

Environmental Behavior of some Key-PFAS and Aromatic Amine Pollutants of Benzidine Type



Dr. Frank KARG / CEO (PDG) HPC INTERNATIONAL SAS / France

Scientific Director of HPC-Group International

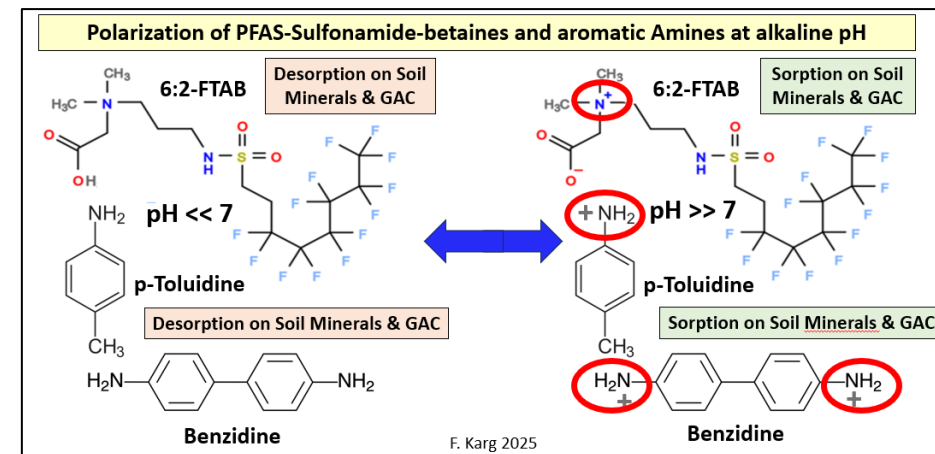
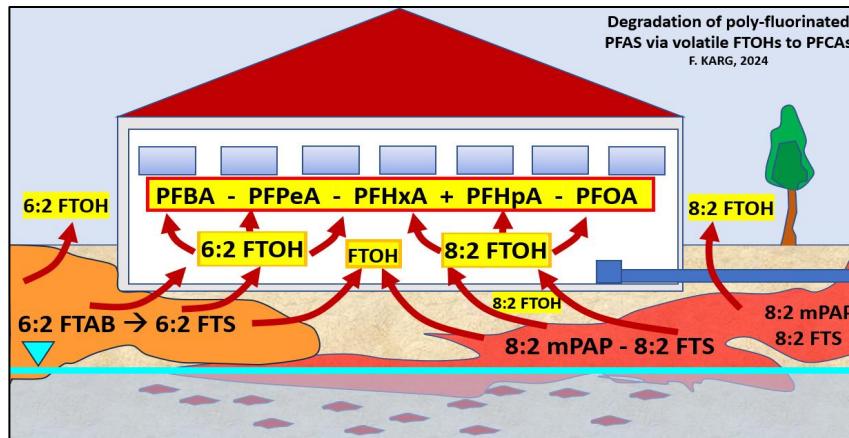
Tél : +33 (0) 607 346 916, Email : frank.karg@hpc-international.com

*Comportement environnemental de quelques polluants
importants des PFAS et des
Amines aromatiques du type Benzidine*

*Environmental Behavior of some Key-PFAS and
Aromatic Amine Pollutants of Benzidine Type*

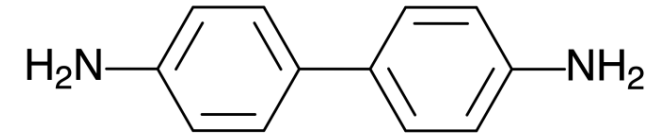
Dr. (PhD) Frank Karg / Scientific Director of HPC-Group (INOGEN JV) and
CEO-President of HPC INTERNATIONAL / France, Germany, Switzerland, Hungary, Balkan, etc.

Email: frank.karg@hpc-international.com / Phone: +33 607 346 916



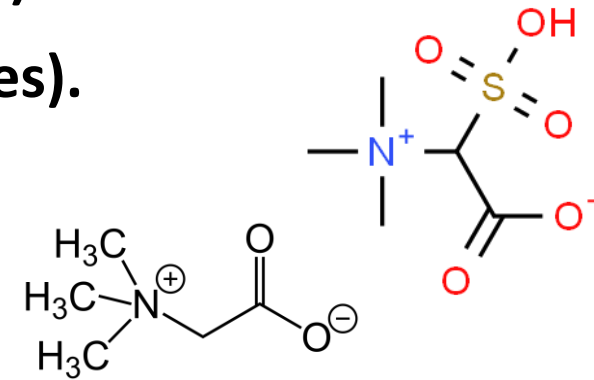
Environmental Chemistry:

- **PFAS and aromatic Amines** have strange behaviors in the environment.
- Concerning some environmental effects,
- they are **similar in chemical reactions**.
- A **comparison** is done **between some key**
- **PFAS products e.g. 6:2-FTAB and Benzidine**.
- Both pollutants are for ex. present in **contaminated groundwater under influence of (hazardous waste) Landfill leachates**.



PFAS (Fluorinated Tensioactifs) contain **hydrophile groups** (strong solubility):

- **Non-ionic** (for ex. Polyethylene glycols, Acrylamide Oligomers).
- **Anionic** (for ex., Sulfonates, Sulfates, Carboxylates, Phosphates).
- **Cationics** (for ex., Quarternary Ammonium).
- **Amphoters** (for ex., Betaines & Sulfo-betaines): base + acid.



- Commercial products mainly contain mixtures.
- The long chain fluoro-telomeres (> C₈) used as substitutes for PFOS (prohibited) and PFOA are transformed into PFOA in the subsoil.
- Short-chain PFAS' (< C₆) can't be transformed into PFOA or PFOS.

Environmental Behavior of some Key-PFAS and Aromatic Amine Pollutants of Benzidine Type

In
minimum
33
Categories

1. Perfluoroalkane-sulfonic-acids (PFASs),
2. Perfluoroalkane-sulfonats (salts),
3. Perfluoroalkane-sulfinic-acid/sulfonates,
4. Perfluoro-cycloalkane-sulfonic-acids & derivats,
5. Perfluoroalkane-sulfonamids (FASAs),
6. Perfluoroalkane-sulfonamide & quaternary ammonium salts,
7. Acrylate de perfluoroalkane-sulfonamide (MeFASACs),
8. Perfluoroalkane-sulfonamide methylacrylates,
9. Perfluoroalkane-sulfonamide phosphates,
10. Perfluoroalkane-sulfonyl halogenureas,
11. Different polyfluoroalkyl-sulfur compounds,
12. Perfluoroalkyl-carboxyl-acids (PFCA),
13. Perfluoroalkyl-carboxyl-acids,
14. Perfluoroalkyl-alcohols/cetones,
15. Halogenurea perfluoroalkyl-carboxylic acids,
16. Perfluoroalkyl-halogenureas,
17. Perfluoroalkyl-ethers,
18. Perfluoroalkyl-amines,
19. Perfluoroalkyl-amino-acides/salts/esters,
20. Perfluoroalkyl-phosphates,
21. Perfluoroalkyl-acrylate,
22. Perfluoroalkyl-methacrylates,
23. Other Perfluoroalkyl-carboxylic esters,
24. Perfluoroalkyl-heterocyclic Compounds,
25. Perfluoroalkyl-silanes,
26. Fluorotelomer-alcools,
27. Fluorotelomer halogenides,
28. Fluorotelomer sulfonates, sulfonyl chlorides and sulfonamides,
29. Fluorotelomer Acrylates,
30. Fluorotelomer Methylacrylates
31. Other Fluorotelomer Acrylates
32. Fluorotelomer phosphates,
33. Other fluorotelomers.

