Residue

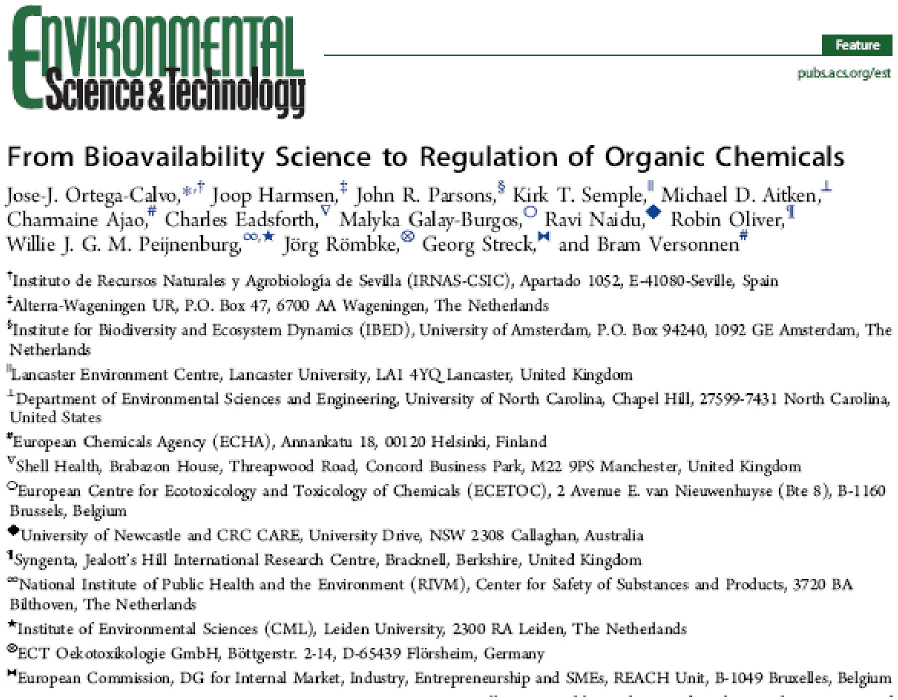
Risk reduction of chemical residues in soils and crops: impact due to wastewater used for irrigation

BIOAVAILABILITY OF ORGANIC CHEMICALS IN SOILS AND SEDIMENTS: POTENTIAL REGULATORY ASPECTS?

José Julio Ortega Calvo, IRNAS-CSIC, 26 April 2022

jjortega@irnase.csic.es

PRIMA PARTNERSHIP FOR RESEARCH AND INNOVATION IN THE MEDITERRANEAN AREA | Fraunhofer IME | Freie Universität Berlin | CSIC CONSEJO SUPERIOR DE INVESTIGACIONES CIENTÍFICAS | PHYTOR | Consorzio Italbiotec | האוניברסיטה העברית בירושלים THE HEBREW UNIVERSITY OF JERUSALEM


Environmental Science & Technology
Feature
pubs.acs.org/est

From Bioavailability Science to Regulation of Organic Chemicals

Jose-J. Ortega-Calvo,[*,†] Joop Harmsen,[‡] John R. Parsons,[§] Kirk T. Semple,[∥] Michael D. Aitken,[⊥] Charmaine Ajao,[#] Charles Eadsforth,[∇] Malyka Galay-Burgos,[○] Ravi Naidu,[◆] Robin Oliver,[¶] Willie J. G. M. Peijnenburg,[∞,★] Jörg Römbke,[⊗] Georg Streck,[⧓] and Bram Versonnen[#]

