# Analytical Insights into Thirteen OPE Variables

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**Abstract**

There are many different parameters that play an integral roll in predictive Organophosphate Esters (OPEs) modelling. Much of this research has revolved around using various physical and chemical properties to determine the Overall Persistance(POV) and Long-Range Transport Potential (LRTP) of these organic chemicals at a screening. While these models have been incredibly beneficial, I wanted to look for ways to better help the predictive patterning of OPEs.To do this, some questions this paper looked to answer was 1) is there a correlation between any of the variables present? 2) How can these relationships (if any) help to improve predictability of OPEs. With that being said, this paper looked to create a basis point for these predictive tools to better understand the relationships between all these parameters. This paper analyzed all the current known available data about each of these parameters for 10 known native OPEs (TPP,TMTP,TPTP,TEP,TPrP,TBP,TBEP,EHDP,TCEP,TCPP) and compared them to one another to see if any sort of relationship can be found. The 14 parameters looked at include: mass, Characteristic Travel Distance in air (CTD_a), Characteristic Travel Distance in water (CTD_w), POV_air, POV_water, Number of Carbon units (C), Number of Hydrogen units(H), Number of Chlorine units(Cl), Number of Oxygen units(O), number of Phosphorus(Ph), air-water coefficient from the literature(KAW), octanol-water coefficient from the literature(KOW), and octanol-air coefficient from

the literature(KOA), Retention Time (RT). Using the pearson test, the most statistically signiifcant results include the: POV_w-CTD_w pair,CTD_a-KOA,H-KOA , KAW-POV_a at higher masses, KOW-RT at lower masses,and KOA-mass, they each had values of 0.999,-0.944,0.952,-0.997,0.952, and 0.910 respectively. These relationships are incredibly important because it aids in giving valuable inisght when it comes to predicting the behavior of similar OPEs. Some noteworthy relationships that may come in aid is the strong correlation between KOA values of OPEs and their respective masses. This relationship can help help predict the extent of the LRTP of OPEs.

# Chapter 1: Introduction The History of OPEs

Organophosphate Esters (OPEs) have been found all across the world. In food webs through bioaccumulation(Du et al., 2019), in sediments(Chokwe et al., 2020), in people via absorption, in the air and in the waters up north in the Arctic through various modes of transport (Castro-Jiménez et al., 2014) (Möller et al., 2011) (Sühring et al., 2016)(Salamova et al., 2013) (Salamova et al., 2013) (Luo et al., 2016) (Lai et al., 2015). Recent research suggests these OPEs have persistent organic pollutant (POPs)-like characteristics (Guigueno & Fernie, 2017). While on the human side, studies have shown that some OPEs can potentially be: mutagenic, carcinogenic, genotoxic and neurotoxic (Zhao et al., 2020). OPEs have the potential to be harmful, also ever since PBDEs were banned, the consumption of these dangerous chemicals has greatly increased (Chupeau et al., 2020). Originally, due to a combination of physio-chemical property assessments and a lack of observational data, OPEs were thought to have been a safe substitute. According to the Danish EPA in the EU Risk Assessment they found that TPP (an OPE) didn't appear to have a greater negative impact than the other flame retardants (FRs) they were using at the time (Pakalin et al., 2007). Other research has also used this same argument, citing that OPEs do not meet the criteria listed out by the Stockholm Convention to be as harmful as the now restricted/banned polybrominated diphenyl ethers (PBDEs) that they are replacing(Fiedler et al., 2019). Under the Stockholm convention there are 4 key criteria listed to be qualified as persistent organic pollutants (POPs) they are: 1) persistence potential i.e persists in the environment and is resistant to degradation, 2) bioaccumulation potential i.e each chemical's potential to accumulate within various organisms, 3) their long-range transport potential (LRTP) i.e the chemical's ability to propagate itself beyond local release locations and 4) Toxicity (Fiedler et al., 2019). The criterion is determined by both observational data and modelling tools. At the time of writing there are modelling tools that underestimate the POP like capabilities of OPEs (Sühring et al., 2020). While on the observational side, it is becoming apparent that OPEs share POP-like characteristics; for example one study found that OPEs persist in indoor dust and bioaccumulate within humans (Y. Wang et al., 2021). Part of these issues in properly predicting POP like properties of OPEs may be attributed to the modelling tools used to assess OPEs. Default parameters of tools such as the Organization of Economic Co-operation and Development (OECD) Persistance (POV) and LRTP Screening Tool ("The Tool") underestimated both the POV and LRTP values for OPEs(Sühring et al., 2020). This is incredibly alarming as predictive modelling tools such as the OECD and POV Screening tool uses data such as OPEs having have half-lives of less than 2 days in air to predict LRTP. Simply based on the knowledge of OPE half-lives being less than 2 days in air, the sheer notion that these OPEs could be found in remote places such as the Arctic would be absurd; and yet emerging data clearly attests to this (Sühring et al, 2021)(Sühring et al., 2016). One way this disparity can be sufficiently explained then is through aerosol absorption. By absorbing into aerosols those same OPEs now had a mode of transport over long ranges (Möller et al., 2012). As noted by Möller et al the half lives presented is only within the gaseous state, this is a factor that must be analyzed more thoroughly to better understand the half-lives of OPEs not just in the gaseous state, but when adsorbed to other aerosols.