**In total > 9 000 – 12 000 PFAS
are existing !**

Environmental Behavior of some Key-PFAS and Aromatic Amine Pollutants of Benzidine Type

Production & Use since 1960

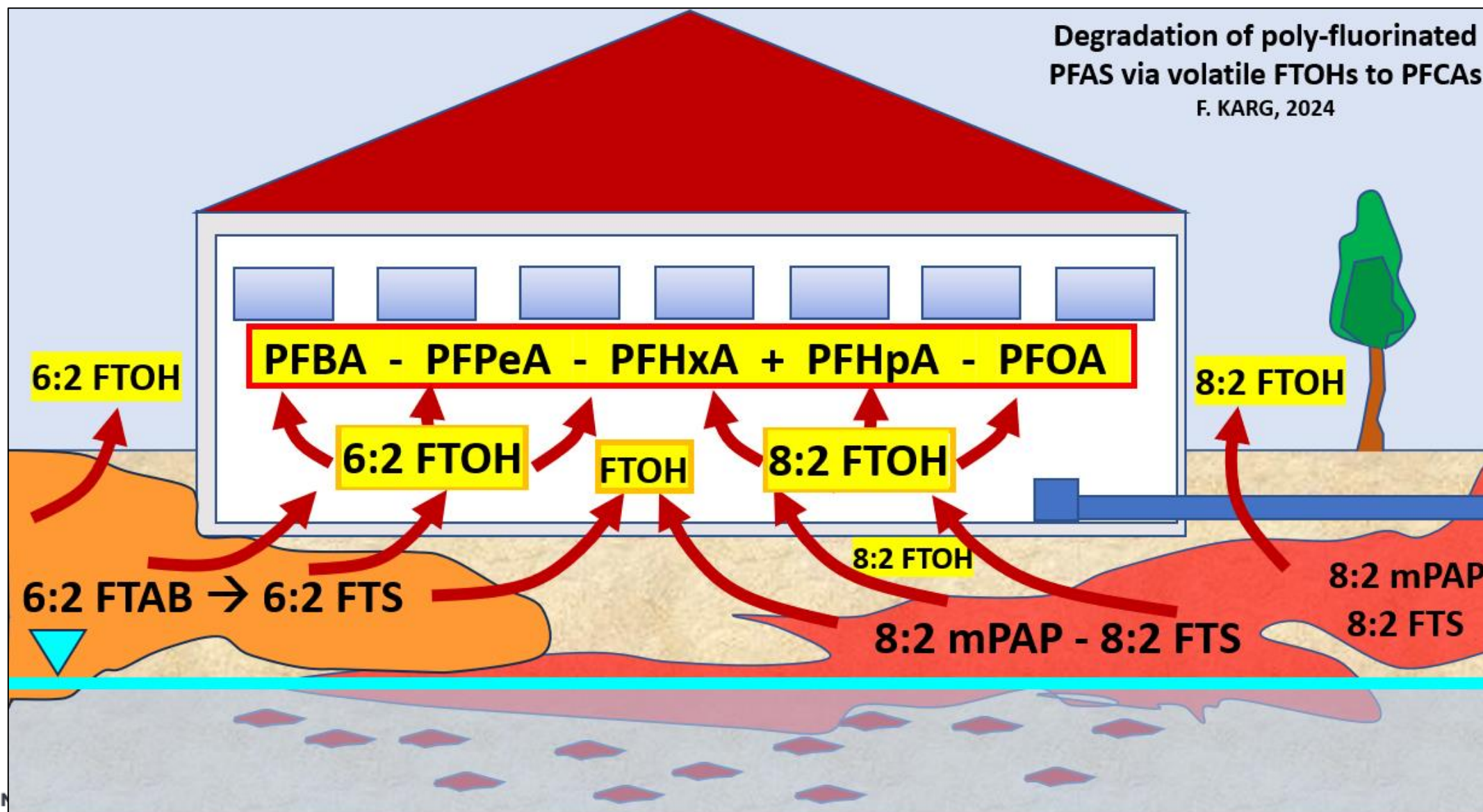
- Galvanization
- Production of Textiles
- Food Packaging (Polymers)
- Surface treated Papiers & Cartons
- Refineries, Photographic Industry
- Construction material (Concrete = Beton):
for ex. C_8 - C_{20} -gamma-omega-perfluoro Thiols)
- Paints, Inks & Lacs
- Electronic modules & semi-conductors
- Hydraulic Oils
- Production of Teflon (Fluoropolymers)
- Fire Fighting Foams (AFFF)



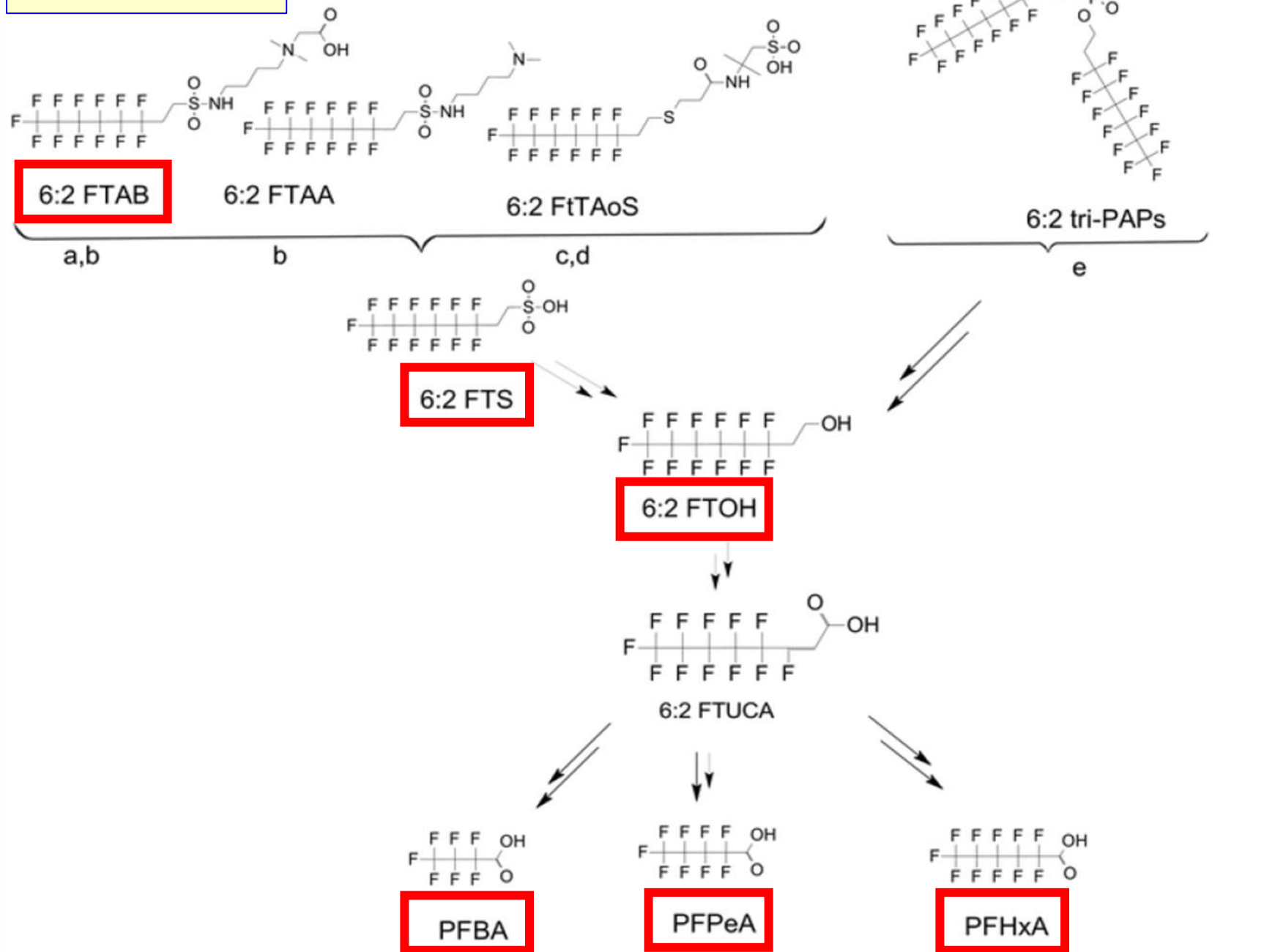
Use of Fire Fighting Foams (AFFF) on former French Air Base BA 103 (700 ha)



Environmental Behavior of some Key-PFAS and Aromatic Amine Pollutants of Benzidine Type