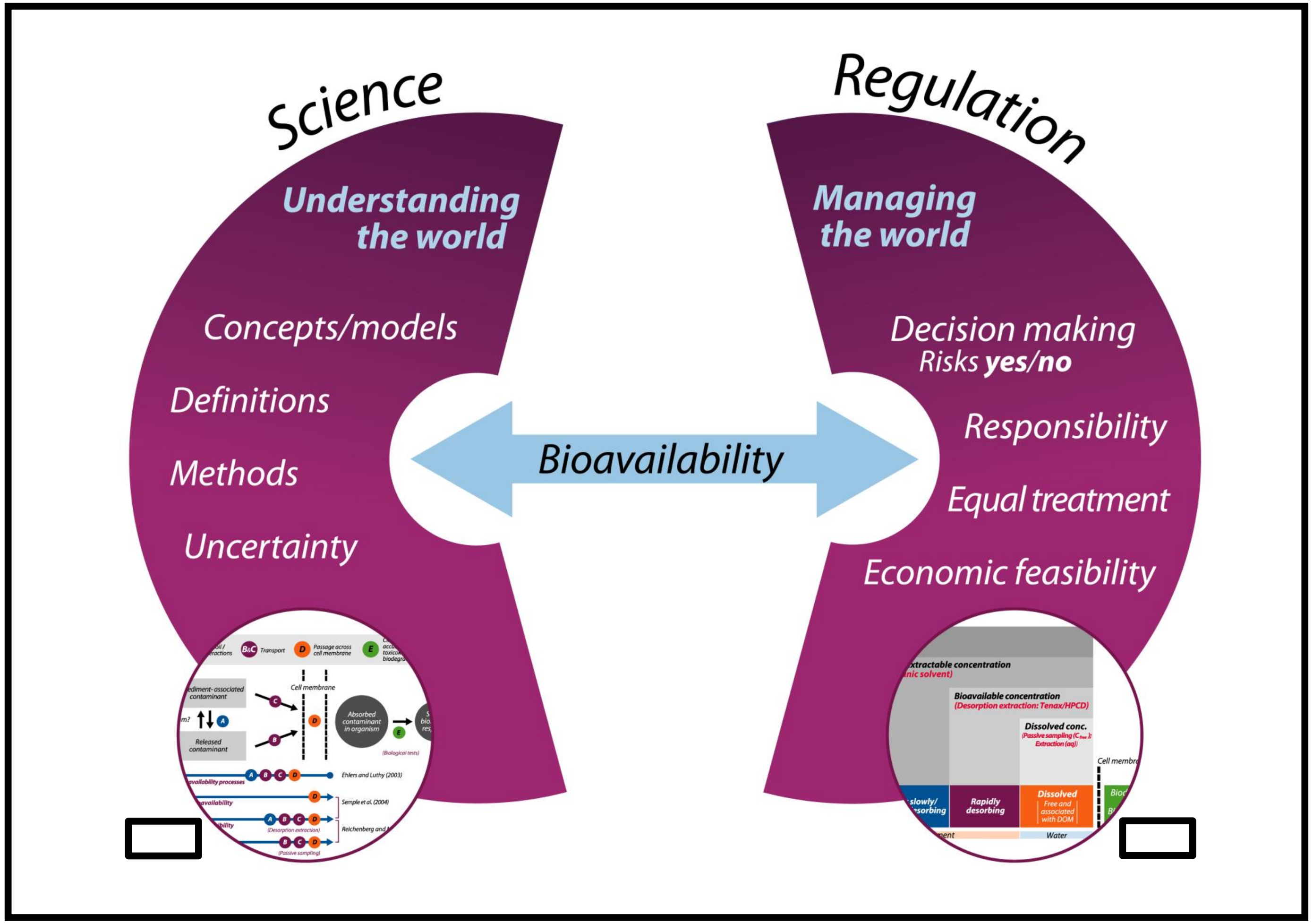
[†]Instituto de Recursos Naturales y Agrobiología de Sevilla (IRNAS-CSIC), Apartado 1052, E-41080-Seville, Spain
[‡]Alterra-Wageningen UR, P.O. Box 47, 6700 AA Wageningen, The Netherlands
[§]Institute for Biodiversity and Ecosystem Dynamics (IBED), University of Amsterdam, P.O. Box 94240, 1092 GE Amsterdam, The Netherlands
[∥]Lancaster Environment Centre, Lancaster University, LA1 4YQ Lancaster, United Kingdom
[⊥]Department of Environmental Sciences and Engineering, University of North Carolina, Chapel Hill, 27599-7431 North Carolina, United States
[#]European Chemicals Agency (ECHA), Annankatu 18, 00120 Helsinki, Finland
[∇]Shell Health, Brabazon House, Threapwood Road, Concord Business Park, M22 9PS Manchester, United Kingdom
[○]European Centre for Ecotoxicology and Toxicology of Chemicals (ECETOC), 2 Avenue E. van Nieuwenhuyse (Bte 8), B-1160 Brussels, Belgium
[◆]University of Newcastle and CRC CARE, University Drive, NSW 2308 Callaghan, Australia
[¶]Syngenta, Jealott's Hill International Research Centre, Bracknell, Berkshire, United Kingdom
[∞]National Institute of Public Health and the Environment (RIVM), Center for Safety of Substances and Products, 3720 BA Bilthoven, The Netherlands
[★]Institute of Environmental Sciences (CML), Leiden University, 2300 RA Leiden, The Netherlands
[⊗]ECT Oekotoxikologie GmbH, Böttgerstr. 2-14, D-65439 Flörsheim, Germany
[⧓]European Commission, DG for Internal Market, Industry, Entrepreneurship and SMEs, REACH Unit, B-1049 Bruxelles, Belgium