# Chapter 2: OECD and POV Screening TOol

One commonly used assessment tool for LRTP and toxicity is the OECD POV and LRTP Screening Tool (The Tool). Designed with extensive research of PBDEs and other POPs in mind the Tool was parameterized to estimate the persistence and LRTP of POPs but would come short in adequately quantifying the persistence and LRTP of many more hydrophilic OPFRs (Zhang and Sühring et al., 2016). Multiple comparative models between The Tool and other models have begun to show the limitations of said parameters. One study found that the poly parameter linear free energy relationships (ppLFERs) tool had the ability to improve the current gas-particle partitioning description for polar chemicals(CW et al., 2008). Another study found that by including other environmental parameters such as wind speed had a significant effect on LRTP(Zhu et al., 2014). Clearly from this it can be seen that the tool must be updated, its ability to predict the fate of OPEs must be broadened as all parameters must be reassessed. This is the goal that this paper sought out attempted to solve as it can be seen throughout the rest of this paper.

# Chapter 3 Figures and Results

Table 1: Summary of OPE Data

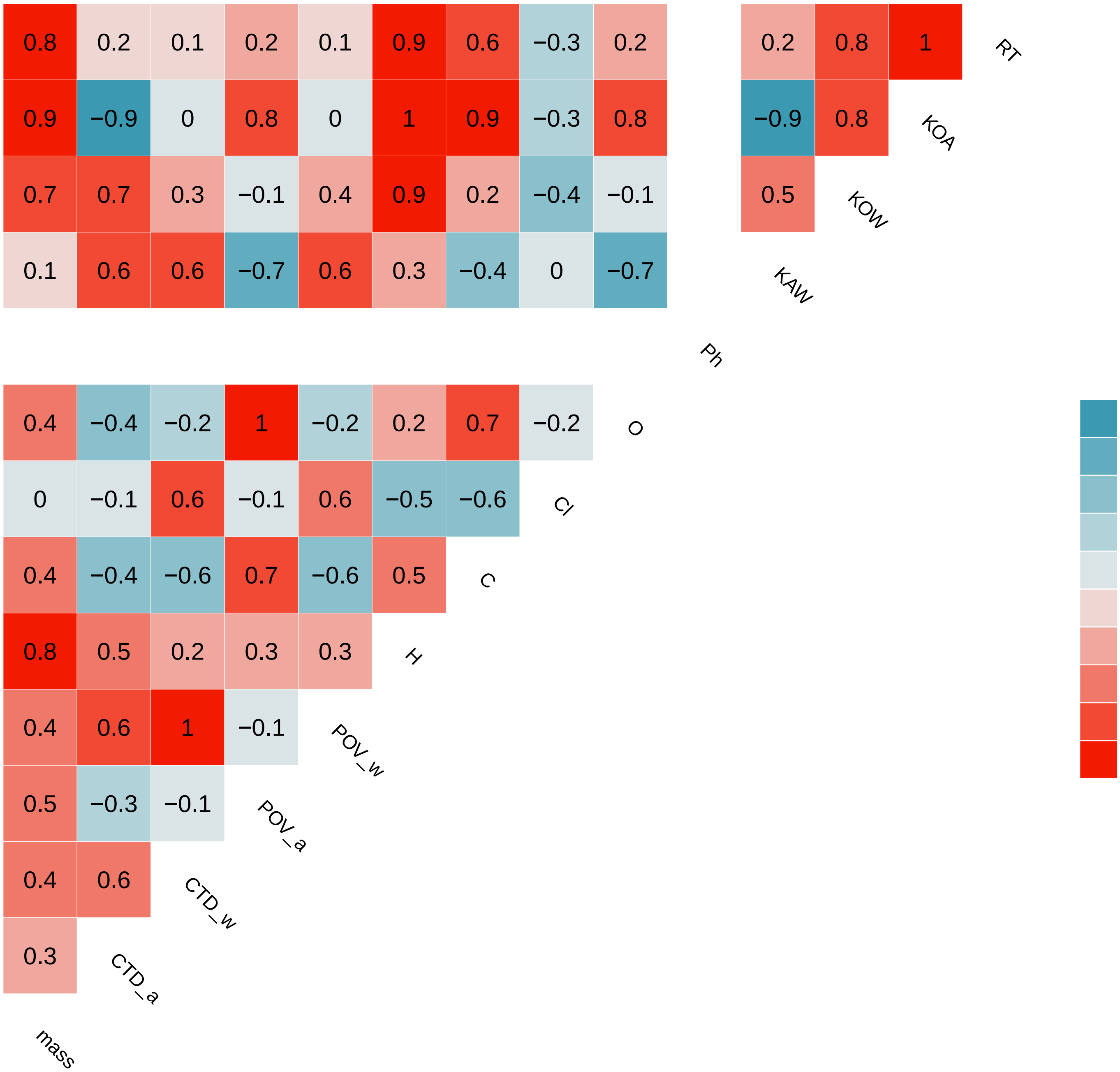