6:2-FTAB



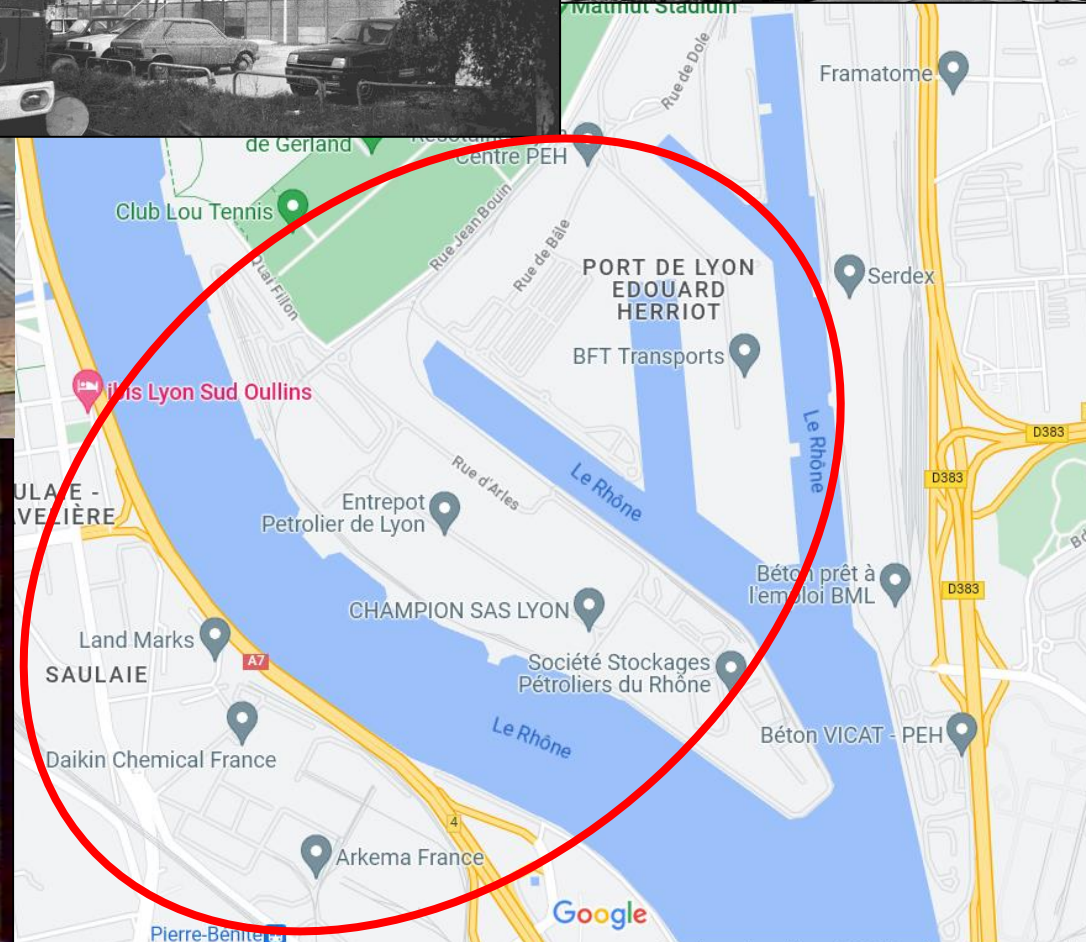
**6 :2 FTAB:
Degradation
via 6 :2 FTS and 6 :2
FTOH to per-
fluorinated PFBA,
PFPeA & PFHxA**

(LaFond et al. 2023, D.M.J.
Shaw et al. 2019 ,Ying Shi,
2018 and V. Mendeza et. al.
2022)

Environmental Behavior of some Key-PFAS and Aromatic Amine Pollutants of Benzidine Type

Fire event Harbor Edouard-Herriot

1987





Bentel et al. 2019 & Masruck, A. et al. 2020)

Ultrashort PFAS:

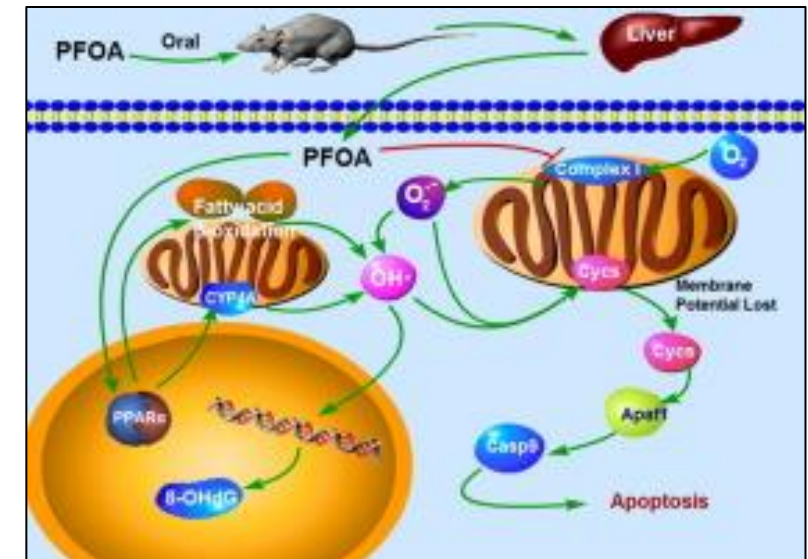
- **TFA: Trifluoro acetic acid:** CAS: 76-05-1
- **TFMS: Trifluoro methane sulfonic acid:** CAS: 1493-13-6
- **PFES: Penta(per)fluoro ethane sulfonic acid:** 354-88-1
- **PFPrA: Perfluoro propanonic acid:** CAS: 422-64-0
- **PFPrS: Perfluoro propane sulfonic acid:** CAS: 423-41-6

TFA

Toxicology: PFAS

Eg. PFOA et PFOS:

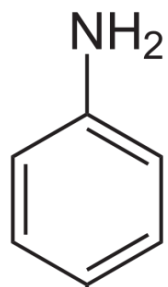
- **Endocrine disruptors** (on the production of steroid hormones, such as reduced testosterone levels, etc.): PFOS + FTOH (Fluorotelomeric alcohols),
- **Carcinogenicity:** Breast & Testicular Cancer Developments (PFOA + PFOS: Apoptosis Suppression),
- **Teratogenicity** (eg.: levels of androgens or abnormal thyroid hormones, etc.),
- **Immunotoxicity** (via thyroid effects and on the immune system),
- **Neurotoxicity** (hyperactivity disorders, etc.).



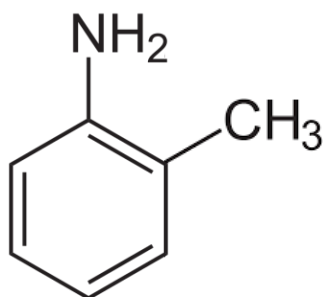
Molecular mechanisms of PFOA-induced Toxicity

Aromatic Amines (Anilines, Toluidines, Benzidines, etc.)

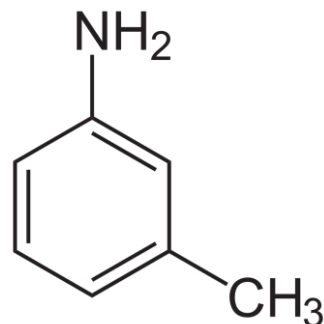
➤ **Cationics** (for ex., Quarternary Ammonium).



