Spatial Distribution and Sources of Total Chromium and Perfluoroalkyl Substances (PFAS) in Northern Italy Rivers

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Abstract. Per- and poly-fluoroalkyl substances (PFAS) and Total Chromium (Cr) in surface waters are polluting factors that can directly or indirectly affect human and animal health. These are conjunctly used in several manufacturing activities such as electroplating, stainless steel welding, leather tanning and the production of electronic components. In this paper we present a study based on the use of the Principal Component Analysis (PCA) statistical technique to explore emission sources of PFAS and Cr in surface water samples taken from a polluted area in Northern Italy. It has been found that the discriminant factor is the link between PFBS and Cr. It is due to electroplating, and stainless steel welding activities. No other links were found between Cr and other PFAS. This information is important both for risk assessment and forensic activities.

1. Introduction
The presence of per- and poly-fluoroalkyl substances (PFAS) in surface waters is an important polluting factor that impacts food safety due to direct (fish and drinking water) and indirect (contaminated vegetables) human and animal consumption. Likewise, chromium containing compounds, have the same impact. Most of the above mentioned classes of products are stable and persistent in the environment, but some of them are mobile being able to contaminate both drinking water and food webs. These contaminants find their association in electroplating, stainless steel welding activities, leather tanning and the production of electronic components. Perfluorooctanesulfonic acid (PFOS) is the most important PFAS used for chrome plating processes, whose many technical formulations contain, in addition, low amounts of perfluorobutanesulfonic acid (PFBS). Moreover, as consequence of the insertion of PFOS in the Annex 2 of the Stockholm Convention as Persistent Organic Pollutants of priority interest due to its persistence, toxicity, bioaccumulation and long-distance transport features, PFBS has been used as a complete alternative to PFOS [1] in order to decrease the surface tension of treatment baths and reduce the formation of toxic chromium VI aerosols by evaporation of hydrogen and oxygen on the electrodes [2, 3]. In contrast, PFBS is water soluble and does not accumulate in organisms; however, when it affects groundwaters, it is persistent and it spreads in the environment. Furthermore, it is associated with thyroid and kidney effects, in addition to reproductive and developmental toxicity [4] PFBS are adsorbed only on fresh activated carbon and fresh anion exchange resins. In order to stop it from spreading into the environment, the frequent replacement of filters in waste water treatment plants has proved to be necessary, even if not efficient from the economic point of view.
Consequently, understanding the source of such pollutants is of uttermost importance, to prevent environmental and food chain contamination. A previous paper [5] reported the seasonal variation of PFAS pollution from a polluted area in Northern Italy. The data analyzed was generated from samples taken in close proximity to a PFAS production plant, as well as several manufacturing sites where PFAS-containing products are used (i.e., leather fabrics, thermoplastics, metal plating, paper, paint, and inks). PCA was coupled to Kriging. It shows that discriminant factors are linked to river basins. The presence of PFBS as discriminant PFAS in the Timonchio river is of particular interest. In this paper, we present a study based on the use of Principal Component Analysis (PCA) technique to explore emission sources of PFAS and Cr in surface water samples taken from the same polluted area. This information could be important both for risk assessment and forensic activities.

2. Materials and methods
Principal Component Analysis (PCA) has been applied on 138 surface water samples from 38 different sampling sites of a rural-industrial district in NE Italy (figure 1).

Figure 1 shows the georeferenced surface water sampling points along the two main river basins (Fratta-Guà Retrone, Timonchio and Adige) that were impacted by PFAS. Data were made available by Regione Veneto through the Regional Environmental Protection Agency portal [6], and they have been georeferenced via QGIS 2.18.0 software tools, with ESPG 3003 as CRS (Coordinate Reference System), for C4 – C12 perfluoroalkylcarboxylic acids (PFCAs, namely PFBA, PFPeA, PFHxA, PFHpA, PFOA), C4 – C8 perfluoroalkanesulfonic acids (PFSAs, namely PFBS, and PFOS) and Chrome. For the C8 compounds, PFOS and PFOA, the sum of the linear and branched isomers was considered in computation. The data used comes from sampling sites where either PFAS and Cr have been analysed in the same period of time (within one week) during 2018. 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)). The statistical analysis was performed on JMP software ver. 14 and SPSS ver. 25.