| OPEs | mass | CTD_a | CTD_w | POV_a | POV_w | H | C | Cl | O | Ph | KAW | KOW | KOA | RT |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| TPP | 327.0781 | 584.00 | 65 | 2 | 39 | 18 | 15 | 0 | 4 | 1 | 0.53 | 6.34 | NA | 14.554 |
| TMTP | 369.1250 | 278.52 | 64 | 1 | 39 | 21 | 21 | 0 | 4 | 1 | 0.53 | 6.34 | NA | 17.902 |
| TPTP | 369.1250 | 584.00 | 65 | 2 | 39 | 21 | 21 | 0 | 4 | 1 | 0.53 | 6.34 | NA | 18.091 |
| TEP | 183.0781 | 155.00 | 24 | 0 | 14 | 6 | 15 | 0 | 4 | 1 | -4.60 | 0.90 | 5.5 | 10.848 |
| TPrP | 225.1250 | 107.00 | 26 | 0 | 15 | 9 | 21 | 0 | 4 | 1 | 0.29 | 1.87 | NA | 14.074 |

| OPEs | mass | CTD_a | CTD_w | POV_a | POV_w | H | C | Cl | O | Ph | KAW | KOW | KOA | RT |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| TBP | 267.1720 | 101.00 | 7 | 0 | 4 | 12 | 27 | 0 | 4 | 1 | - 5.80 | 4.20 | 10.0 | 16.540 |
| TBEP | 399.2506 | 8.00 | 28 | 21 | 16 | 18 | 39 | 0 | 7 | 1 | - 9.30 | 3.00 | 12.3 | 17.076 |
| EHDP | 363.1720 | 201.00 | 28 | 1 | 16 | 20 | 27 | 0 | 4 | 1 | 0.58 | 6.30 | NA | 18.616 |
| TCEP | 284.9612 | NA | NA | NA | NA | 6 | 12 | 3 | 4 | 1 | - 6.00 | 1.60 | 7.6 | 12.969 |
| TCPP | 327.0081 | 179.00 | 88 | 1 | 51 | 9 | 11 | 4 | 4 | 1 | 0.27 | 2.59 | NA | 14.565 |

## 3.1 Table Results

As it can be seen from the table, there are a total of 14 variables being compared to here for the given 10 OPEs. Not all data was present for each OPE so some appear blank.