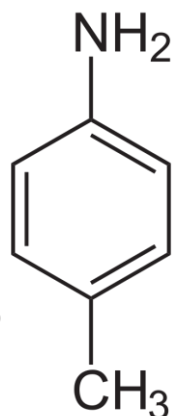
Aniline



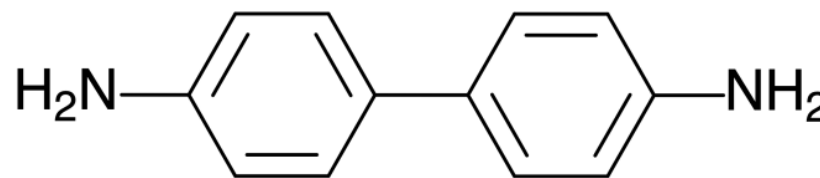
o-Toluidine



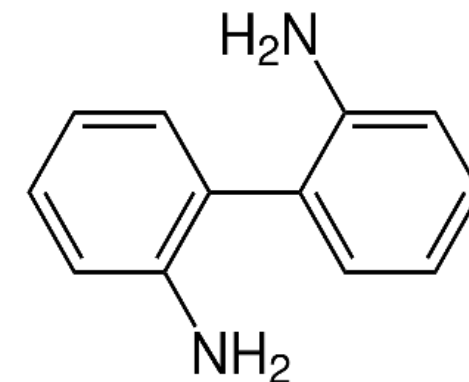
m-Toluidine



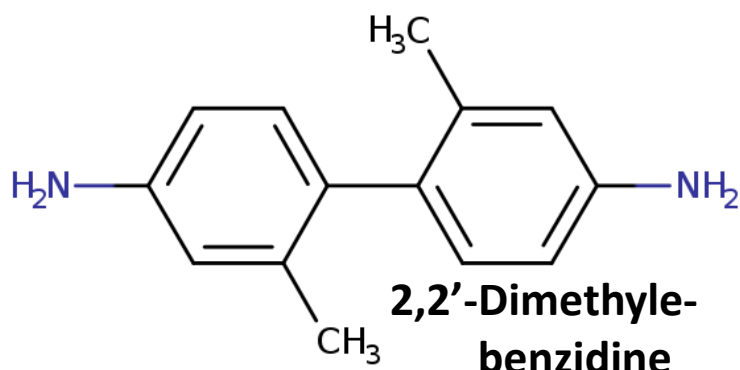
p-Toluidine



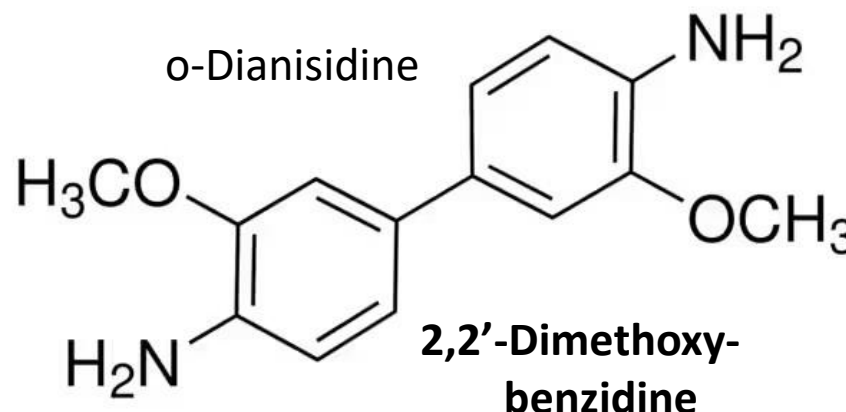
Benzidine



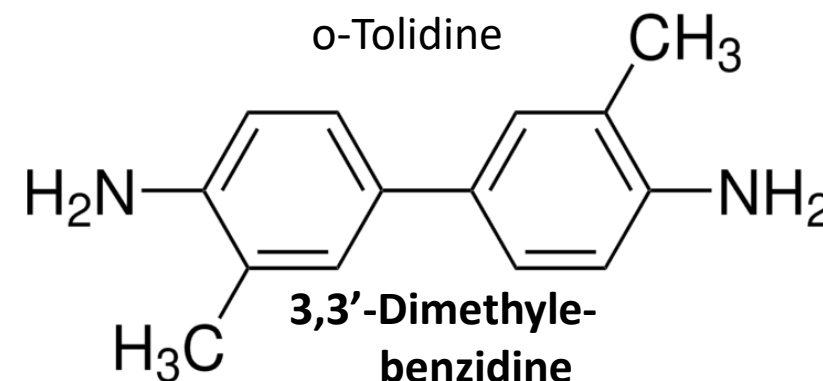
2,2'-Diamino-biphenyle



2,2'-Dimethylebenzidine



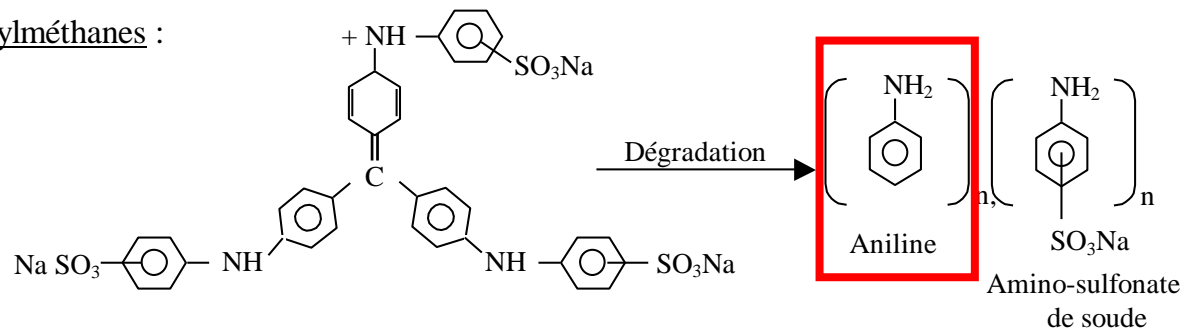
2,2'-Dimethoxybenzidine



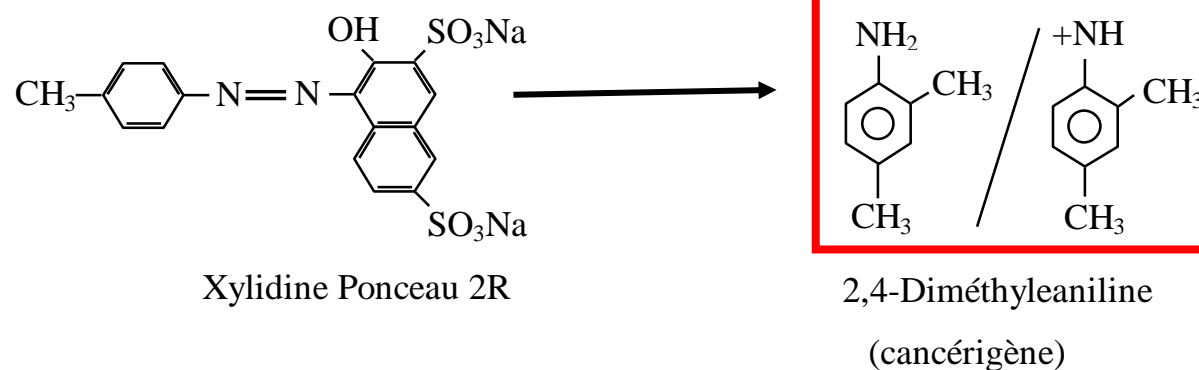
3,3'-Dimethylebenzidine

Environmental Behavior of some Key-PFAS and Aromatic Amine Pollutants of Benzidine Type

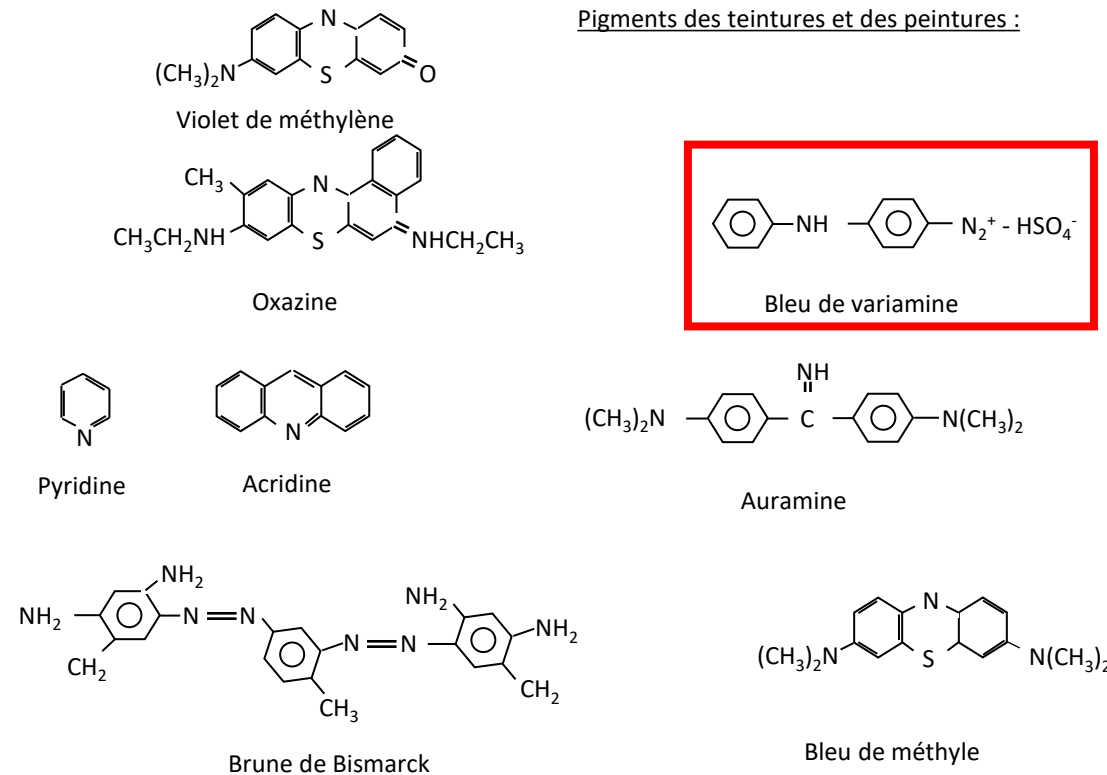
Triarylméthanés :



Exemple de dégradation par hydrolyse du xylidine Ponceau 2R :

