Before giving specific replies to the reviews it is worthwhile to reiterate the focus of the manuscript. The Crist campaign was an investigation of in-plume reduction of RGM - an attempt to establish whether such reduction is occurring and if so, the rate of such reduction. It is worth noting that, to the best of our knowledge, prior to this work there have been no published reports that identify the chemical speciation of RGM in flue gas. This is a critical issue in understanding the mechanism of mercury oxidation in coal-fired power plants (CFPPs) and in modeling any subsequent reduction chemistry in the emitted plume. Although preliminary in nature, our work contributes to the understanding of the speciation of RGM in stack gas and plumes. We would emphasize that this work is not an attempt to address mercury deposition in Florida. Although CFPP Crist is located in Florida this is a study on the chemistry of mercury in CFPP flue gas. We've noted the uncertainties associated with a preliminary study. We show supplemental data that demonstrates a great improvement in the quality of Programable Thermal Dissociation (PTD) profiles. If we were given an opportunity to repeat the Crist experiment we believe we could produce more definitive data. Unfortunately, we will not have that opportunity. This was a unique field experiment and the results are highly relevant to anyone who is attempting to study the oxidation chemistry of mercury in combustion environments, or examining potential mechanisms of in-plume reduction. For example, in the supplemental material we show a PTD profile of an atmospheric sample of unidentified RGM that dissociates at much lower temperature than $HgCl_2$. The presence of such a species in a stack plume could help explain homogeneous gas phase reduction of RGM. In contrast, because of the stability of $HgCl_2$ it is difficult to propose any realistic chemical or photolytic routes to homogeneous gas phase reduction. We will emphasize some of these points again in specific replies to the points raised by each review.

In addition we have now become aware of several papers that have addressed the use of programmable thermal dissociation or desorption to attempt to speciate mercury in solids. One issue in attempting to calibrate the PTD technique as utilized here for gas phase sampling is that the mercury halides are the only candidate RGM species that have appreciable vapor pressures. Although these papers address a somewhat different issue, the analysis of solids, as opposed to attempting to sample and speciate gas phase RGM they clearly require citation. In addition they provide useful information on the thermal dissociation and desorption properties of several mercury compounds. The two most relevant citations are:

Feng X, Lu JY, Gregoire DC, Hao Y, Banic CM, Schroeder WH. Analysis of inorganic mercury species associated with airborne particulate matter/ aerosols: method development. Anal Bional Chem 2004;380:683–9.

Lopez-Anton, M. A.; Yang, Y.; Ron, P.; Maroto-Valer, M. M. Analysis of mercury species present during coal combustion by thermal desorption. Fuel 2010, 89, 629–634.

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Replies to specific review points (original reviewer comments in bold italics)
Review 1:

It addresses an important issue (identification of oxidized Hg compounds in power plants) but arrives at no conclusions.

We list two important conclusions in the "conclusions" section.

a)Thermal dissociation profiles for RGM were obtained in both stack and in-plume samples that suggest that it is possible to track a specific chemical form of RGM from the stack and follow its evolution in the stack plume.
b)The PTD profiles of the stack and plume samples are consistent with $HgCl_2$ being the chemical form of the sampled RGM.

In section 3.2 we noted: "Given the large uncertainty in the dilution ratios these efficiencies suggest that the RGM sampled in-plume is consistent with the levels measured by the CEMS instrument in the stack. This, together with the PTD profiles of the stack and plume samples shown in Fig. 6 suggests that it is possible to use PTD to measure a component of RGM in the stack and follow its evolution in the plume."

In section 3.3 we noted: "One possible explanation of the observations of Edgerton et al. (2006) would be a component of the RGM that undergoes slow thermal decomposition at ambient temperatures. No evidence for a significant component of the RGM sample that has a significantly lower decomposition temperature than $HgCl_2$ was observed. "

These are all significant conclusions, however we plan to strengthen the conclusions section noting that "the RGM sampled in-plume is consistent with the levels measured by the CEMS instrument in the stack", and that "there is no evidence for a component of the RGM sample that has a significantly lower decomposition temperature than $HgCl_2$ "

We propose to add the following to the abstract:
Thermal dissociation profiles for RGM were obtained in both stack and in-plume samples that suggest that it is possible to track a specific chemical form of RGM from the stack and follow its evolution in the stack plume. The PTD profiles of the stack and plume samples are consistent with $HgCl_2$ being the chemical form of the sampled RGM.

The PTD method, as presented in this manuscript, cannot be used to

qualitatively identify RGM compounds, nor can it be used to quantify RGM.

Although PTD cannot be used to qualitatively identify RGM it can indicate that a sample is consistent with or not consistent with an RGM compound. We've used this sampling from the gas phase and as a result the only available gas-based standards are the mercuric halides. These are the only mercury compounds with an appreciable vapor pressure. We have shown supplemental data of atmospheric samples of RGM. One of the samples shows a peak decomposition temperature below 150 C that is clearly not consistent with $HgCl_2$ or $HgBr_2$. While we have greatly improved the quality and reproducibility of our PTD profiles, we would suggest that the data obtained during the Crist campaign, and shown in Figs 4-7 indicates that the RGM sampled, both in stack in plume, are consistent with identifying the RGM as $HgCl_2$. $HgBr_2$ is not an option because of the absence of a significant amount of bromine in the coal.