Figure 1: OPE Correlation Chart

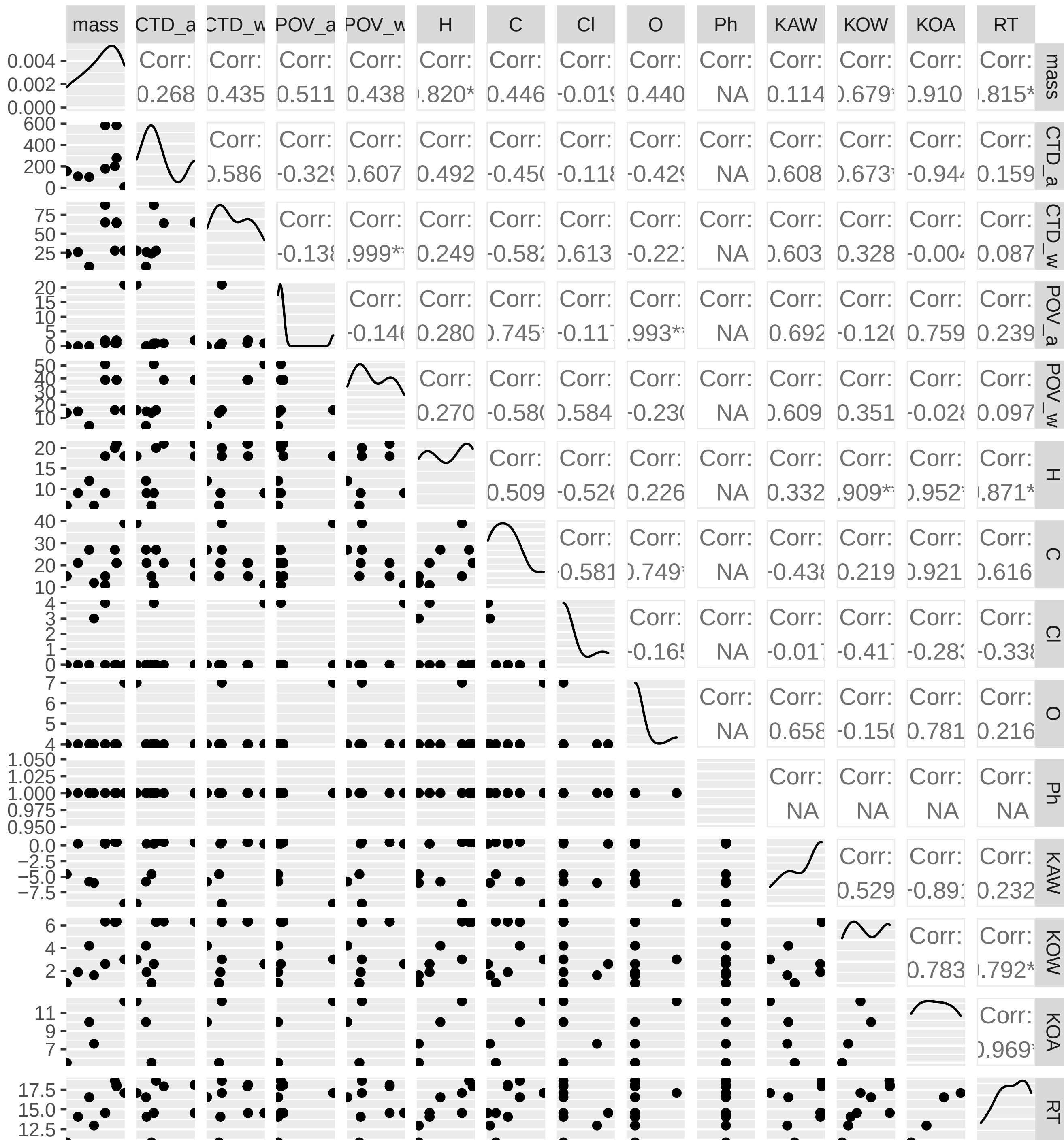



Correlation Data for all 13 variables analyzed for all OPEs

## 3.2 Chart Results

An easy to read summary data chart of the correlation potential between the OPE variables. The chart starts with mass on the left, all the way down to RT on the right. The chart was broken down into 10 categories of correlation values, with +/-(0.8,1) having the highest degree of absolute coefficients. Due to rounding to 1 significant digit some values have a complete correlation.