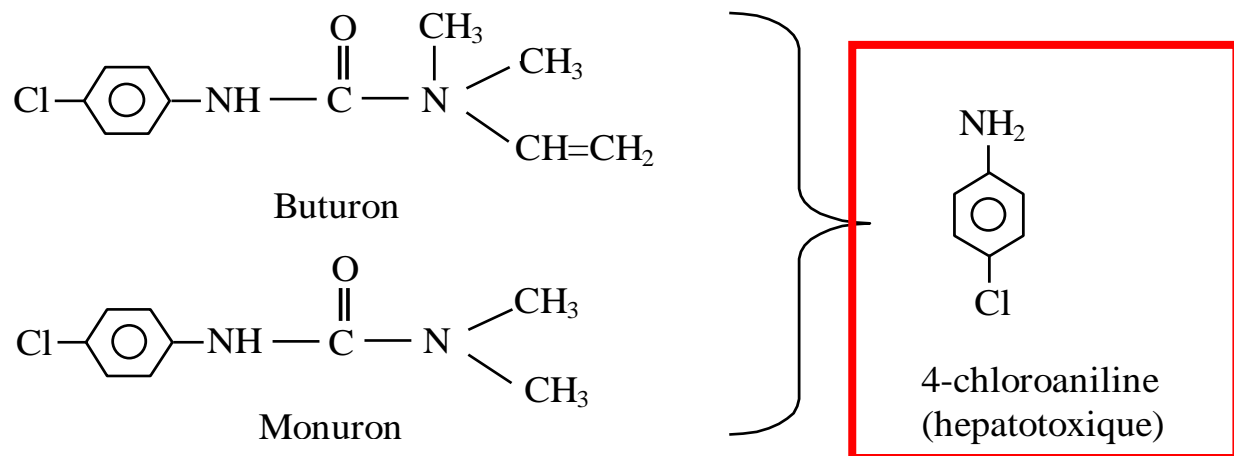
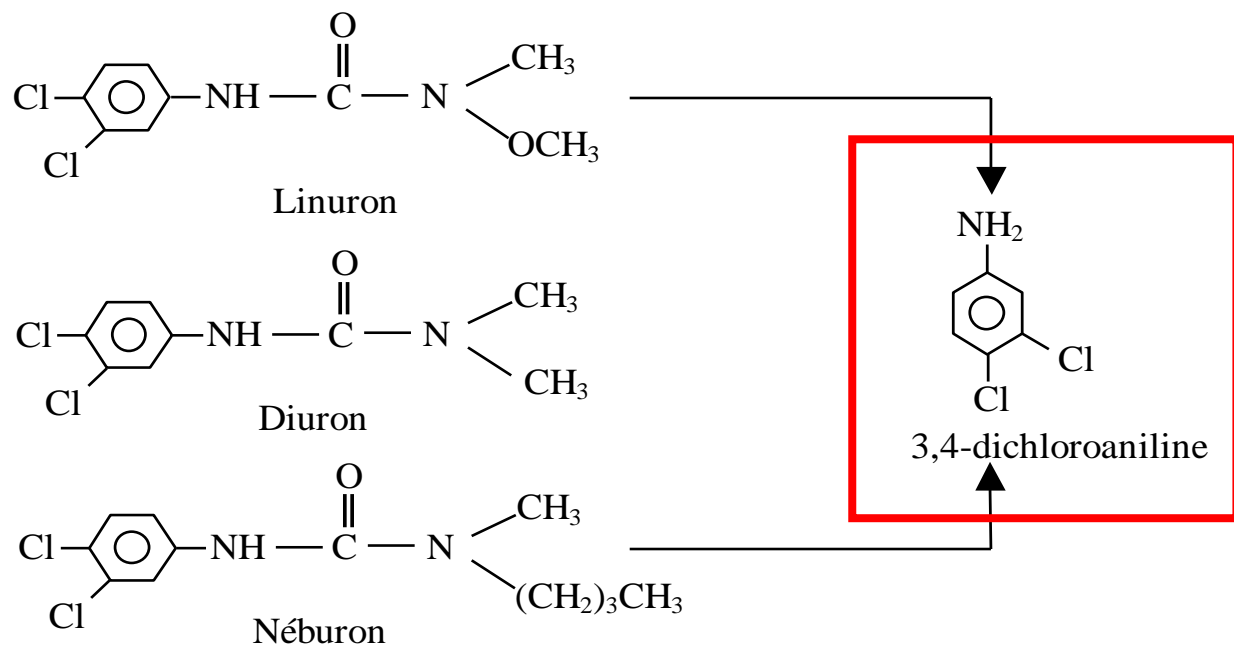


Pigments des teintures et des peintures :



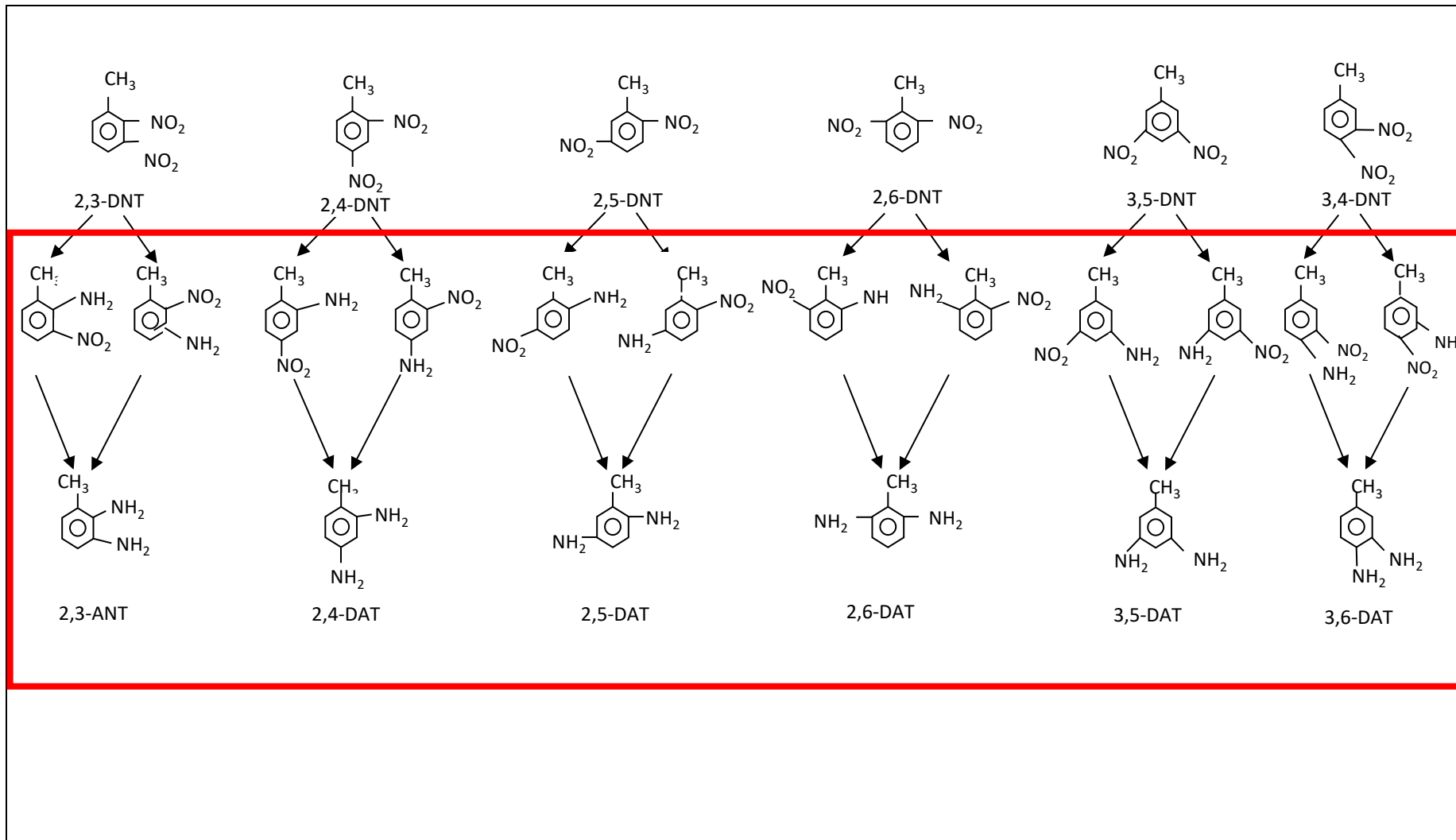
Toluidines & Dimethylanilines from Hydrolysis of Azo-Pigments

Environmental Behavior of some Key-PFAS and Aromatic Amine Pollutants of Benzidine Type



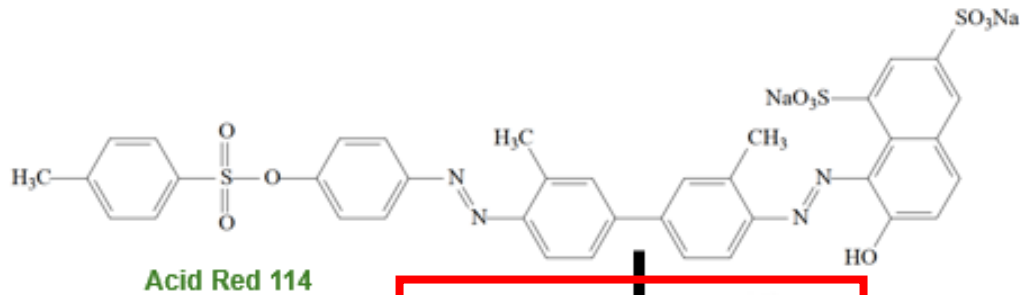
***Chloro-anilines from
Pesticides'
Hydrolysis
(Phenylureas &
Carbamates)***

