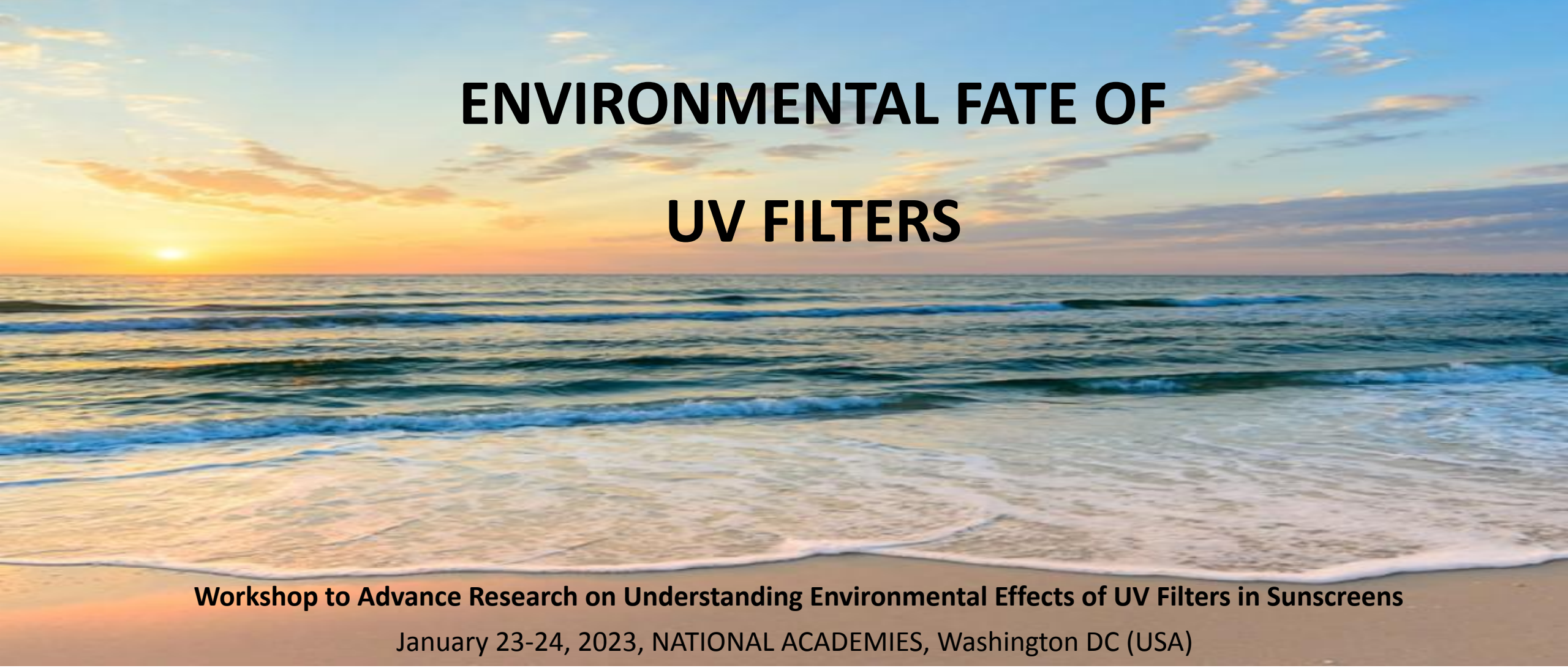

ENVIRONMENTAL FATE OF UV FILTERS

Workshop to Advance Research on Understanding Environmental Effects of UV Filters in Sunscreens

January 23-24, 2023, NATIONAL ACADEMIES, Washington DC (USA)

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- Exposure for any receptor is impacted by the **interaction** of UVFs with the environment.
- UVFs undergo several **processes** once released to the environment.
- The **physico-chemical** properties of UVFs in combination with **environmental factors** drive those processes, ultimately defining **where** UVFs may reside, how long they will **persis**t, and whether they will **degrade** into other products (TPs).