Figure 2: OPE Correlation Chart of all Variables

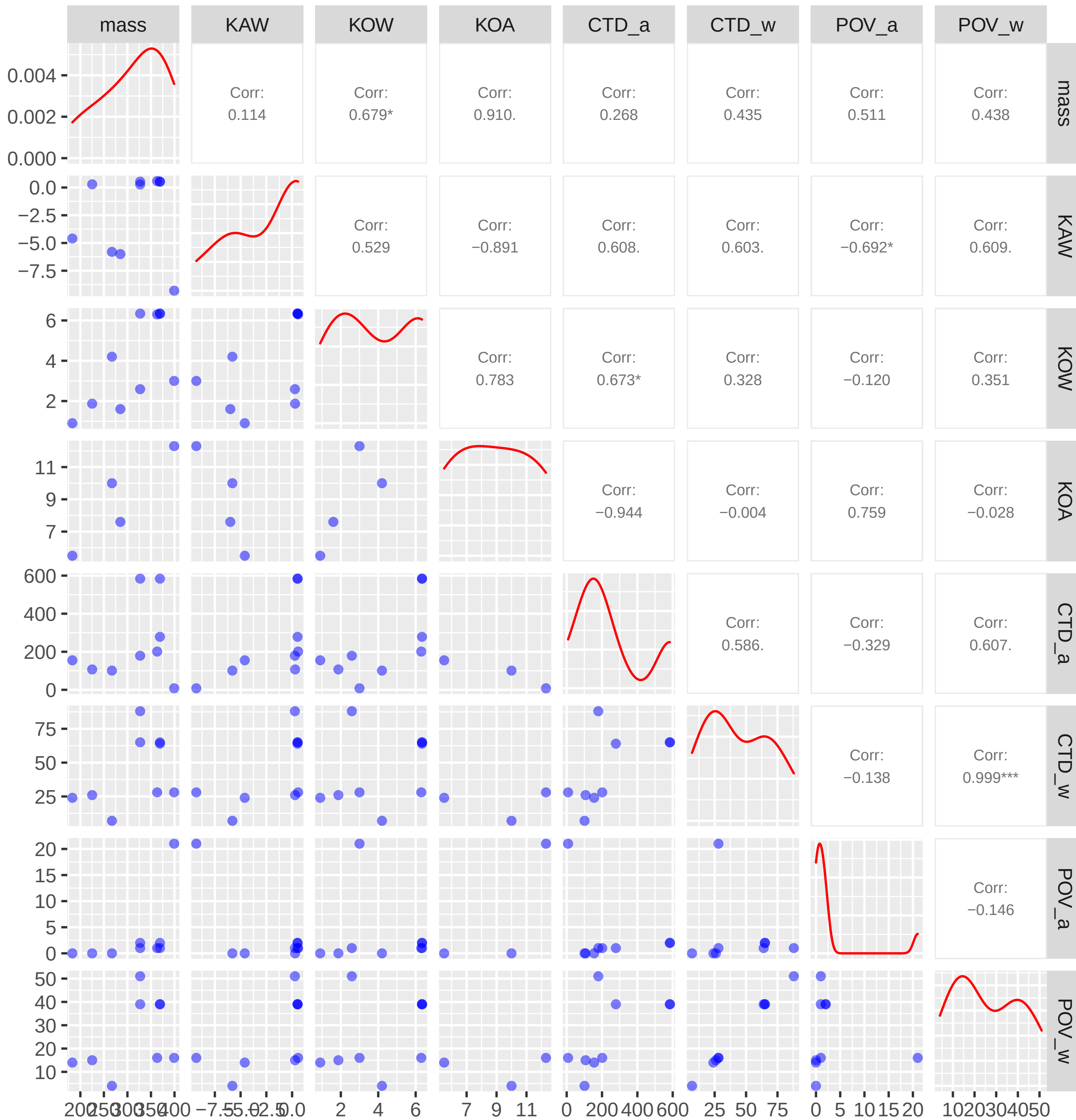



Correlation Data for all 14 variables analyzed for all OPEs

## 3.3 GGPairs OPE Correlation Data.

Here we can see the total analysis of all the OPEs pitted against each other. Due to the sheer number of variables it becomes difficult to read so this chart is simply used as a demonstration. More comprehensive graphs are designed below breaking down the variables within smaller categories