Environmental Behavior of some Key-PFAS and Aromatic Amine Pollutants of Benzidine Type

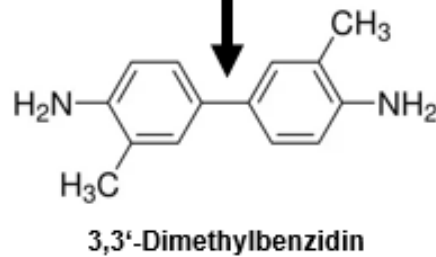


***Amino-nitro- &
Diamino-
toluines from
Explosifs
(Nitro-
aromatics)
Anaerobic
micro-
biological
Degradation
(DNTs)***

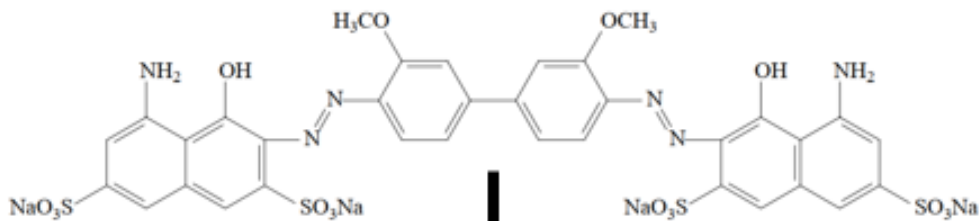
Environmental Behavior of some Key-PFAS and Aromatic Amine Pollutants of Benzidine Type



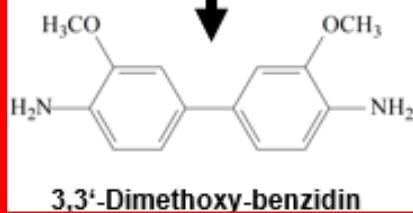
Acid Red 114



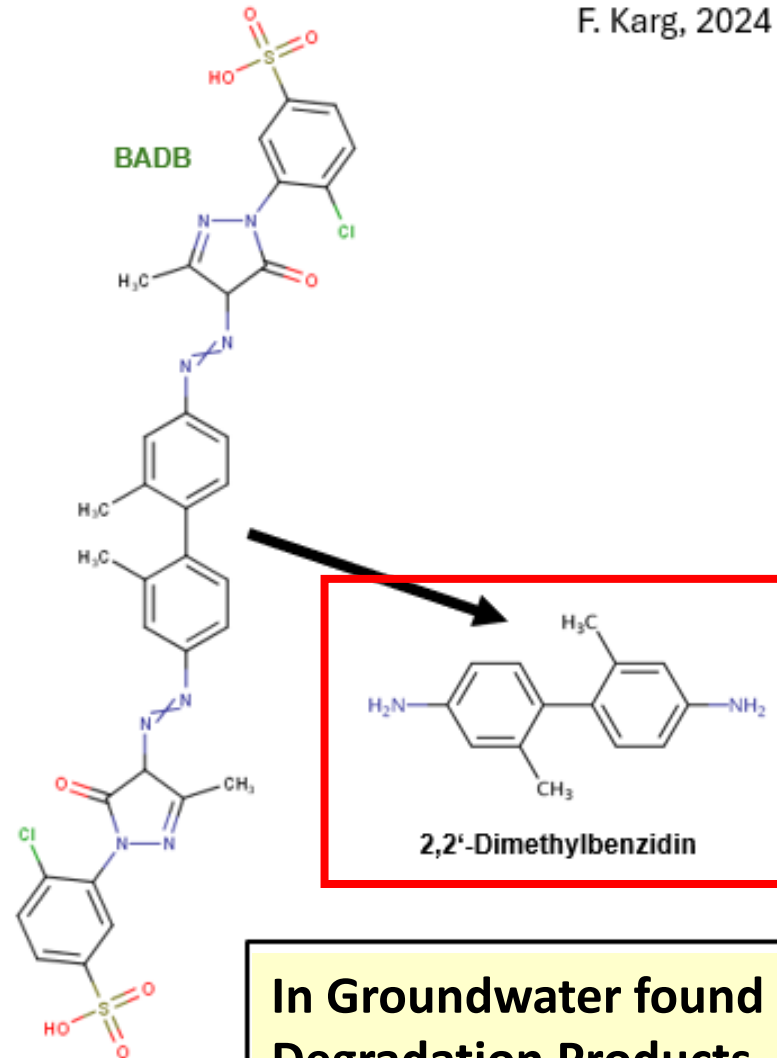
3,3'-Dimethylbenzidine



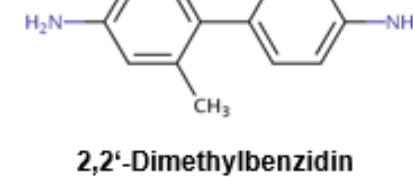
Direct Blue 15



3,3'-Dimethoxy-benzidine



F. Karg, 2024



2,2'-Dimethylbenzidine

In Groundwater found
Degradation Products

***Benzidines
from Azo-
Dyes & Azo-
Pigments***

*(Textiles, Leather,
Wood, Inks, Paints,
Cosmetics, etc.)*

HPC 
HPC INTERNATIONAL SAS

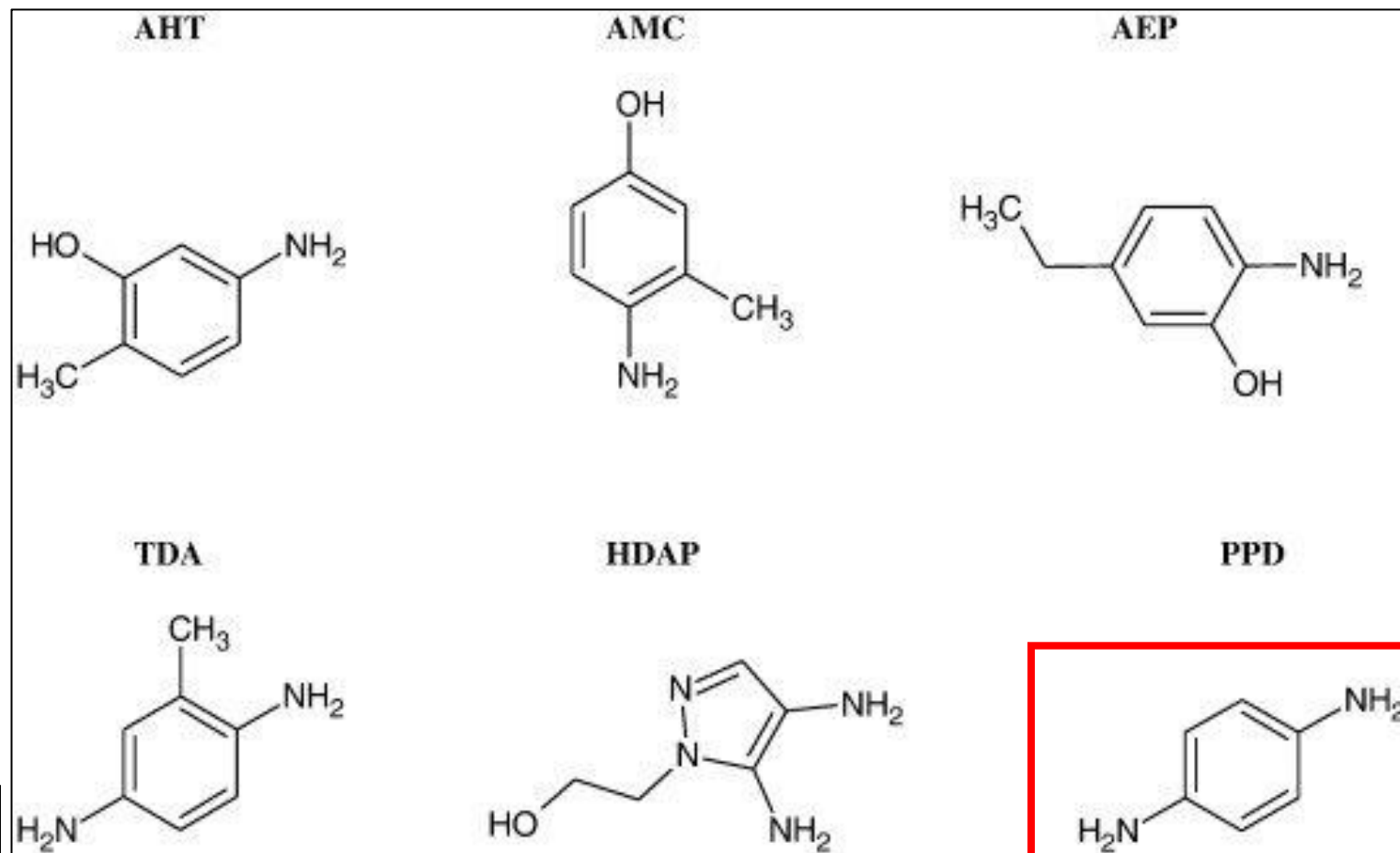
The diagram illustrates the metabolic pathway of benzidine, starting from the parent compound and branching into various degradation products. The products are categorized by their stability and whether they have been measured or are theoretical.