SOURCES AND PATHWAYS OF UV FILTERS INTO THE ENVIRONMENT

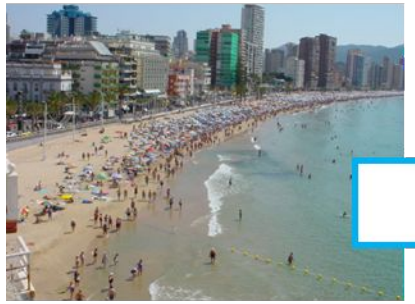
Rain

Direct entry

Indirect entry

Recreational activities

Domestic and industrial use



Bath

Transference (clothes, towels)

Percutaneous absorption and excretion

Bath (shower)

Industrial discharges

ENVIRONMENT

WWTPs

SOURCES AND PATHWAYS OF UV FILTERS INTO THE ENVIRONMENT

Direct release of UV Filters during Surface-Water contact activities

- **Many studies**
- Concentrations of some UV filters have been **correlated** with the **time, location, season and intensity of recreational activities.**

Direct release of UV Filters from Stormwater

- **No studies** have systematically measured stormwater concentrations of **organic UV filters**, and there are **limited studies** on **inorganic UV filters**.

Indirect release of UV Filters by WWTPs discharges

- **Many studies** reporting the extent of **organic UV filter removal** at centralized wastewater treatment plants (WWTPs).
- **No studies on inorganic UV filters**, as they do not biodegrade.

SOURCES AND PATHWAYS - REMARKS

- **Measured concentrations do not necessarily reflect UV filters solely from sunscreen** since they are present in a range of products, (cosmetics, hair products, paints,..) being the category of product most likely to have **similar fates as sunscreens.**

- The influence of the **hydrography** of a given location is not usually considered. Assessing risk will require inclusion of the unique **dynamics of the water bodies considered**. These dynamics may include **residence time** of the waterbody, **rates of mixing and directionality** (currents and downstream transport), **vertical stratification** of the water column, and **sediment type and patterns of sediment movement.**

- **Stormwater** is the "invisible" pathway, **lack of studies for both organic and inorganic** UV filters.