2.1. Principal component analysis
Principal Component Analysis (PCA) is a statistical technique often used in environmental analysis to detect pollution sources in ambient air and in soil. PCA is a dimension-reduction tool that can be used to reduce a large set of variables to a small set (called “principal components”) that still contains most of the information and summarizes the features of the original dataset [7]. Principal components are uncorrelated and ordered so that the kth PC has the kth largest variance among all PCs [8]. So, the first component has the maximum variance. Successive components progressively explain smaller portions of the variance and are all uncorrelated with each other. In this work PCA was used to identify the different contaminant sources of surface waters in the considered site.

3. Results and discussion

3.1. Correlation analysis

A preliminary correlation analysis by Pearson's coefficients has been performed to study the linearity in a set of 10 variables: PFBA, PFPeA, PFBS, PFHxA, PFHpA, PFOA (Linear PFOA), PFOA (Total PFOA), PFOS (Total PFOS), PFOSL (Linear PFOS) and Cr. Results have been illustrated in table 1.

|       | PFBA  | PFPeA | PFBS  | PFHxA | PFHpA | PFOA  | PFOAL | PFOS  | PFOSL | Cr    |
|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| PFBA  | 1     | .941**| .208  | .982**| .891**| .978**| .978**| .791**| .853**| -0.251|
| PFPeA | .941**| 1     | .219  | .970**| .934**| .913**| .919**| .718**| .860**| -0.246|
| PFBS  | 0.208 | 0.219 | 1     | 0.241 | .342  | 0.187 | 0.181 | 0.143 | 0.172 | -0.164|
| PFHxA | .982**| .970**| .241  | 1     | .929**| .966**| .969**| .782**| .866**| -0.246|
| PFHpA | .891**| .934**| .342  | .929**| 1     | .906**| .913**| .755**| .865**| -0.231|
| PFOAL | .978**| .913**| 0.187 | .966**| .906**| 1     | .999**| .876**| .908**| -0.258|
| PFOAT | .978**| .919**| 0.181 | .969**| .913**| .999**| 1     | .872**| .909**| -0.251|
| PFOSL | .791**| .718**| 0.143 | .782**| .755**| .876**| .872**| 1     | .954**| -0.272|
| PFOS  | .853**| .860**| 0.172 | .866**| .865**| .908**| .909**| 1     | .954**| -0.268|
| Cr    | -0.251| -0.246| -0.164| -0.246| -0.231| -0.258| -0.251| -0.272| -0.268| 1     |

**: Pearson correlation test at significant level p < 0.01. Values below LODs were treated as zero and were induced in the Pearson correlation test. Any PFAS was found to have correlation with PFBS and Cr.

High and significative correlations have been determined between PFAS congeners, except for PFBS. Specifically, PFBS such as Cr, has statistically no significant correlation to the other variables. It is also noted that even if the correlations are not statistically significant, Cr is inversely proportional to all PFAS.

3.2. PCA results

PCA has been applied to the original data set of 10 variables, corresponding to the 9 PFAS congeners and Cr. Principal Components (PCs) were chosen according to eigenvalues-greater-than-one rule [9], identifying in this way two PCs (table 2). In fact, when the eigenvalue is less than 1, the factor explains less information than a single item would have explained.

In the sampling sites, PC1 and PC2 accounted for 71% and 85% of the cumulative variance, respectively. The Principal components (PCs) describe the latent structure of the original data set through a component matrix (table 3), which contains estimates of the correlations between each of the variables and the estimated components.

It could be possible, as in the case of Cr, that a variable is not clearly related to one of the PCs. Generally, a rotated component matrix (table 4) determines a better component representation [10]. In this analysis, the first component is highly correlated to all PFAS congeners, except for PFBS. In table 4, PC2 is better related to Cr and PFBS, negatively and positively respectively. The relationship between original variables and PCs is graphically represented in figure 2.
Table 2. Total variance explained