ES&T (2015) 49, 10255-10264

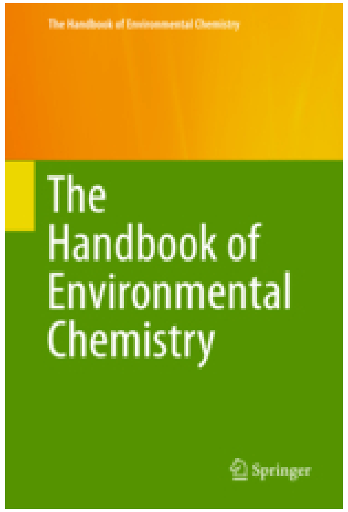
SETAC Europe setac.org sesss10.setac.org

Residue

BRINGING DIFFERENT WORLDS TOGETHER



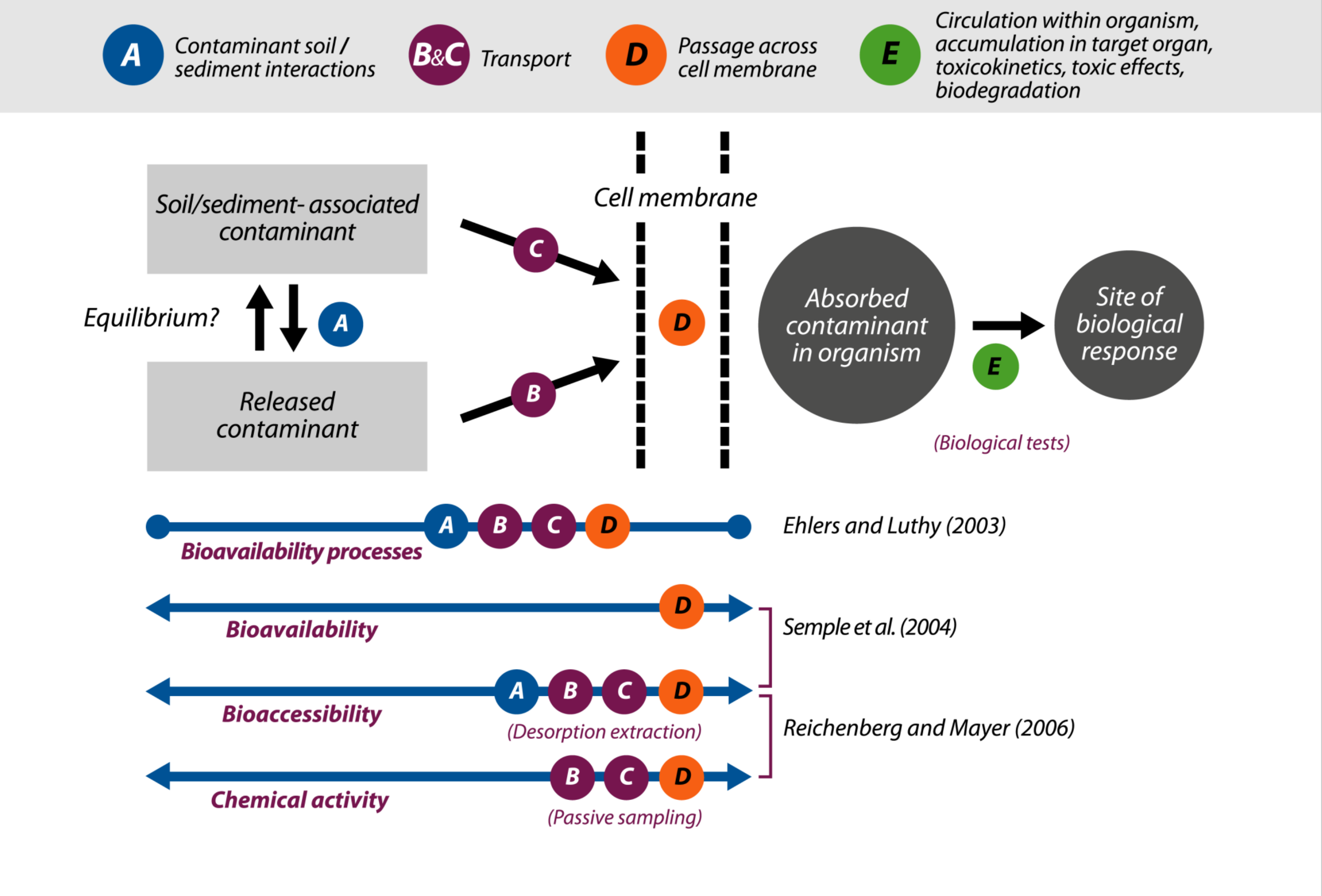
Ortega-Calvo et al. ES&T, 2015. 49, 10255-10264