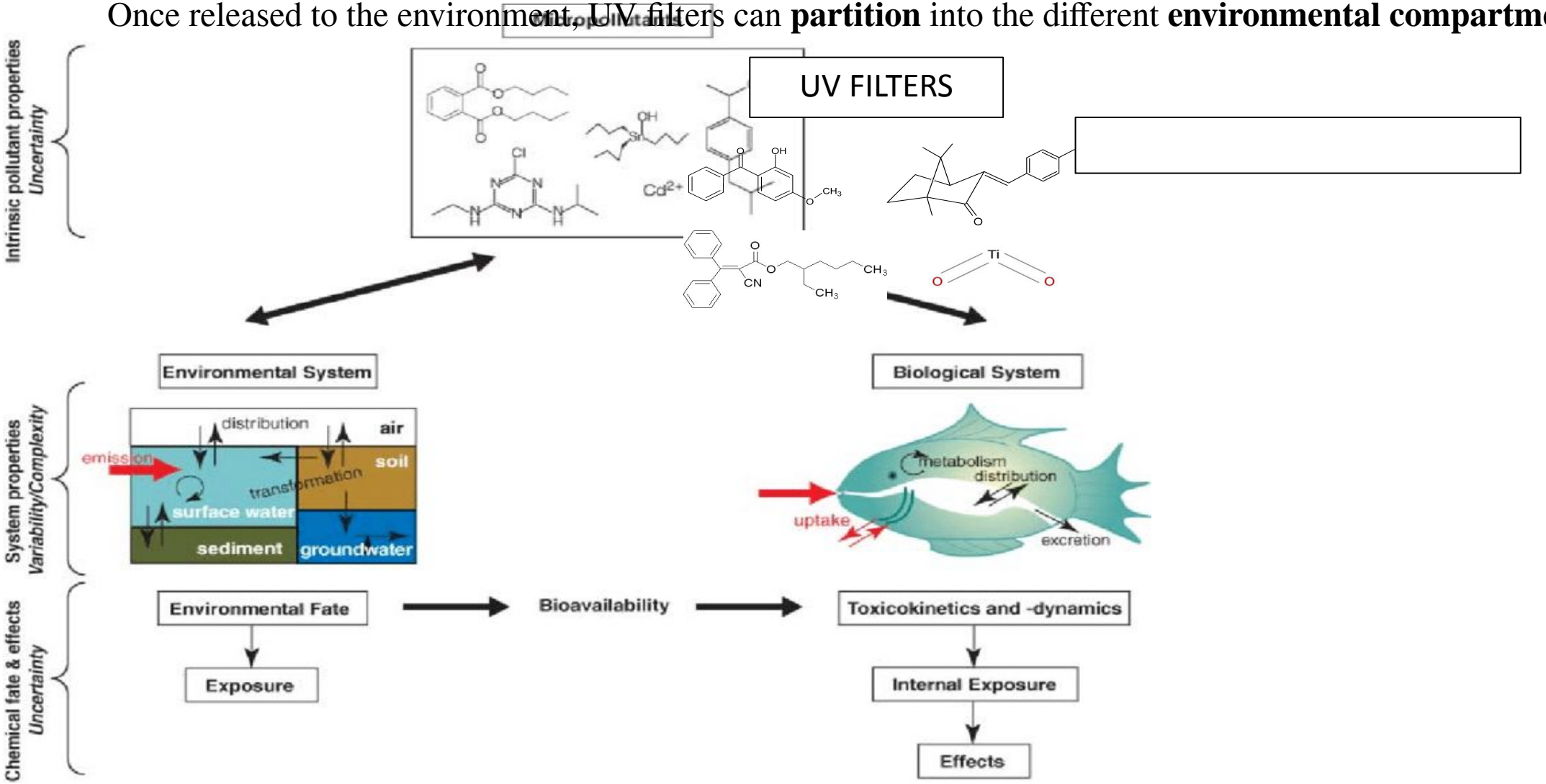
- **Inorganic UV filters occur naturally in water and sediments hindering measurements** of the incremental contribution from sunscreens.

- Difficult to consider input from unidentified **illegal dumping.**

- **Disinfection by-products** of **organic UV filters released by WWTPs should be studied; chlorinated and brominated** derivatives have **high potential to be toxic.**

FATE CHARACTERISTICS OF UV FILTERS

Once released to the environment, UV filters can **partition** into the different **environmental compartments.**

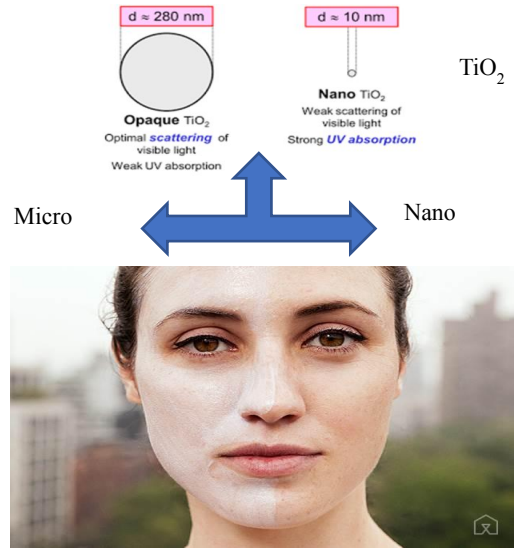


Adapted from Science 313, 1072 (2006); René P. Schwarzenbach, et al. Systems The Challenge of Micropollutants in Aquatic Systems. DOI: 10.1126/science.1127291

1. Solubility in water (S)

- For organic UV filters, reported values are usually in **pure (deonized) water, 25°C**. (Maximum solubility).
- Testing conditions for "**freshwater solubility**" or "**saltwater/marine solubility**" are **not standardized** leading to **high variability** in these **predictions** and/or **measurements**. (Lower than in pure water, less in freshwater and much less in saltwater).
- Solubility for some **organic UVF** can also vary with **temperature and the pH of the medium for ionogenic compounds-pKa (additional factors).** Ionic forms favour solubility, neutral tend to adsorb.