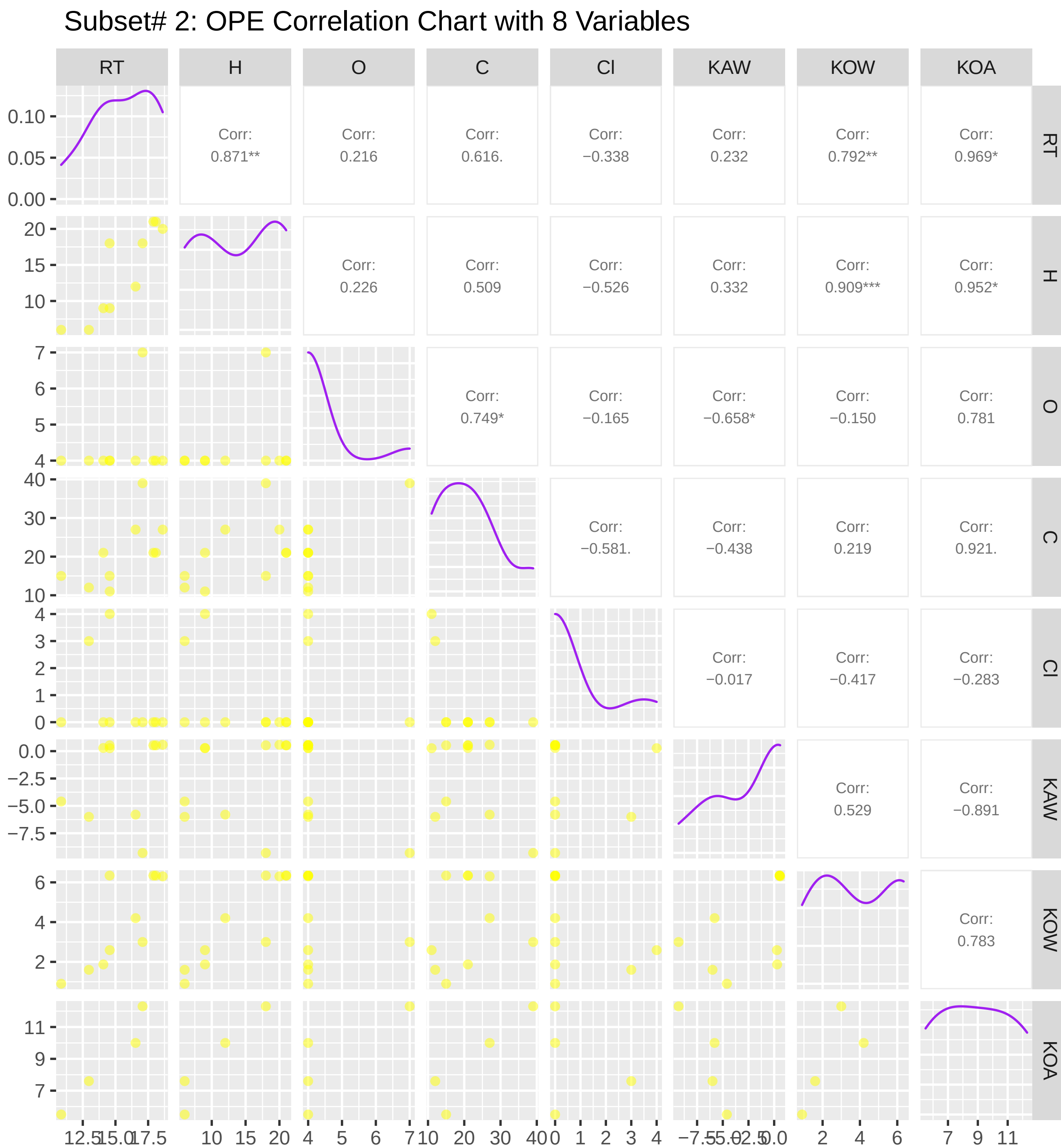
Subset# 1: OPE Correlation Chart with 8 Variables




The 8 variables being anaylzed here for correlation values are: mass,

KAW, KOW, KOA, CTD_w, CTD_a, POV_a, and POV_w

\# 3.4 GGPlots Subset Chart 1. This subset compares KAW, KOW, KOA, CTD_w, CTD_a, POV_a,POV_w, and mass. Some notable values here are between the pairs: CTD_w-POV_w, KOA-mass,KOA-KAW, and CTD_a-KOA with values: 0.999,0.910,-0.891 and -0.944 respectively.