- Measured and proven substances (Gemessene & nachgewiesene Stoffe):**
 - 3,3'-Diamino-benzidin
 - 2,2'-Diamino-biphenyl
 - 3-Amino-biphenyl
 - 4-Amino-biphenyl
 - 4-Hydroxy-phenylamin
 - Anilin
 - 1-Amino-2-hexen
 - Mineralisierung
 - Phenol
 - Catechol
 - 2-Ethylhexan-1-ol (2-Ethyl-1-hexanol)
 - Mineralisierung
- Measured but less stable substances (Gemessene aber weniger stabile Stoffe):**
 - o-Benzidin
 - para-Semidin (4-Aminodiphenylamin)
 - ortho-Semidin (2-Aminodiphenylamin)
- Measured but not stable substances (Gemessene aber nicht stabile Stoffe):**
 - 2,4'-Diamino-biphenyl (Diphenylin)
 - 3-Hydroxy-benzidin
 - 4-Amino-4'-hydroxy-biphenyl
 - 4,4'-Dihydroxy-biphenyl
 - 3,3'-Dihydroxy-benzidin
 - Hexa-2,4-dien-4-phenyl-1,6-Dicarboxylsäure
 - 2-Acetyl-4-methylen-5-Anilin-1-pentansäure
- Presumed intermediate products (Vermutete Zwischenprodukte der Fachliteratur):**
 - N-Hydroxy-benzidin
 - 4-Amino-4'-nitro-biphenyl
 - N,N'-Dihydroxy-benzidin
 - 4,4'-Dinitro-biphenyl
 - N,N'-Diacetyl-benzidin
 - 4-Nitro-biphenyl
- Theoretical synthesis impurities (Berichtete theoretische Synthese-Verunreinigungen):**
 - 3-Hydroxy-benzidin
 - N-Hydroxy-benzidin
 - 4-Amino-4'-nitro-biphenyl
 - N,N'-Dihydroxy-benzidin
 - 4,4'-Dinitro-biphenyl
 - N,N'-Diacetyl-benzidin
 - 4-Nitro-biphenyl

F. Karg, 2024

Toxicology: Aromatic Amines: Amino-Benzenes, -Biphenyls, -Toluidines, Benzidines, etc.

- Aromatic amines : For Production of Textiles & Leather Azo-Dyes, Paper Pigments, Inks, Rubbers, Plastics, Cutting oils, Pesticides, Cosmetics, etc.
- Well-established causes of Bladder Cancer and one of the first Carcinogens to be associated with an occupational exposure.
- Environmental Pollution (Soil and Surface - & Ground-water) by Dye Waste Landfills, Wastewater, Textile & Paper Production.



Leaching Increasing or Reduction of of some PFAS-Fluortelomeres by pH-changing

Example: Seawater Intrusion into the Aquifer (HH): Analyses according DIN 38407-42

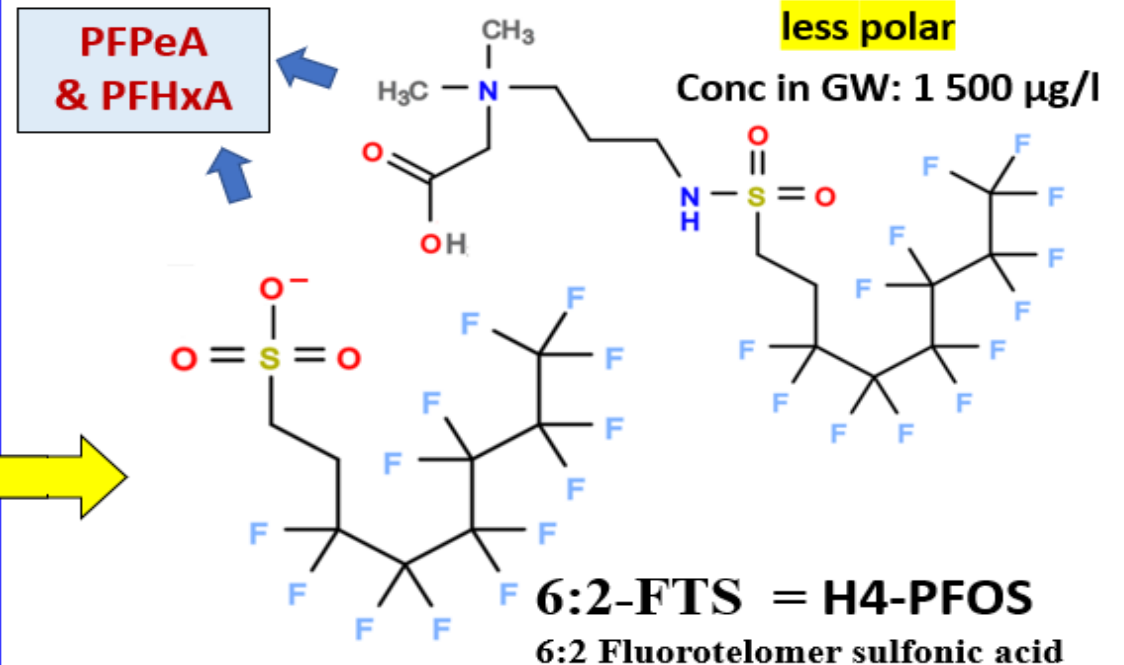
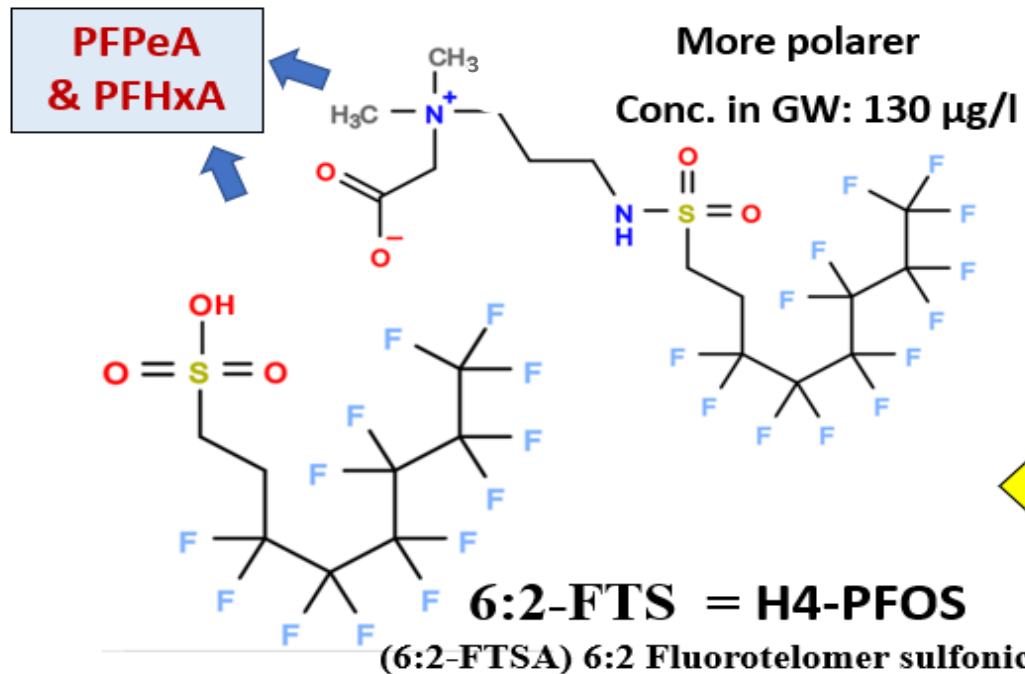
pH 6,7