- As metal oxide particles, **inorganic UV filters** tend to **aggregate** with other particles or colloids in water, including bacteria, algae, clays, and mineral oxides.
- Some studies highlight the **importance of surface coatings** in controlling the release and fate of TiO2 particles into the environment.
- ZnO undergoes dissolution to release zinc ions. The **dissolution rate of ZnO** is impacted by the **particle size** and **morphology** as well as the **media. Lower pH levels favours its solubilization**
- **Inorganic UV filters** are used in both **nano (< 100 nm) and macro sized** forms in sunscreens (there is no distinction in their regulation by FDA, but it exists in EU). **Increased use of nano-size**.



2. Volatility (Henry's Law constant, KH)

- For **organic UV filters**, in light of the low vapor pressures and moderate to low solubilities, losses to the atmosphere may be **negligible.**
- **Inorganic UV filters are not volatile**.

3. Dissociation (Acid dissociation constant, Ka)

- **Wide range** of pKa **for organic UV filters.**
- Besides **pKa** informs whether an organic chemical will be neutral or ionic in a given water, the **pH of** the media **must be known**.
- The **neutral** (uncharged) form of organic UV filters is usually the **more toxic,** and the **more bioaccumulative.**
- **Inorganic UV filters do not dissociate.**

4. Adsorption:
Hydrophobicity and lipophilicity (octanol-water partition constant, pKow)

- Distribution constant, **Kd,** generally used. But, more appropriate to use **Koc** to normalize for **organic content** of the solid or **Dow,** which is **Kow pH dependent,** for **ionogenic organic UV filters**.
- **Few studies** on **organic UV filters** adsorption, mainly **to sediments.**
- Information on **non-settling particles** (i.e., suspended solids including phytoplankton) or **surface microlayer** (SML) is much more limited.
- A new phase of interest: **Microplastics.**
- **Adsorption onto Inorganic UV filters.** Natural organic matter and other dissolved chemicals that may change their surface charge characteristics (and thus adsorption capacity).
- **Inorganic UV filters** can **aggregat**e with each other (homoaggregation) or with other suspended solids leading to larger particles that can **settle out of the water column**.

FATE CHARACTERISTICS OF UV FILTERS: ENVIRONMENTAL PROCESSES (I)

1. Physical processes: transport and adsorption.

2. Chemical processes: Acid-base, precipitation, oxidation/reduction and **PHOTOTRANSFORMATION.**

- **DIRECT** phototransformation
  - Production of **transformation products of organic** UV filters.
  - **Sunlight** reacts with **inorganic UV filters** in the water column and produce **reactive oxygen species**, ROS, which may initiate toxicity to organisms or transformation of chemicals.
  - Also can **change the pH of the media by generation of oxygen peroxide (H_2O_2).**

- **INDIRECT** phototranformation.
  - **UV filters and other substances may impact phototransformation of other UV filters.**

FATE CHARACTERISTICS OF UV FILTERS: ENVIRONMENTAL PROCESSES (II)

- **Most phototransformation** studies are in **organic solvents** (tests in formulations), far from **real dilute aqueous** environments.
- **Environmental factors** such as **pH and disolved organic matter**, impact **photolisis**.
- **Phototransformation products of organic UV filters** are rarely studied (occurrence and **toxic potential**).

FATE CHARACTERISTICS OF UV FILTERS: ENVIRONMENTAL PROCESSES (III)

3. Biological processess:

- **Bioaccumulation/biomagnification** (Predator/Prey):

Relationships between routes of exposure and bioaccumulation metrics.