The 8 variables being anaylzed for correlation values are: RT, H, O, C, Cl, KAW, KOW, KOA

# 3.5 GGPlots Subset Chart 2. This subset compares "RT","H","O","C","Cl", "KAW", "KOW", and "KOA". Some notable pairs here not already previously mentioned are: KOA-

RT,KOA-H,KOA-C, and KOW-H, with values: 0.969,0.952,0.921, and 0.909 respectively. #note how significant this is because the pairs KOA-H and KOA-C may be a good predictive factor for what mode of transport other similar OPEs may use. With OPEs high in Carbon, oxygen and hydrogen likely to be in air while not so much in water. While OPEs with Cl have a higher likely hood of using water as their mode of transport

Subset# 3: OPE Correlation Chart with 9 Variables


The 9 variables being anaylzed for correlation values are: RT,

H, O, C, Cl, CTD_a, CTD_W, POV_a, POV_w

# 3.6 GGPlots Subset Chart 3. This subset compares RT","H","O","C","Cl", "CTD_a", "CTD_w", "POV_a","POV_w". The main point of this subset is to compare the chemical compositions with the POV. Some notable pairs here not already previously mentioned are:

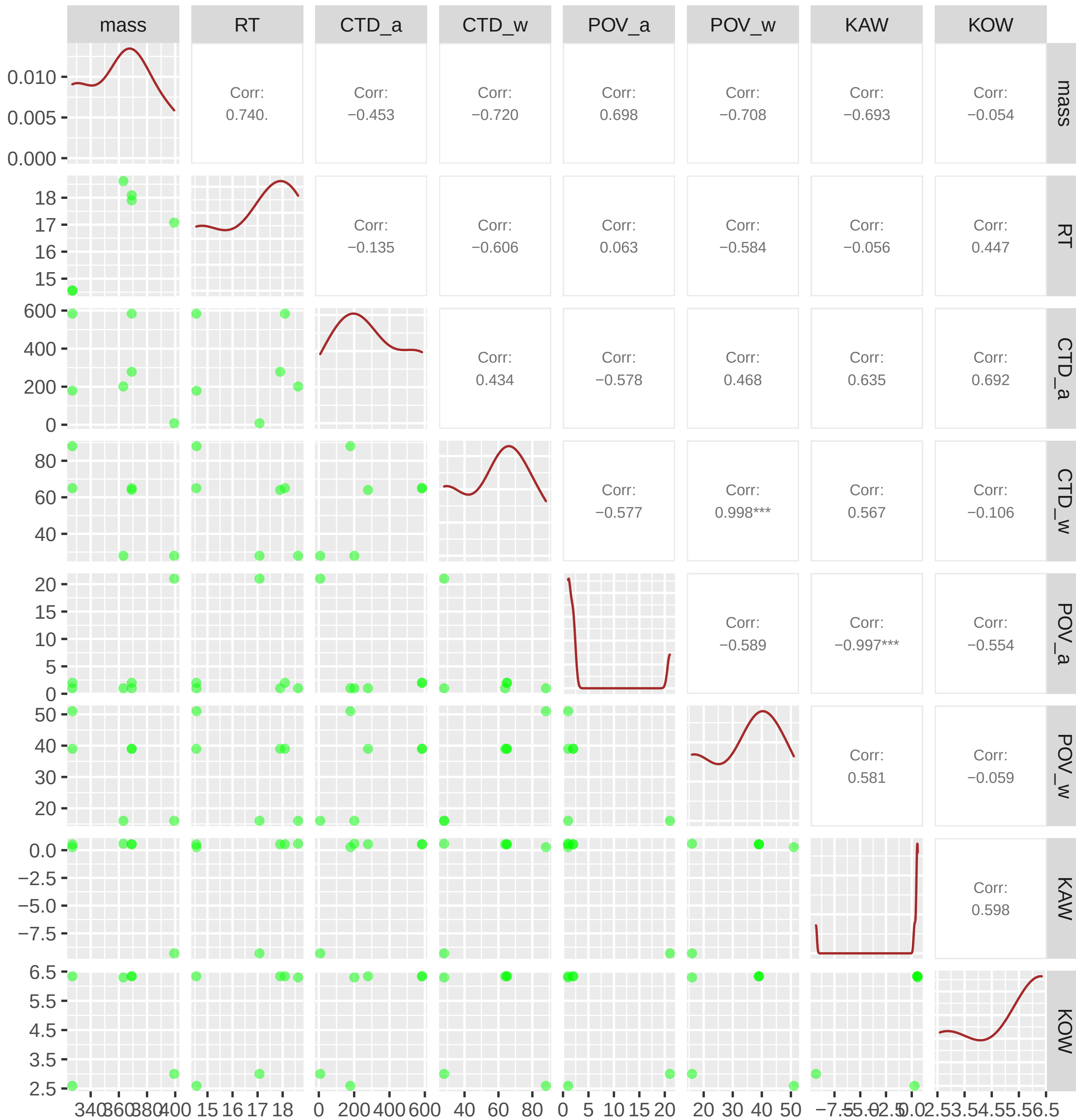
POV_a-POV_w, and POV_a-O, with values: 0.999, 0.993 respectively. #note how significant this is, the POV_a match up with O at such a high value matches up with its CTD_a-O as well. Showing that O is an indicator of both and likely needed for atmospheric transport


