Reassessing atmospheric deposition rates of polycyclic aromatic compounds to the Athabasca River (Alberta, Canada) watershed from oil sands related activities

Sierra Rayne [a] *

Keywords: *polycyclic aromatic compounds, atmospheric deposition, oil sands, Athabasca River*

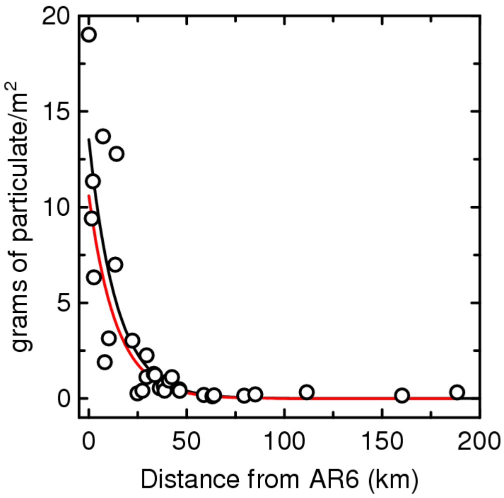
Abstract: *In an earlier study (Kelly et al., PNAS, 2009, 106, 22346-22351), spatial patterns for the concentrations of particulate matter, particulate polycyclic aromatic compounds (PAC), and dissolved PAC in the snowpack around the Syncrude and Suncor upgrader facilities near the oil sands development at Fort McMurray, Alberta, Canada were determined. A reassessment of the datasets employed in this work yields significantly different deposition rates (by up to an order of magnitude) than reported, as well as reveals substantial sensitivity in deposition rate estimates depending on a range of equally valid regression types chosen. A high degree of uncertainty remains with regard to the quantities of particulate matter and PAC being deposited in the Athabasca River watershed from oil sands related activities.*

In their article, Kelly et al. [1] report on the spatial patterns for concentrations of particulate matter, particulate polycyclic aromatic compounds (PAC), and dissolved PAC in the snowpack around the Syncrude and Suncor upgrader facilities near the oil sands development at Fort McMurray, Alberta, Canada. From their sampling data and subsequent analysis, estimates of total loadings of these contaminants to snowpack over a 4 month period in 2008 were developed for a radius of 50 km around the oil sands upgrading facilities.

Based on their data, the authors conduct negative exponential regression analysis and obtain the following equation describing the relationship between distance from the upgrading facilities and concentration of particulate matter: particulates=$10.6\times e^{-0.0714x}$ g/m^2 where x is the distance in km from site AR6. In ref. [1], the number of samples is given as 23. A data request from the authors of ref. [1] for their data behind Figure S2 in this work obtained a spreadsheet with 31 datapoints for each of the three variables. It is clear from Figure S2(a) in ref. [1] that this published figure also has 31 datapoints, of which 23 datapoints are within a 50 km radius of the upgraders.

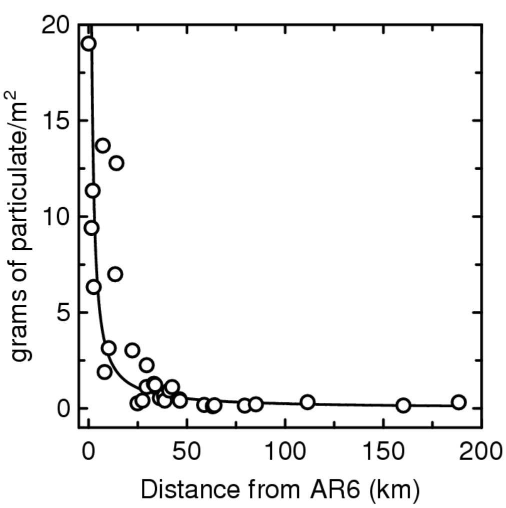
However, Fig. S2(a) in ref. [1] does not show an exponential regression with the equation y=$10.6\times e^{-0.0714x}$, as such an equation would have a y-intercept of 10.6. Instead, Fig. S2(a) in ref. [1] shows a regression equation with a y-intercept of between 13 and 14. In the figure below is shown a negative exponential regression with the use of either 23 or 31 datapoints (as obtained from Kelly et al. [1]) from Fig. S2(a) as a black line (y=$13.5\times e^{-0.0707x}$; r=0.844; both n=23 and n=31 yield the same regression equation, as the datapoints at >50 km distance play negligible role in the regression constant fitting), and the authors' claimed regression fit with an equation y=$10.6\times e^{-0.0714x}$ as a red line.