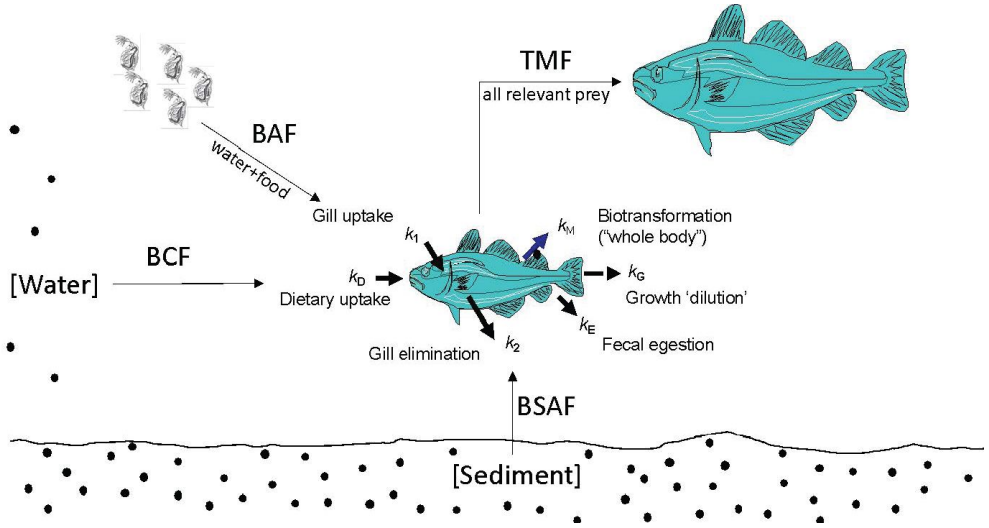
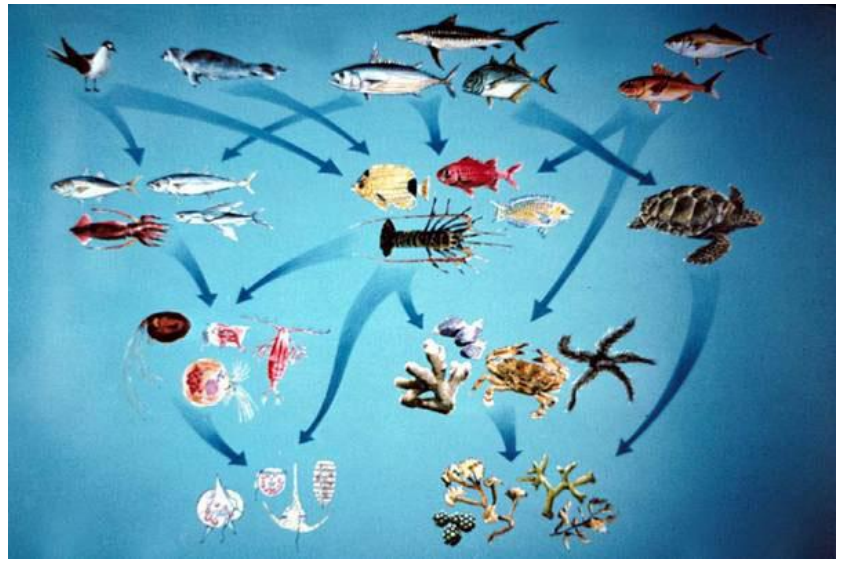


TABLE 5.1 Summary of Key Bioaccumulation Assessment Endpoints, Metrics, and Standard Calculations

Bioaccumulation endpoint	Bioaccumulation metric (units)	Calculation
BCF	$BCF_{WD/LW}$ (L-water/kg-lipid)	$C_{B\text{-}LW}/C_{WD}$
BAF	$BAF_{WD/LW}$ (L-water/kg-lipid)	$C_{B\text{-}LW}/C_{WD}$
BSAF	$BSAF_{OC/LW}$ (kg-organic carbon/kg-lipid)	$C_{B\text{-}LW}/C_{S\text{-}OC}$
BSSAF	$BSSAF_{OC/LW}$ (kg-organic carbon/kg-lipid)	$C_{B\text{-}LW}/C_{SS\text{-}OC}$
BMF	$BMF_{LW/LW}$ (kg-lipid/kg-lipid)	$C_{B\text{-}LW}/C_{D\text{-}LW}$
TMF	TMF (unitless)	e^m or 10^m



https://celebrating200years.noaa.gov/breakthroughs/ecopath/food_web_600.html

BCF = bioconcentration factor;

BAF = bioaccumulation factor;

BSAF =biota-sediment accumulation factor;

TMP = trophic magnification factor;

"k" = kinetic rate constant for the tissue or physiological compartment being addressed.