| Component | Initial Eigenvalues | Extraction Sums of Squared Loadings | Rotation Sums of Squared Loadings |
|-----------|---------------------|-------------------------------------|----------------------------------|
|           | Total               | % of variance | cumulative % | Total               | % of variance | cumulative % | Total               | % of variance | cumulative % |
| 1         | 7.505               | 75.053        | 75.053       | 7.505               | 75.053        | 71.416        | 71.416           |
| 2         | 1.044               | 10.437        | 85.491       | 1.044               | 10.437        | 14.075        | 85.491           |
| 3         | 0.841               | 8.411         | 93.902       | 0.841               | 8.411         | 14.075        | 93.902           |
| 4         | 0.384               | 3.841         | 97.743       | 0.384               | 3.841         | 14.075        | 97.743           |
| 5         | 0.139               | 1.385         | 99.129       | 0.139               | 1.385         | 14.075        | 99.129           |
| 6         | 0.064               | 0.642         | 99.771       | 0.064               | 0.642         | 14.075        | 99.771           |
| 7         | 0.012               | 0.124         | 99.894       | 0.012               | 0.124         | 14.075        | 99.894           |
| 8         | 0.007               | 0.068         | 99.962       | 0.007               | 0.068         | 14.075        | 99.962           |
| 9         | 0.003               | 0.033         | 99.995       | 0.003               | 0.033         | 14.075        | 99.995           |
| 10        | 0.001               | 0.005         | 100.000      | 0.001               | 0.005         | 14.075        | 100.000          |

Table 3. Component matrix

| Variable | PC 1 | PC 2 |
|----------|------|------|
| PFBA     | 0.972| 0.046|
| PFPeA    | 0.949| 0.026|
| PFBS     | 0.247| -0.847|
| PFHxA    | 0.981| 0.019|
| PFHpA    | 0.944| -0.061|
| PFOAL    | 0.985| 0.082|
| PFOAT    | 0.987| 0.088|
| PFOSL    | 0.883| 0.117|
| PFOST    | 0.945| 0.102|
| Cr       | -0.555| 0.529|

Extraction method: Principal Component Analysis

Table 4. Rotated component matrix

| Variable | PC 1 | PC 2 |
|----------|------|------|
| PFBA     | 0.955| 0.186|
| PFPeA    | 0.928| 0.2  |
| PFBS     | 0.039| 0.882|
| PFHxA    | 0.957| 0.215|
| PFHpA    | 0.903| 0.283|
| PFOAL    | 0.976| 0.154|
| PFOAT    | 0.98  | 0.149|
| PFOSL    | 0.886| 0.095|
| PFOST    | 0.943| 0.125|
| Cr       | -0.22| -0.599|

Rotation method: Varimax with Kaiser normalization

The graph in figure 2 shows a cluster consisting of PFBA, PFPeA, PFHxA, PFHpA, PFOAL, PFOAT, PFOS and PFOSL. PC 1 perfectly identifies PFOAT, while the second component represents the latent variable that connects PFBS – positively - and Cr - negatively.

3.3 Contamination sources

The PFAS contamination of the surface water in the Veneto Region has been linked to industrial production [11] and PFAS industrial use, in particular to a chemical plant that has been active in the area since 1968, producing chemicals for crop production (herbicides), pharmaceuticals, and PFAS. PFAS and Cr are also used in a leather tanning district laying in the same area. The above sources could be the reason of the PFAS cluster. However, the PCA results suggest the presence of another factor of contamination for the examined sites, conjunctly correlated to PFBS and Cr, referable to electroplating and stainless-steel welding activities also carried out in the investigated area.
Figure 2. Component plot in rotated space. PC 1 perfectly identifies PFOAT, while the second component represents the latent variable that connects PFBS – positively - and Cr - negatively.

Figure 3. PFAS relative composition profile in the investigated area.

PFAS relative composition profile is very different diverse in the different river basins of the investigated region. Moreover, it is possible to determine an extensive seasonal variability [5] of the
above mentioned parameter. Figure 3 shows the relative composition profile, in spring 2018, for Agno, Brendola-Guà, Retrone-Bacchiglione and Timonchio rivers sampling sites, shown left to right with direction of the current flow, generally NW-SE. It is possible to see that Timonchio river sampling points show a very different profile than the others, with a strong prevalence in PFBS; the sampling points are a few kilometers away from each other and they show a very different PFAS concentration, but almost exactly the same concentration profile. This might be explicable by a PBFS point source. This information strengthens the PCA results. Moreover, the first two sampling point are also quite different than the others. They are located very close to one of the European biggest PFAS production sites, now closed.

4. Conclusions
The reduction of the release from point sources of mobile and persistent contaminants such as Cr and PFBS is of pivotal relevance to prevent impacts of (eco) toxicological relevance on water bodies, the food webs, and human health. The approach proposed is able to differentiate and thus geo-reference the contribution from the different manufacturing activities present on the selected territory, thus addressing environmental, food, and human (bio)monitoring plans on risk-oriented basis.

5. References
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Acknowledgments
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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