*Corresponding author: Tel/Fax: 1.250.487.0166 Email: sierra.rayne@live.co.uk. [a] Chemologica Research, PO Box 74, 318 Rose Street, Mortlach, Saskatchewan, Canada, S0H 3E0.

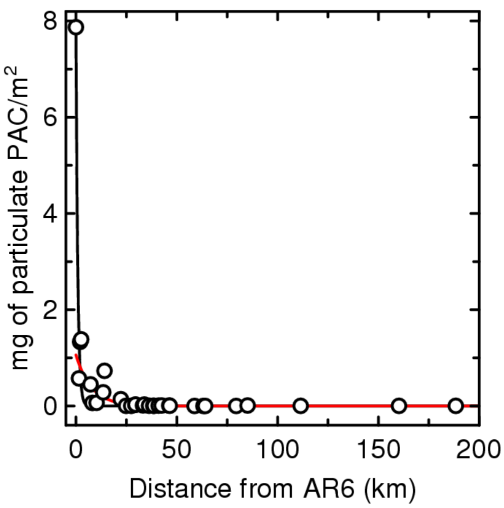


Using the regression equation given by the authors (y=10.6×e$^{-0.0714x}$) and integrating the particulate concentration versus distance relationship to 50 km radius yields a total estimated deposition of 11,400 tons, equivalent to the value of 11,400 tons stated in ref. [1]. On the other hand, using the regression equation obtained from an analysis of the authors' own data (black line in the figure above; y=13.5×e$^{-0.0707x}$), which appears to match the regression equation shown in Fig. S2(a) of ref. [1], yields an integrated total deposition of 14,800 tons (i.e., 30% higher than the estimate in ref. [1]).

An equally plausible fit (r=0.839) of the data is shown in the figure below, using the equation y=31.15×x$^{-1.048}$. When integrated, this fit yields a total particulate deposition of 8,400 tons (i.e., 26% lower than the estimate in ref. [1]). Based on the significant sensitivity of loadings estimates to the type of regression equation chosen, quoting deposition estimates to 3 significant figures (as was done in ref. [1]) is not valid. A reasonable particulate loadings estimate range is probably best assigned as between 8,000 and 15,000 tons.

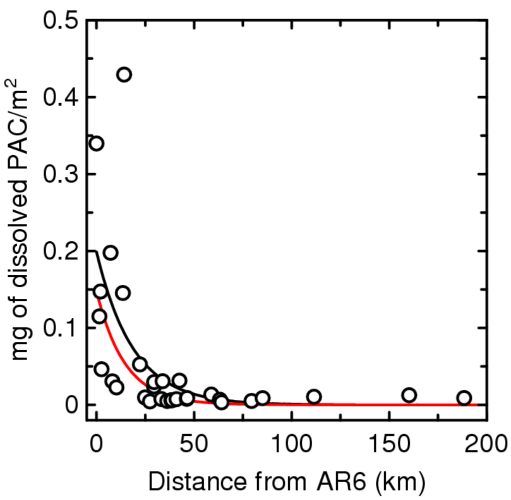


Issues also exist with the analysis of particulate PAC (Fig. S2(b)) and dissolved PAC (Fig. S2(c)) loadings estimates. Kelly et al. [1] report the following particulate PAC concentration versus distance relationship, yet their own graph (Fig. S2(b) in ref. [1]) shows a regression line with a y-intercept of about 8: y=1.06×e$^{-0.130x}$. When either all 31 datapoints are regressed using a negative single exponential fit, or just the n=23 at <50 km distance from the upgraders, the following equation is obtained (shown as a black line in the figure below, with the claimed in-text regression fit from ref. [1] shown as a red line in this figure): y=$7.81\times e^{-1.12x}$ (r=0.976).