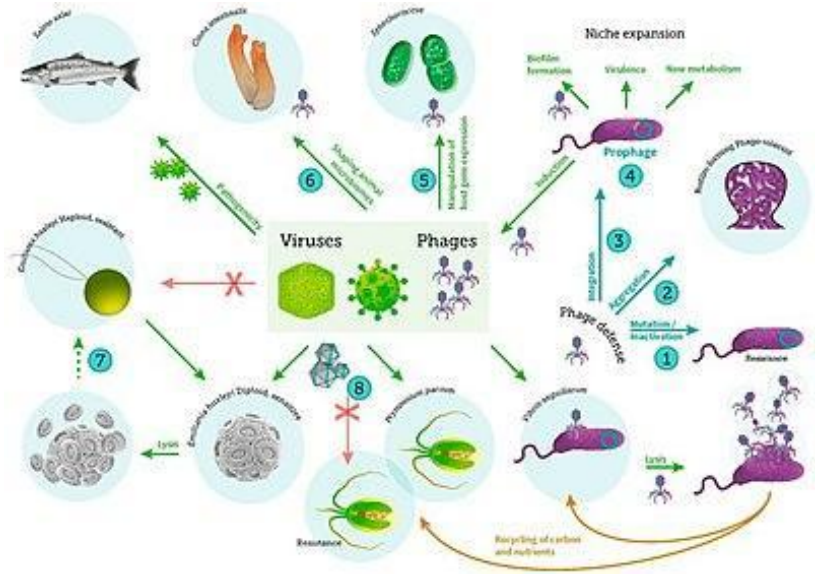
From the report (Fig. 5.1 and Table 5.1).

FATE CHARACTERISTICS OF UV FILTERS: ENVIRONMENTAL PROCESSES (IV)

3. Biological processess:

- **Biotransformation/biodegradation**: generally are **hydrolysis, oxidation, reduction** and **addition** (conjugation) reactions producing **transformation products** (metabolites and conjugates).

    - **Microorganisms**: bacteria, fungi, algae and insects. Are affected by pH (Aerobic bacteria 6,5-8,5, and Anaerobic bacteria 6.5-7.5) and temperature (5-35ºC).



From Bar-on et al., 2018.
doi:10.1073/pnas.1711842115. PMC 6016768

    - **Higher organisms:** fish, dolphins, turtles, penguins…

FATE CHARACTERISTICS - REMARKS

- The **organic UV filters** are generally **hydrophobic** (important exception, oxybenzone, that is moderately water soluble) and thus tend to partition to **organic fractions**, including particles and sediments.
- **Inorganic UV filters** are expected to **aggregate** in the water column and **deposit into sediments**. Increasing **salinity** leads to **more rapid aggregation** of particles.
- More studies on **sediments** are needed, especially for inorganic UV filters, particularly addressing **impact on soil organisms and filter feeding aquatic organisms**.
- **ZnO** does **dissolve** to zinc ions in water, after which the fate of the ions is influenced by **pH, redox potential, solids, and anions** present in the water.
- **Limited** data exists on the role of coatings (aluminum, silica, polydimethylsiloxane) applied to **inorganic UV filters** on aggregation or dissolution.
- Several studies of **biodegradation and photostability in laboratory settings.** However, empirical evidence of processes reaction rates **in the environment** is limited.
- **Laboratory settings do not accurately recreate environmental conditions (ex. pH and temperature).**
- Some UV filters and/or their **metabolites** were found to be present in tissues of aquatic **animals and plants.**
- **Transformation products also bioaccumulate**, toxicity evaluations are needed.
- **Biomagnification is poorly** studied, despite some authors suggest it.
- Biodegradation by aquatic **microorganisms** is not explored, and very few data from soil organsims (fungi).