The 9 variables being anaylzed for correlation values are: RT,

H, O, C, Cl, CTD_a, CTD_W, POV_a, POV_w

# 3.7 GGPlots Subset Chart 4. This subset compares “mass”,“RT”, “CTD_a”, “CTD_w”, “POV_a”,“POV_w”,“KAW”,“KOW”. Due to the absence in all data for each OPE, this data is less accurate for the representation of OPEs with a mass less than 300. Despite this,some notable pairs here are: KOW-RT(0.952),KOW-CTD_w (-0.926), KOW-POV_w(-0.931), CTD_a-mass(-0.912),and CTD_a-RT(-0.941) with values: 0.952, -0.926,-0.931,-0.912,-0.941 respectively.

Subset# 5: OPE Higher Mass Correlation Chart with 9 Variables




The 9 variables being anaylzed for correlation values are: RT,

H, O, C, Cl, CTD_a, CTD_W, POV_a, POV_w

# 3.8 GGPlots Subset Chart 5. This subset compares “mass”,“RT”, “CTD_a”, “CTD_w”, “POV_a”,“POV_w”,“KAW”,“KOW”. Due to the absence in all data for each OPE, this data is less accurate for the representation of OPEs with a mass over 300. Despite this,some

notable pairs here are: POV_a-KAW, and POV_w-CTD_w with values: -0.997 and 0.998 respectively.

## Conclusion and Discussion

As noted throughout the entirety of the results, many of the variables within the OPE parameters have some sort of relationship with each other, whether that be positive or negative. Looking deeper into these results in section 3.5 note how significant the statistical relationship is between the pairs KOA-H and KOA-C. This is important because it may be a good predictive factor for what mode of transport other similar OPEs with high units of hydrogen and carbon atoms may use. Implying that OPEs high in Carbon, oxygen and hydrogen likely to be in air while not so much in water. Section 3.5 also highlights to a lesser degree that OPEs with Cl have a higher likely hood of using water as their mode of transport.In section 3.6 there was also another pair with statistical significance: POV_a-O. This is because it supports the previous findings of 3.5, higher concentrations of oxygen have a strong positive coefficient value with the overall persistence of the OPE in air. Implying once more that this type of OPE is more likely to use an atmospheric mode of transport. This adds evidence to the fact that specific compounds may be indicators for certain modes of transports.These results are profound in that sense that when isolated for each significant relationship a crude model can be made to predict future OPEs. Future work I would love to do is to attempt these concepts on other OPEs to see how well it stands up, as well as expand the database to get more accurate results.

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# TOC Graphic

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