

# MULTIVARIATE STATISTICAL ANALYSIS TO TRACE SEASONAL VARIATION OF PERFLUOROALKYL ACID CONTAMINATION IN SURFACE WATERS

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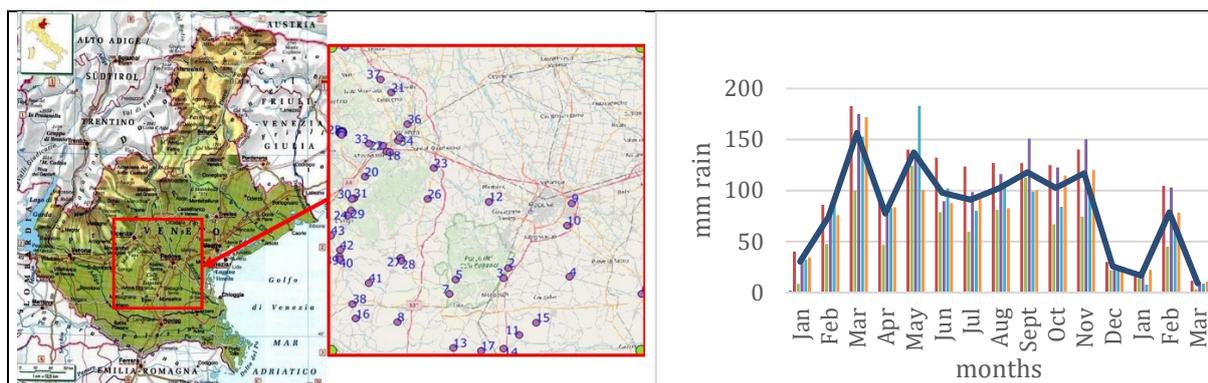
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## Introduction:

The ecotoxicological implications of per- and poly-fluoroalkyl substances (PFAS) in surface waters are an important issue facing environmental researchers, but impacts on food safety through the consumption of fish and drinking water sourced from contaminated water bodies, as well as indirect exposure via the ingestion of contaminated vegetables, cannot be overlooked<sup>1-2</sup>. It is also important to consider that seasonal changes may impact the concentration of PFAS in water systems, thus creating various risk scenarios of potential relevance for the toxicological assessment of pre- and perinatal human exposure, as has been described for PFOS and PFOA<sup>3</sup>. In this paper we present a study based on the combined use of Principal Component Analysis (PCA) and Kriging techniques to explore sources and seasonal variation of PFAS concentrations in surface water samples taken from a polluted area. The data analyzed were generated from samples taken in close proximity to a PFAS production plant and several manufacturing sites where PFAS-containing media are utilized (i.e., leather, fabrics, thermoplastics, metal plating, paper, paint, and inks).

## Materials and methods:

In 2018, data describing the occurrence of PFAS in the surface waters of a rural-industrial district in NE Italy were made available by Regione Veneto through the Regional Environmental Protection Agency portal<sup>4</sup>. The data have been georeferenced via QGIS 2.18.0 software tools, with EPSG 3003 as CRS (Coordinate Reference System), for C4 - C12 perfluoroalkylcarboxylic acids (PFCAs, namely PFBA, PFPeA, PFHxA, PFHpA, PFOA, PFNA, PFDA, PFUnA, PFDoA) and C4 - C8 perfluoroalkanesulfonic acids (PFSAs, namely PFBS, PFHxS, and PFOS). For the C8 compounds, PFOS and PFOA, the sum of the linear and branched isomers was considered in computation. Data have been framed within 4 seasonal periods (winter, spring, autumn, and summer) according to the reported differences in rainfalls in 2018. The mean value of contamination refers to the same time-frame and same georeferenced sampling site (1-3 data points). Left-censored data are computed in Upperbound (not determined values are set at the analytical limit of determination of the corresponding PFAS -5 ng/L)) were utilized. PCA was performed on JMP software ver. 14 and SPSS ver. 25. Kriging was performed on Surfer software ver. 14.