ENVIRONMENTAL OCCURRENCE

CONCENTRATIONS IN WATER AND SEDIMENT

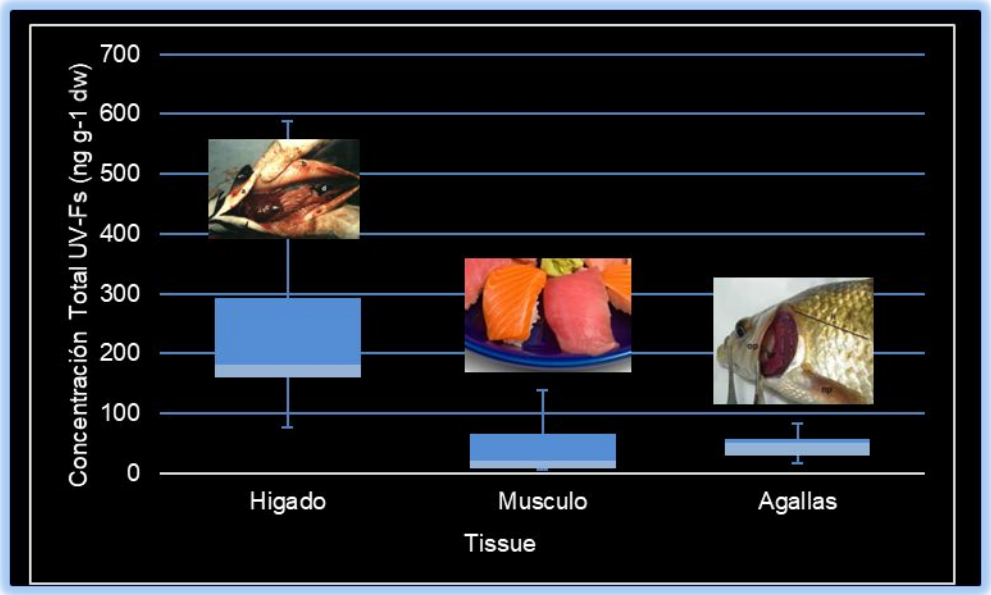
- Measurements are typically **snapshots in space and time**.
- Predicted (modelled) and experimental concentrations of UV filters reflect **spatial and temporal variability.** Maximum measured concentrations occur in **shallow waters, near recreational activities areas and during the day in summer**.
- Some UV filters (BP3) have high number of aquatic measurements available compared to other. Usually concentrations < 1µg/L.

- There are fewer observations for organic UV filters in sediments. Usually < 0.1µg/g dw.
- The elements used in inorganic UV filters (titanium, zinc) occur naturally in water and sediments at concentrations that vary regionally, complicating measurements of the incremental contribution from sunscreens.

ENVIRONMENTAL OCCURRENCE

CONCENTRATIONS IN BIOTA

- UV filters exhibit a **wide range of bioaccumulation potential**, driven primarily by the **lipophilicity** of the compound and the **metabolism** of the parent compound by the organism.
- **Bioaccumulation** can be predicted by **hydrophobicity**, though this **does not take metabolism** within an organism into account.
- **Metabolites also bioaccumulate** in tissues.
- For many UV filters, **reliable** laboratory-based or experimental **BAFs or BCFs** are not available.
- **Magnification potential is poorly** investigated.
- **Limited** studies in aquatic **plants.**

