

Interactive comment on “Principal component analysis of summertime ground site measurements in the Athabasca oil sands: Sources of IVOCs” by Travis W. Tokarek et al.

Anonymous Referee #1

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This manuscript measured a variety of air pollutants at a surface site in the oil sands region in summer 2013. PCA approach was used to elucidate major sources of these air pollutants, in particular, IVOCs. Using the 95% cumulative percentage of variance criterion, ten components were categorized, among which 3 components correlated with IVOCs, most likely related to the unearthing and processing of raw bitumen. The authors also found the association of secondary variables with the primary components, implying rapid formation of these secondary products on a time scale that is similar to the transit time of the pollutants to the measurement site. The study was specifically carried out in an oil sand region, which constrained the extension of the implication of the findings to other regions. The PCA with different number of sources was tested,

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and the identification of source types was discussed and elucidated in detail. Though this manuscript was for a special issue of ACP, this manuscript still needs significant improvement, and could only be considered for potential publication after the following major concerns are well addressed. 1) The aim of this study was to identify IVOC sources. However, none of the peaks of IVOC species in Ion Chromatograms was identified, which subsequently biased or even wronged the identification of the IVOC sources. 2) It is doubtful that CO was mainly generated from VOC oxidation given many industrial sources in the oil sand region. 3) The criteria for the degree of correlations, i.e., correlation coefficient r value, are unclear. $r = 0.3$ indicated very poor correlation to me. Specific comments: 1. Page 9, Figure 2. The gray area showed unsolved HCs in the volatility range of C11-C17 with saturation vapor concentration from $105 \mu\text{g m}^{-3} < C^* < 107 \mu\text{g m}^{-3}$. It is not clear how the retention time for C11, C12, ..., C16 was obtained in the figure. The marked retention time for C11-C16 n-alkanes is actually doubtful, because for n-alkanes IVOCs, the distance between C11 and C12, C12-C13, C13-C14, ... C15-C16 in the chromatograms should be generally equal. Also, their retention time in Figure 2 seems too high (25 min later) as they usually appear at ~ 10 -15 mins (of course it depends on the methods and columns used). Furthermore, why were some IVOC species not identified (even could not be quantified) when this study was designed because the focus of this manuscript is about IVOC sources? If the focus was based on something unknown, the speculation could be very wrong. In this study, the headspace sample of bitumen indeed showed an unsolved signal in the IVOC range, but this does not mean bitumen is definitely the IVOC source in this study because n-alkanes IVOCs have many other sources such as vehicular emissions, biogenic IVOCs (e.g. sesquiterpenes) and petroleum enterprises. In fact, there are mature analytical methods such as TAG-GC-ToF-MS for gas- and particle-phase IVOCs, SVOCs and SOA tracers. 2. I have to admit that the PCA results in this study were quite impressive no matter how many factors were extracted (5-11 factors) because it is common that PCA often gives collocated factors and it is very difficult to identify 10 or above individual sources with this method, especially when 22-28 variables were input. Certainly

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more than 200 samples as input could enhance the PCA extraction. 3. Page 12, Table 3. 4 AVOC and 3 BVOC species were quantified. What were the reasons to select these specific VOC species in this study, due to the limit of GC-ITMS or selection of tracers? In particular, isoprene was not measured (used) in this study as its level in the atmosphere is usually much higher than other BVOCs. 4. Lines 284-289 stated that CH₄ and CO₂ originated from distinct sources while both correlated well with Factor 6 in Table 5, indicating their similar sources/patterns. They are contradictory. Please clarify it. 5. Table 5 claims that coefficients with Pearson correlation coefficients $r > 0.3$ are interpreted as being moderately or strongly associated with a component, which I do not agree. What are the criteria to select $r > 0.3$ to indicate moderate or strong association? To me, r value around 0.3 means very poor correlation. At least r value should be > 0.5 to indicate somewhat correlations. 6. Page 24, Table 6. Component 5 was identified as “surface exposed bitumen and hot-water based bitumen extraction”. This is only based on the headspace sample of bitumen without any identification of IVOC species. Could it be other sources? If TAG-GC-ToF-MS was used, this source could be better identified. Furthermore, IVOCs correlated well with LO-OOA (Table 5), implying that some IVOCs might be secondarily formed or the PCA results were collocated. Please comment on these. 7. Page 24, Table 6. Component 9 “enhancement of CO” was categorized as “VOC oxidation”. This is questionable. Why? It is apparent that on some days the nighttime CO was quite high, which should not be formed via VOC oxidation due to the fact that nighttime VOC oxidation chemistry is weaker than daytime photochemistry. Moreover, if CO was from VOC oxidation, it would destroy the correlations among VOCs (due to various photochemical reactivity of VOC species), leading to poor factor loadings, while the correlations among AVOCs and BVOCs were strong in Table 5. Though CO did not have correlations with other combustion tracers, could it be caused by the weakness of the PCA method, or the correlation of CO with other combustion tracers is the “must” for the identification of a combustion source? 8. Page 25, Figure 4. (B) (component 2) vehicles emit aromatics and n-alkanes but component 2 did not in Table 5. (D) (component 4) Upgrader facilities emitted TS and

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SO₂ only? There was flare stack. Were there no VOC emissions (Table 5)? 9. Page 26, lines 382-385. Not true. $r=0.27$ only for Ox in component 5! Moreover, why didn't Ox have high correlations with any variables in Table 7? 10. Page 43, lines 718-720. Could any measurements be done downwind to verify this hypothesis? 11. Page 44, lines 740-742. This also fits CO. But no discussion at all. 12. Page 44, lines 749-750. TAG-GC-ToF-MS technique has already been applied to identify and quantify many IVOC species. Many papers have been published in the society. In the "Supplement" document 13. Lines 54-55. Again, what are the selection criteria for these specific VOCs? Can GC-ITMS measure more VOCs such as C₂-C₁₀ HCs and so on for better source identification? 14. Line 330. No solid evidence for this. 15. Figs S2-S4, S7-S11 caption: Table 4 should be Table 5 in the text? 16. Figure S5 caption: Table 4 should be other Table in the text? 17. Figure S6 caption: Table 4 should be Table 5 in the text?

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