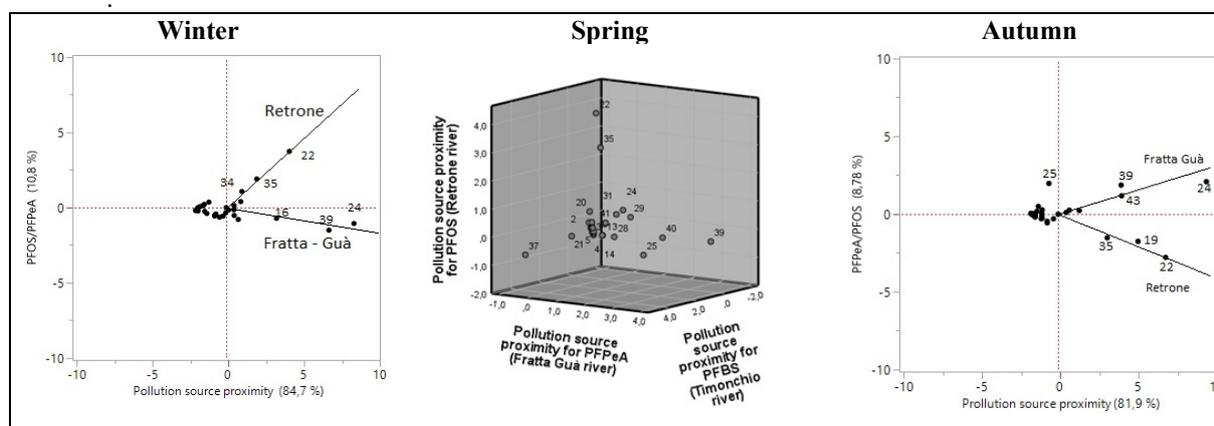


**Figure 1.** Sampling points considered in the impacted area. Points 1 and 25 indicate the presence of PFAS production plants.

**Figure 2.** Average variation in rainfalls (mm per month) in the considered georeferenced area, starting from Jan 2018.

## Results and discussion:

The utilized database contained 258 reports related to the 9 PFAS analytes being investigated. The surface water samples were collected over 4 seasons in 2018 from 48 different sampling sites. **Figure 1** shows the georeferenced surface water sampling points along the two main river basins (Fratta-Guà and Retrone) that were impacted by PFAS and **Figure 2** shows the mean rainfalls (seasonally recorded during the considered period). PCA analysis (**Figure 3; Table 1**) reveals the highest correlation for PFPeA and PFOS with principal components during all four seasons despite the rainfall variation which could affect PFAS concentrations in the surface waters. PCA also revealed differences between the two main river basins examined (Fratta-Guà and Retrone) during the Winter and Summer-Autumn periods. The inverted ratio of PFOS/PFPeA observed for the Winter and Autumn surface water samples suggests the presence of an additional PFAS emission source. PCA also reveals the rise of another PFAS emission in the Spring characterized by a PFBS concentration linked to Timonchio river that is 10x higher than that measured in the other locations investigated (**Figure. 3; Table 1**). This finding requires further investigation to ascertain a potential source of the PFBS contamination. Iso-concentration maps of PFPeA illustrating seasonal variation (**Figure 4**) suggest that the contaminated area tends to expand in Spring as result of an increased PFAS mobility driven by rainfalls.



**Figure 3.** Bi-dimensional (Winter and Autumn) and tri-dimensional (Spring) PCA analysis indicating PFPeA and PFOS as discriminants of different PFAS pressures on Fratta-Gua and Retrone rivers, with seasonal changes in their ratio. In spring, presence of PFBS as discriminant for the additional Timonchio river.

**Table 1.** Rotated components matrix of PCA carried out on Spring data. Values with  $r \geq 0.95$  bolded.

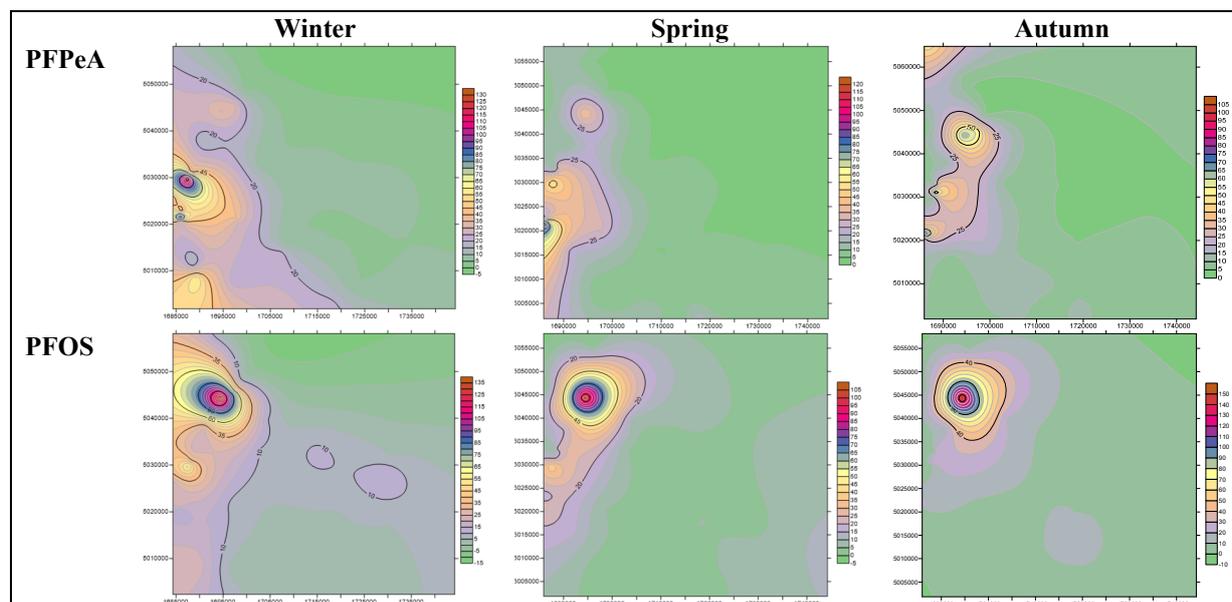
Carbon length	PFAS	Components		
		1	2	3
C4	PFBA	0.704	0.026	-0.180
C4	PFBS	0.069	-0.002	<b>0.977</b>
C5	PFPeA	<b>0.950</b>	0.223	0.089
C6	PFHxA	0.929	0.304	0.129
C7	PFHpA	0.913	0.241	0.267
C8	PFOS (total)	0.238	<b>0.964</b>	-0.002
C8	PFOA (total)	0.784	0.607	0.049

