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Reply to Gulson's comments on 'Tracing changes in atmospheric sources of lead contamination using lead isotopic compositions in Australian red wine'

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We thank Emeritus Professor Gulson for bringing to the readers' attention our recent paper 'Tracing changes in atmospheric sources of lead contamination using lead isotopic compositions in Australian red wine' (Kristensen et al., 2016).

The data presented in our study are supported and cross-tested using a variety of independent samples and measures, all of which reflect the dominant atmospheric source (petrol lead) and its reduction and removal from use since the 1970s. To this end, our study relies on:

(1) independently calculated total lead emissions derived from petrol sales data (Kristensen, 2015);
(2) time-matched air filter samples from Adelaide, the closest city with substantial lead in air emissions from petrol;
(3) assessment of local soils – both natural (at depth) and surface to reflect possible sources and external inputs of lead;
(4) strontium isotopes to evaluate the uptake of metals from local soils;
(5) multiple analyses of the same wine;
(6) consistent, reliable and published verification of the isotope analyses by the National Measurement Institute (NMI).

In contrast to assumptions or untested assertions presented by Gulson, our reply to his letter, along with our original study, relies on data generated to specifically to assess the sources of contamination in the wine samples analysed. We did not use data derived from *other* wine analysis, which have their own confounding factors.

We are perplexed as to why Gulson questions the quality of the National Measurement Institute's ICP-MS data used in Kristensen et al. (2016),given he recently put his name to a paper (Wu et al., 2016a, b) that uses lead isotope composition data collected at the same laboratory with the same ICP-MS. The analyses conducted in Wu et al. (2016a) involved lead extraction and analysis of a 150-year lichen and fungi record from Central and Southern Victoria, Australia. Like the wine anlaysed in our study, these too are also organic matrices.

Overall, we contend that no study is 'perfect' but we have taken care to limit potential confounders in our study such that the data are fit for purpose. We assert that the multitude of evidence in our study corresponds to the known and anticipated effect of removing lead in petrol from the environment: total lead in air values fell, which was also associated with a clear shift in the isotopic composition of environmental samples reflecting the removal of a dominant source of atmospheric contamination (Facchetti, 1989; Marx et al., 2010; McConnell et al., 2014; Serrano et al., 2016; Wu et al., 2016a, b).

In regards to the specific concerns raised by Gulson, we address

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each of his points to demonstrate the reliability of the data used in Kristensen et al. (2016) and to show that the conclusions presented are the most logical in light of all the evidence compiled. Information on vintages, vineyards and number of wine and soil samples is provided in the supplementary tables S1 and S3 and in Table 4 of Kristensen et al. (2016).

Gulson's point 1 suggests lead in wine (including port) is sourced from the vinification process such as the plumbing, giving rise to a uniform lead isotopic composition. We do not discount the potential for other sources of lead to have contaminated wines, including those from the vinification process. However, the overall changing pattern of lead concentration and isotopic compositions not only coincide with leaded petrol emissions and available lead in air filter measurements, but also mirror other environmental proxies from Australia including peat bogs (Marx et al., 2010) and lichens and fungi (Wu et al., 2016a, b).

The study benefited from the fact that two vineyards were able to provide a large set of samples (n = 35, 58% of the sample set, Winery A and B). Analysis of these samples revealed that within a single winery, where no reported changes to the wine-making apparatus had occurred, there was both declining lead concentrations (Fig. 1) and changing lead isotopic compositions (Fig. 2).

We also note that in Fig. 1, other elemental concentrations have remained largely constant during the period of the atmospheric lead reductions, including arsenic, which was used previously in lead arsenate agricultural sprays (see Gulson et al., 1981). The identified changes in atmospheric lead concentration and its composition in our study correspond remarkably well to the anticipated effect of removing petrol lead from the environment in Australia. Equivalent environmental responses have been identified in other similar international studies of wine (Médina et al., 2000), atmospheric lead compositions (Facchetti, 1989), blood lead levels (Annest et al., 1983; Brunekreef, 1984), and numerous environmental proxy studies (Barbante et al., 1997; Inoue and Tanimizu, 2008; Kelly et al., 2009; Flegal et al., 2010; Hosono et al., 2010; Marx et al., 2010; Larsen et al., 2012; Deljanin et al., 2014; Lee et al., 2014).