→ zu →

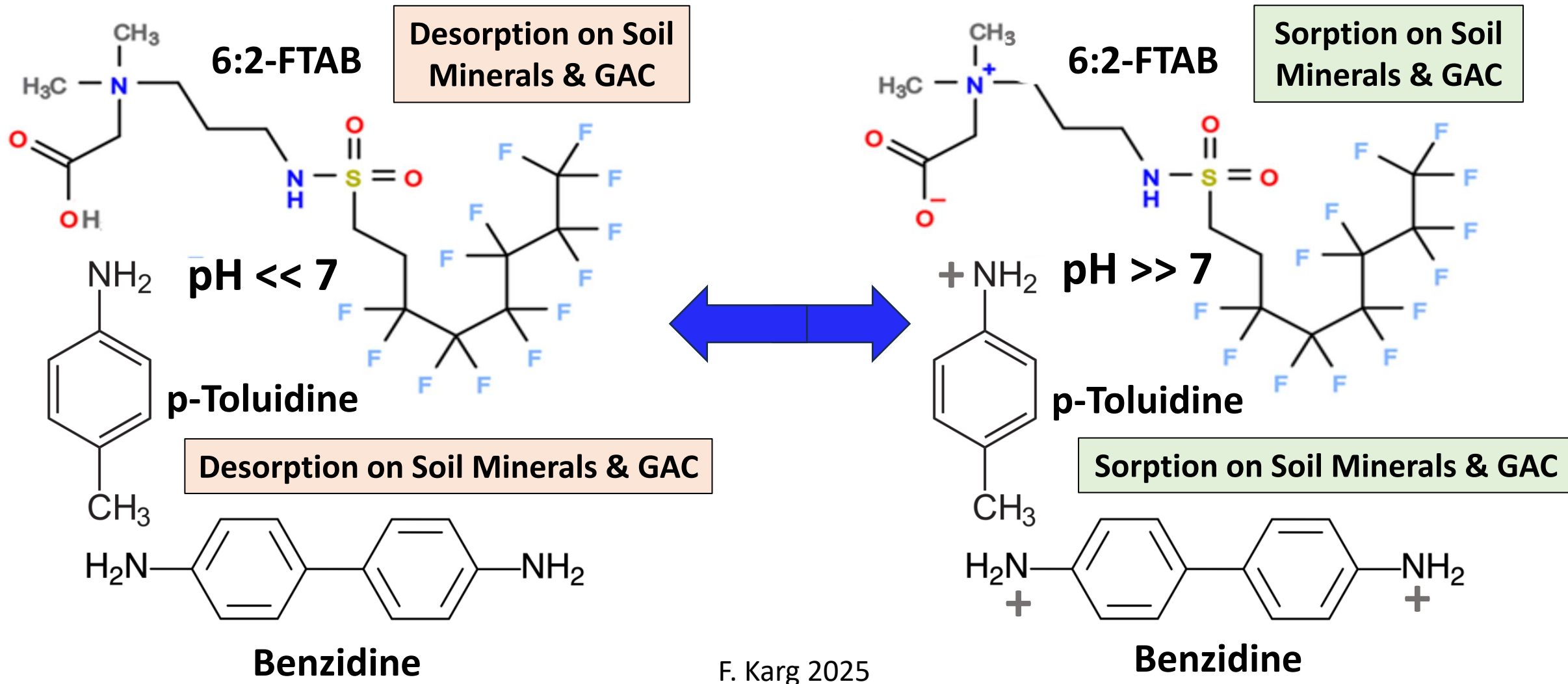
pH 7,3

6:2-FTAB = Capstone B (AFFF)
6:2 Fluorotelomer-sulfonamid-propyl-betain

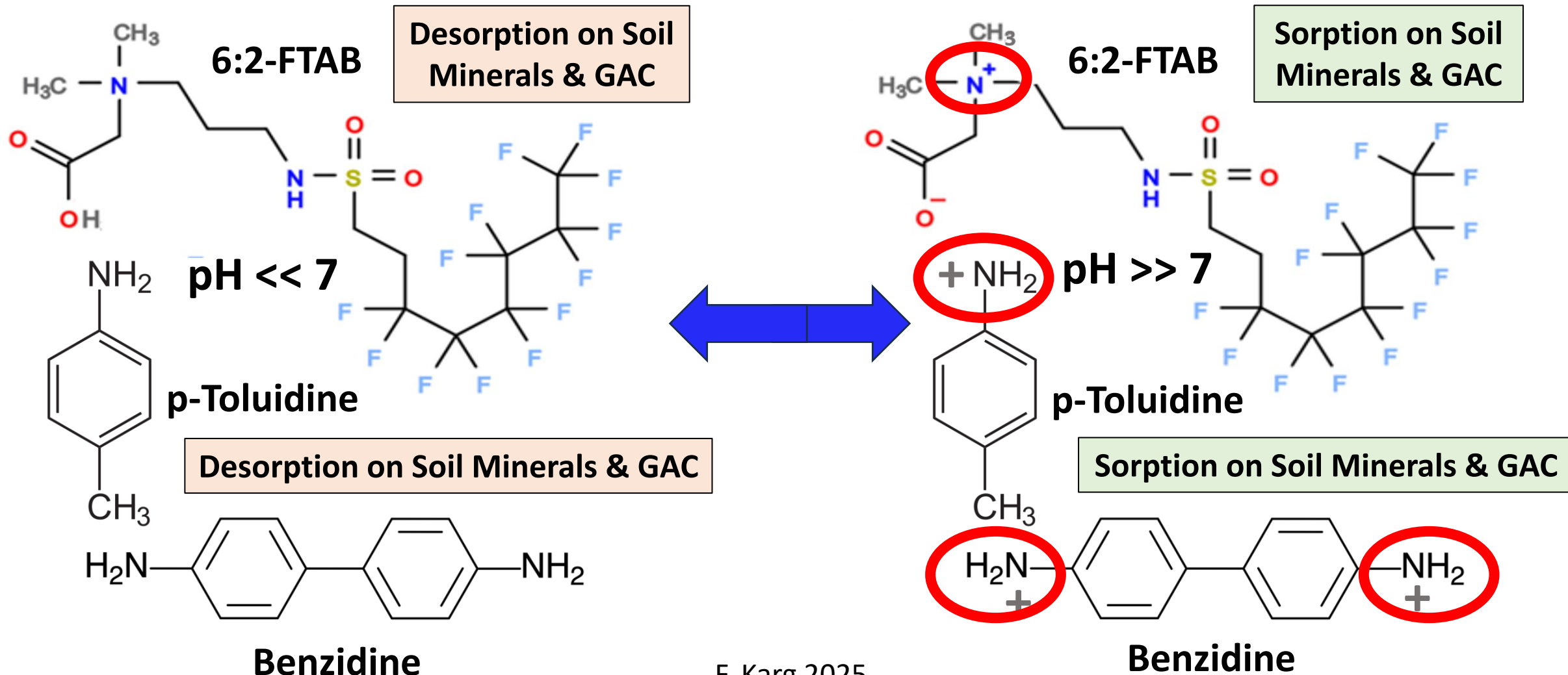
6:2-FTAB = Capstone B (AFFF)
6:2 Fluorotelomer-sulfonamid-propyl-betain
Factor 11,5 x higher Concentrations



Polarization of PFAS-Sulfonamide-betaines and aromatic Amines at alkaline pH



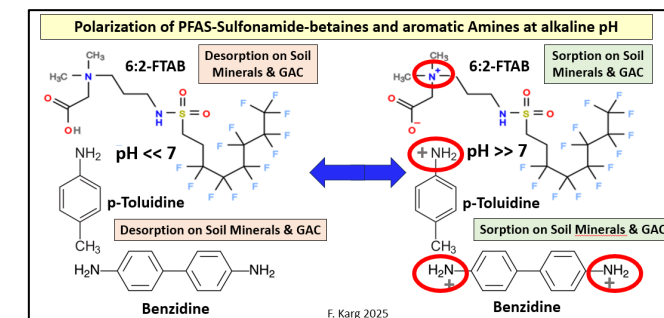
Polarization of PFAS-Sulfonamide-betaines and aromatic Amines at alkaline pH



Conclusion:

Contact: frank.karg@hpc-international.com

- About 2 000 PFAS of > 12 000 are **Sulfonamid-betaines under strong pH Influence.**
- **All Aromatic Amines** are under strong pH Influence.
- **Chemical Analysis must be done under slight alkaline conditions, otherwise Extractions, Detection and Site Investigations are nearly impossible.**
- If slight acid pH change to (slight) alkaline pH conditions, Polarization will be neutralized, **and Desorption will be happened. Sulfonamid-betaines PFAS and aromatic Amines will do Desorption from Soil & GAC to Water.** Aromatic Amines could even be volatilized **to Soil gas and Ambient Air.**
- **The pH-Dependent Environmental Chemistry Behavior of those PFAS and Aromatic Amines must be considered in Pollution Investigations, Risk Assessment and Remediation.**



Management of PFAS: Per- & Polyfluoro-Alkyl Substances: Environmental Contaminations & Health Risk

Thank You !

Questions? Remarks? Requests?

Dr. (PhD) Frank Karg / Scientific Director of HPC-Group (INOGEN JV) and
CEO-President of HPC INTERNATIONAL / France, Germany, Hungary, Balkan, etc.

Email: frank.karg@hpc-international.com / Phone: +33 607 346 916