A comparison of the iso-concentration maps for PFOS and PFPeA divided by season indicates that PFPeA has a higher mobility during spring. This could be attributed to the increased rainfalls and PFPeA's higher hydrophilicity relative to that of PFOS (**Figure 4**). On the contrary, PFOS seems to be residual contamination from the PFAS production plant, where its synthesis has been ceased since 2004<sup>5</sup>. It is worth noting the PFAS plant is settled on an undifferentiated aquifer with its recharge area, that represents the water reservoir of the downhill plain, mostly devoted to agriculture and animal farming practices.

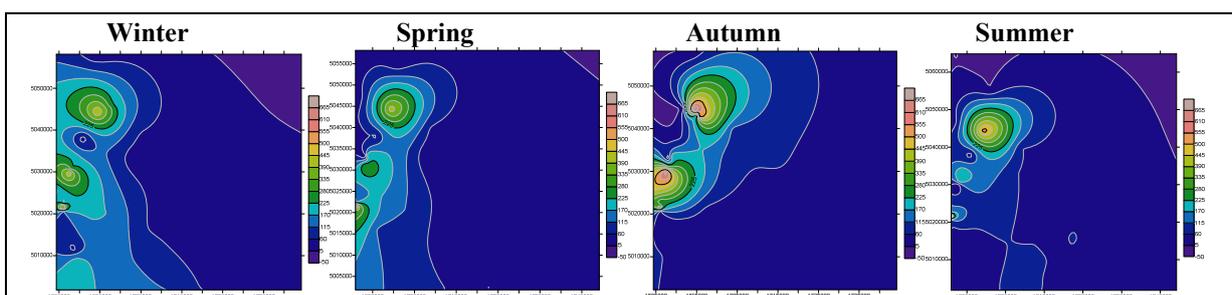
PFOA contamination in the surface waters of the impacted area represents a major issue, but PCA does not identify it as a discriminant factor like PFOS, PFPeA, and PFBS. A possible explanation could be the impact from multiple PFOA sources. **Figure 5** highlights the presence of two possible PFOA point sources unrelated to the PFAS production plant. This finding is clearer than the kriging outcomes in the case of PFOS (**Figure 4**). These additional PFOA sources could be attributed to the manufacturing district and the effluents of a pipe collecting run-off waters from five different northern-bound wastewater treatment plants. Such pressures seem to decline in summer, possibly as consequence of the 3-week vacation period.

The observed seasonal variations in the amount, extension, and profile of PFAS in surface waters should be accounted for in exposure assessments since contaminated surface waters are used to water agricultural fields. The seasonal relevance of short chain PFAS, which can be taken up by plants more efficiently than medium- and long-chained PFAS, should be matched with the cultivation cycle and harvesting of leafy vegetables, cereals, and fodders intended for food production and animal nutrition which usually occurs in the spring to autumns period.

Moreover, the use of surface water in local agriculture activities that are settled on very permeable soil may contribute to the contamination of groundwater intended for drinking purposes. This could be a serious issue for residents that draw water from private wells without filtration systems equipped to reduce PFAS contamination.



**Figure 4.** Iso-concentration maps (ng/L) of PFPeA and PFOS variation in surface waters during different seasons. Summer data are very similar those shown for Autumn.



**Figure 5.** Iso-concentration maps (ng/L) of PFOA variation in surface waters during different seasons.

To conclude, the multivariate statistical analysis approach is proposed for risk assessment and management activities for an industrial/rural area contaminated with PFAS. This approach takes into account seasonal influences and their impact on the profile and amount of PFAS in surface water. In addition, this approach can be used to trace the transition from long- and medium-chained PFAS to short-chained PFAS in local manufacturing activities, as in the case of PFBS, independently from their formation and release as degradation products of precursors from waste-water treatment facilities.

#### Acknowledgements:

ARPA Veneto open access dataset on PFAS concentration in water bodies sampled by ARPA Veneto, available at : <http://www.arpa.veneto.it/dati-ambientali/open-data/idrosfera/concentrazione-di-sostanze-perfluoroalchiliche-pfas-nelle-acque-prelevate-da-arpav> , last update March 31, 2019 is acknowledged under Creative Commons 3.0 License.

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