A review of all the wine samples analysed in the study shows clearly an increase in the average decadal wine lead concentration from the 1960s–1970s. This rise corresponds to the rise in the sale of leaded petrol over that time period (Kristensen, 2015). The decline in wine lead concentrations coincides with the implementation of unleaded petrol in the mid-1980s and the introduction of regulations limiting the allowable concentrations of lead in petrol in South Australia in the mid-1990s (Kristensen, 2015; Kristensen et al., 2016).

Gulson's point 2 suggests that variations measured in lead isotopic compositions in Sydney petrol should be identifiable in the wine from South Australia. We note that petrol sold in Adelaide was sourced from the Port Stanvac refinery (Gulson et al., 1981). Moreover, Gulson et al. (1981) states the refinery used 'mainly Broken Hill and Mount Isa lead with some Canadian lead' while the petrol used in Sydney came from Clyde and Kurnell refineries (Australian Institute of Petroleum (AIP) 1985). While Gulson does not specify which Canadian ore was used, lead isotopic compositions of Canadian ore have generally more radiogenic compositions than Broken Hill and Mount Isa ore (Sangster et al., 2000). However, there is no reason to rationalise that these refineries all sourced lead from the same locations at the same time. Previously Gulson and a representative from Shell Petroleum stated 'any old lead from any old source' was added to petrol (Carrass and Johnson, 1983). Moreover, the lead isotopic compositions of aerosols collected at the same time in Sydney and Adelaide differed from each other (i.e. $^{206}Pb/^{204}Pb$ for Sydney was 16.45 and for Adelaide it was 16.29) (Bollhöfer and Rosman, 2000). Comparison of lead isotopic compositions of average monthly air filters from both Adelaide and Sydney show there is a marked difference across multiple years (Fig. 3).

In regard to petrol lead sources, Gulson adduces no new data to support his argument and anticipates that his data from Sydney is sufficiently explanatory for Adelaide. Although we stated in our article that the dominant source of lead used in petrol was from Broken Hill/Mount Isa lead ores, the authors have acknowledged previously that various sources of lead have been used in petrol (Kristensen, 2015, 2016). However, in our study we preferred to rely on locally collected environmental data, including air filters to ascertain the *local* relationship between air lead and that found in wine. Air filters are a reliable strong predictor for lead sources used locally in petrol and the resulting atmospheric lead composition (Facchetti, 1989; Chiaradia et al., 1997; Bollhöfer and Rosman, 2000; Wu et al., 2016a, b). Therefore, analysis of air filters from Adelaide provided a more accurate assessment of local atmospheric

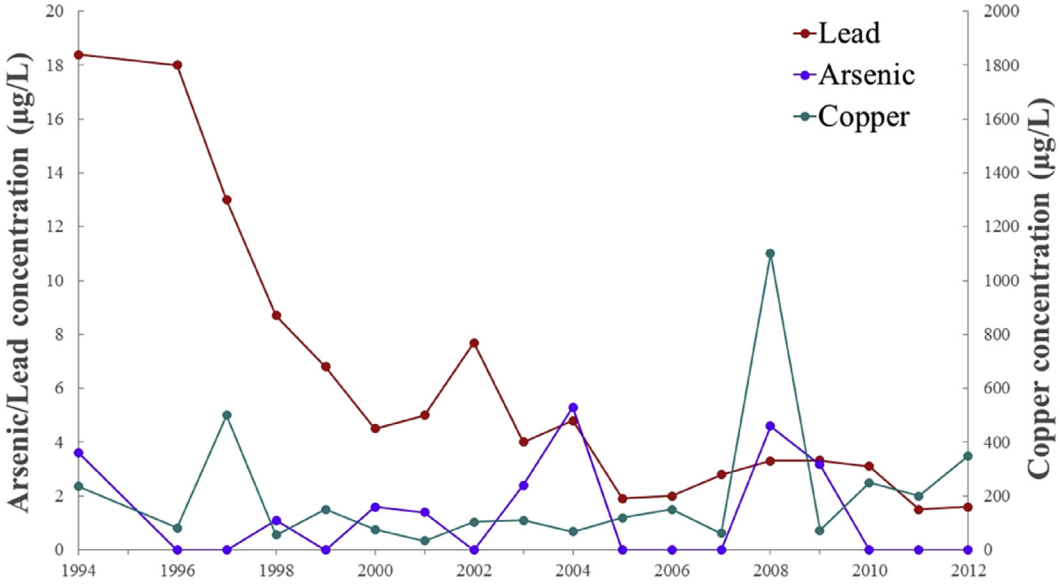

Fig. 1. Copper, arsenic and lead concentrations of wine from a single winery (Winery A from Kristensen et al. (2016)).