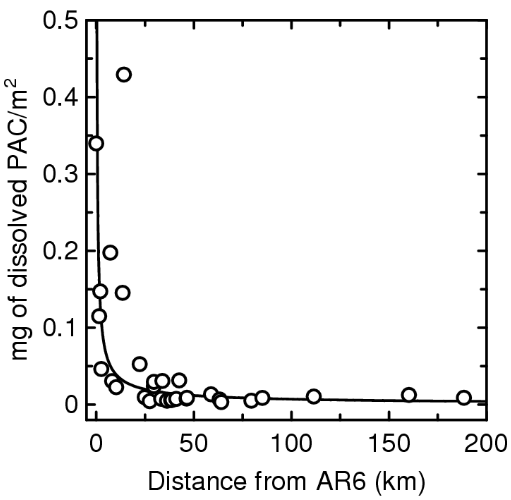
If the quoted Kelly et al. [1] regression equation for particulate PAC (y=$1.06\times e^{-0.130x}$) is integrated between 0 and 50 km, a total particulate PAC deposition of 391 kg is obtained, equivalent to what the authors quote in ref. [1]. However, when the negative single exponential regression that actually matches the data in Fig. S2(b) is integrated, a total particulate PAC deposition of 39 kg is obtained (i.e., 90% lower than the estimate in ref. [1]).

For dissolved PAC (Fig. S2(c) in ref. [1]), Kelly et al. quote the following regression equation in-text: y=$0.148\times e^{-0.0691x}$. This does not match the regression equation shown in the authors' own plot (Fig. S2(c)). Instead, when either all datapoints are regressed using a negative single exponential function, or just the n=23 datapoints at <50 km distance from the upgrader, the following equation is obtained (shown as a black line in the figure below, with the claimed in-text regression fit from ref. [1] shown as a red line in this figure): y=$0.199\times e^{-0.0531x}$ (r=0.624).



When the quoted Kelly et al. [1] regression equation for dissolved PAC (y=$0.148\times e^{-0.0691x}$) is integrated between 0 and 50 km, a total dissolved PAC deposition of 168 kg is obtained, equivalent to what the authors quote in ref. [1]. However, when the negative single exponential regression that actually matches the data in Fig. S2(b) is integrated, a total particulate PAC deposition of 332 kg is obtained (i.e., 98% higher than the estimate in ref. [1]).

A more plausible fit (r=0.693) of the dissolved PAC data is shown in the figure below, using the equation $y=0.221\times x^{-0.747}$. When integrated, this fit yields a total particulate deposition of 152 kg between 0 and 50 km radius around the upgraders.



In conclusion, the source of the in-text quoted regression equations used to obtain 0-50 km integrated deposition quantities of particulate matter, particulate PAC, and dissolved PAC in the snowpack around the Syncrude and Suncor upgrader facilities near the oil sands development at Fort MacMurray, Alberta, Canada from Kelly et al. [1] is not clear. An analysis of the authors' own data yields significantly different deposition rates (by up to an order of magnitude), as well as reveals substantial sensitivity in deposition rate estimates depending on a range of equally valid regression types chosen.

Acknowledgements

Thanks are extended to KF and DD for project management assistance.

References

[1] Kelly, E.N., Short, J.W., Schindler, D.W., Hodson, P.V., Ma, M., Kwan, A.K., Fortin, B.L., Oil sands development contributes polycyclic aromatic compounds to the Athabasca River and its tributaries, Proceedings of the National Academy of Sciences USA, 2009, 106, 22346-22351.