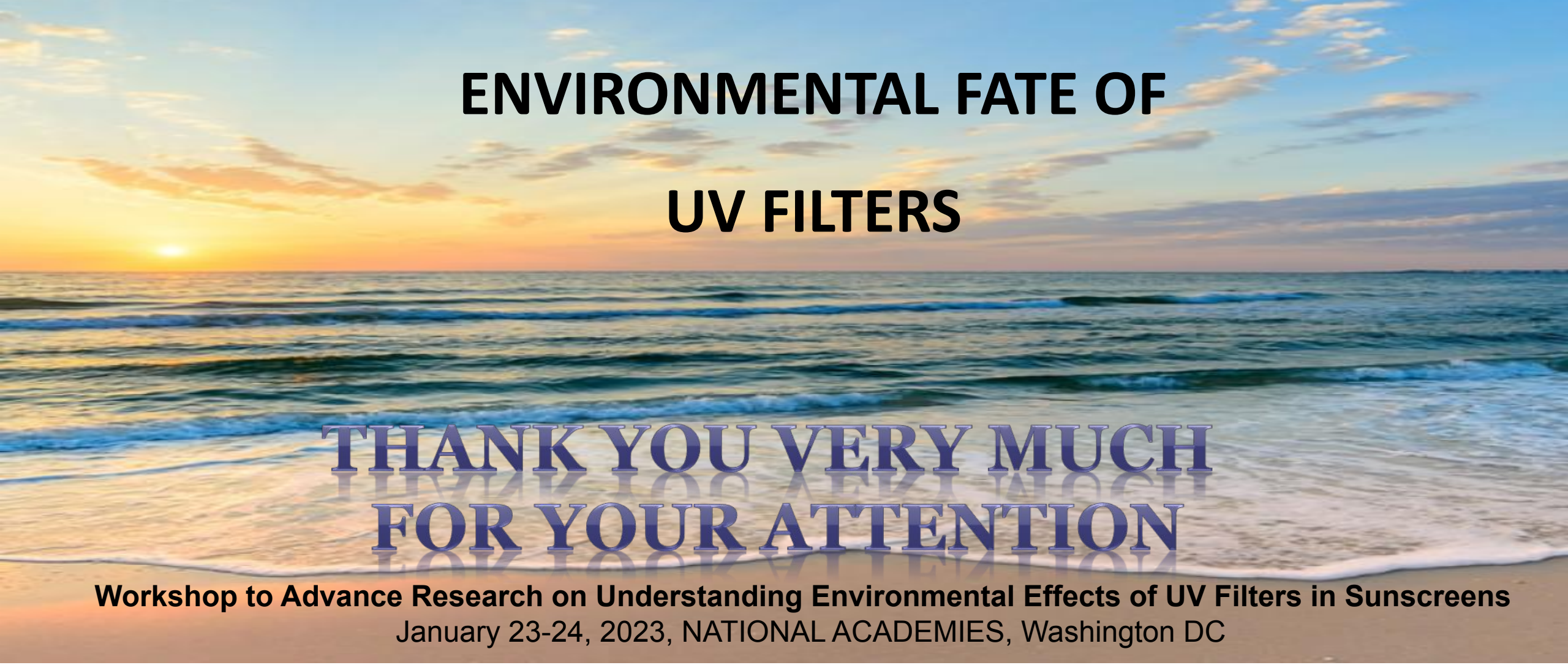


ENVIRONMENTAL OCCURRENCE - REMARKS

- Current **monitoring programs** provide limited data, especially in regard to identifying sources, a particular problem for the inorganic UV filters. Particular **areas dynamics** should be considered.
- Monitoring efforts should include **repeated and replicated measures in space and time** for an accurate occurrence data. Standardized methods, field blanks and quality controls are required. **Analytical Chemistry.**
- The analysis of **inorganics** UV filters is **complex** because they are **present in the environment** (naturally occurring or other sources beyond sunscreens), and specially for the **nano-sized** ones, analytical instrumentation to differentiate metal size is scarce.
- **Limited** data exists on the **role of coatings**, not only for inorganic but also for organic UV filters.
- Lack of systematic **studies on metabolites/**transformation products.
- **Limited occurrence data of many UF filters** in a wide range of matrices, mainly biological.
- **Additional research,** ex. determination of **critical body burdens,** may clarify if accumulations of UV filters **contribute to long-term stress of biota.**
- **Longer food chains for proper biomagnification studies** should be perform, including fish-eating birds and sediment-dwelling organisms, because sediment is a sink to many UV filters, that settle down or adsorb.
- **Production volumes, uses and amounts allowed in formulations** are also **determinats of occurrence**.

ENVIRONMENTAL FATE OF

UV FILTERS



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