking for people who are not coauthors of this paper
Done.

4907 line 24 "we stumbled across" sounds too informal, please rephrase this sentence
Done.

4909 line 4 – 12 Please let the reader know whether or not this is the standard SP2 setup and if not what is different.
Done.

Reference

Schwarz, J. P., Spackman, J. R., Gao, R. S., Perring, A. E., Cross, E., Onasch, T. B., Ahern, A., Wrobel, W., Davidovits, P., Olfert, J., Dubey, M. K., Mazzoleni, C., and Fahey, D. W.: The Detection Efficiency of the Single Particle Soot Photometer, Aerosol Science and Technology, 44, 612-628, 10.1080/02786826.2010.481298, 2010.

Bladh, H., Johnsson, J., Rissler, J., Abdulhamid, H., Olofsson, N.-E., Sanati, M., Pagels, J., and Bengtsson, P.-E.: Influence of soot particle aggregation on time-resolved laser-induced incandescence signals. Appl. Phys. B, 104, 331-341, 2011.