PTD profiles of a variety of more stable mercury compounds such as HgO and $HgSO_4$ are shown in the papers by Feng et al. and Lopez-Anton et al. referenced above. These are not directly comparable because they use solids but they show that these compounds dissociate at much higher temperatures than $HgCl_2$.

Review 2

My first impression of the ms is that it is really rather long-winded and in the end also rather inconclusive. The final sentence of the abstract illustrates my point, "The PTD profiles from these samples were compared with PTD profiles of HgCl2." Yes, and …?

As noted above we plan to add the following to the abstract.
"Thermal dissociation profiles for RGM were obtained in both stack and in-plume samples that suggest that it is possible to track a specific chemical form of RGM from the stack and follow its evolution in the stack plume. The PTD profiles of the stack and plume samples are consistent with $HgCl_2$ being the chemical form of the sampled RGM."

We will also strengthen the conclusions section.

The ms describes in a lot of detail a method for collecting RGM, in this case in stack plumes, with the intention of then using programmable thermal desorption of the sample to obtain a desorption profile which could be compared to the desorption profile of a number of oxidized Hg compounds. However the description of the sampling and results is confusing, it is difficult to keep in mind whether the denuders are quartz or pyrex, etched or unetched, and which were used where. The thesis also seems to suggest that uncoated denuders and pyrex tubes have very different desorption profiles for HgCl2 (pp 227-228), but there seems to be no

mention of this in the manuscript. However it may just be the rather confused presentation that means I missed that part.

There may be confusion here because the Donohoue thesis uses the term “denuders” to describe “annular denuders” as manufactured by URG and “pyrex tube” to refer to tubular denuders. All the work reported here used tubular denuders i.e quartz or pyrex tubes with no inner annulus. It is clear that we need to make this distinction much apparent, particularly because the terms “denuder” and “annular denuder (URG version)” may have become synonymous in the mercury community.

In section 3.3 the authors state that the PTD profiles of HgCl2 and HgBr2 are identical on uncoated denuders, but they are not in figure 7.23 of the thesis, and p 231 states quite clearly that they are different. Also in section 3.3 the authors say that HgO desorbs at a higher temperature than HgCl2. I assume this is on uncoated denuders because in Donohoue's thesis the opposite is seen for KCl coated denuders. The desorption profiles from uncoated denuders in Donohoue's thesis seem to differ significantly from those in the manuscript. In the figures in the thesis it seems that the onset of HgCl2 desorption (on uncoated denuders) is around 200°C whereas in the article the authors state that there is significant desorption from (on uncoated denuders) is around 200°C whereas in the article the authors state that there is significant desorption from 100°C.”

The work reported in the thesis of Donohoue was a limited study with almost all of the work performed on KCl coated annular denuders. In contrast, all the work at Plant Crist utilized uncoated tubular denuders. As the current manuscript makes clear, issues related to the large temperature differential within the oven, the limited reproducibility of temperature ramps, and issues related to flow direction affected the reproducibility and shape of the PTD profiles reported in the manuscript. These issues also affected the work reported by Donohoue on the PTD’s obtained using KCl coated annular denuders since that work was done well before the Crist campaign. We have not attempted to reproduce the work in the Donohoue thesis but, based on our current (unpublished) work on both KCl coated and uncoated tubular denuders we would conclude that the PTD profiles of $HgBr_2$ and $HgCl_2$ are identical. The 10 C differences in peak decomposition temperature in fig 7.24 in the Donohue thesis are, we now believe, due to irreproducibility in oven ramps. The three HgO profiles reported by Donohoue were based on RGM loads of 470-760 pg, more than an order of magnitude lower than those of $HgBr_2$ and $HgCl_2$ and were most likely due to contamination in the Teflon tubing used in the experiments.

The ms is often really quite confusing to read, and it is possible that some of my comments are out of place as a result of this. There are very few

references, and not one refers to the general problem of Hg in the environment (or the forthcoming UNEP meeting to discuss a legally binding agreement). One of the main references is a PhD thesis, which I managed to find online, but given that theses are long it was not always obvious where the reader was supposed to find the detail referred to in the article. One other reference which was quoted a lot, Landis et al., 2009, was presented at Air Quality VII, in Washington, and I failed to find a copy on the internet. The manuscript describes a lot of work, contains a lot of technical detail (possibly not of very general interest), is not very clearly written, and concludes that in all probability the RGM emitted from CFFPs is in the form of HgCl2. I am not really sure that this manuscript is suitable for ACP. Certainly I would suggest a major rewrite and and resubmission before even considering publishing in ACPD.

We do not think that references that deal with mercury deposition in Florida, or artifacts of quantitative RGM sampling on KCl coated annular denuders are appropriate in this manuscript given its focus. As we note above, it seems clear that some of the reviewer's confusion stems from the differences between the use of annular and tubular denuders and issues in the results reported in the thesis of Donohoue. We plan to add text to address these issues in a revised manuscript. The references focus on Hg and the speciation of RGM in combustion environments since this is the topic of the manuscript although, as noted above, we were unaware of PTD work on solid mercury compounds and this will be addressed in a revised manuscript. This paper is a little different from typical ACPD papers since it focuses very specifically on RGM in CFPPs and their plumes. However the paper was submitted to a special issue on presentations from 10th International Conference on Mercury as a Global Pollutant.