BIOAVAILABILITY OF ORGANIC CHEMICALS IN SOIL AND SEDIMENT

- **Editors:**
  J.J. Ortega-Calvo (CSIC) & J. R. Parsons (UvA)
- **16 chapters on:**
  - **Chemical distribution in soil and sediment**
  - **Bioavailability and bioaccumulation**
  - **Impact of sorption processes on toxicity, persistence and remediation**
  - **Methods for measuring bioavailability**
  - **Bioavailability in chemical risk assessment**
- **Publication: May 2020**

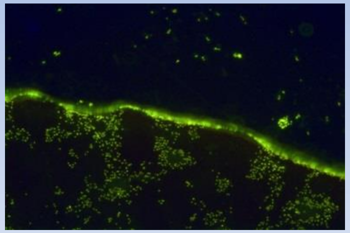
BIOAVAILABILITY SCIENCE



Ortega-Calvo et al. ES&T, 2015. 49, 10255-10264

Residue

ADHESION

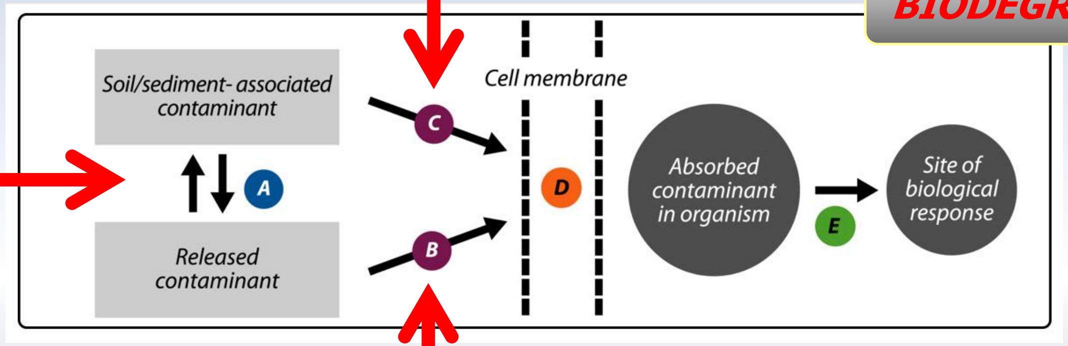


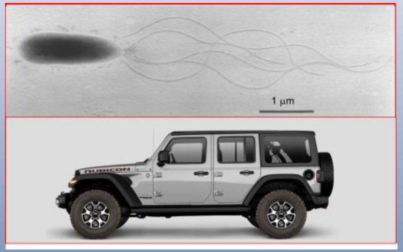
ES&T 2011, 45:1074-1081
ES&T 2017, 51:11935–11942

SOLUBILIZATION

ES&T 2011, 45:3019-3026
ES&T 2014, 48:10869-10877

BIODEGRADATION





ES&T 2008, 42:1131-1137
ES&T 2015, 49:4498-4505
ES&T 2016, 50:7633-7640
ES&T 2018, 52:10673−10679

MOBILIZATION

Ortega-Calvo et al. , 2020. Handbook of Environmental Chemistry, Springer

Residue

Soil quality — Environmental availability of non-polar organic compounds — Determination of the potentially bioavailable fraction and the non-bioavailable fraction using a strong adsorbent or complexing agent

INTERNATIONAL STANDARD

ISO 16751

First edition
2020-06

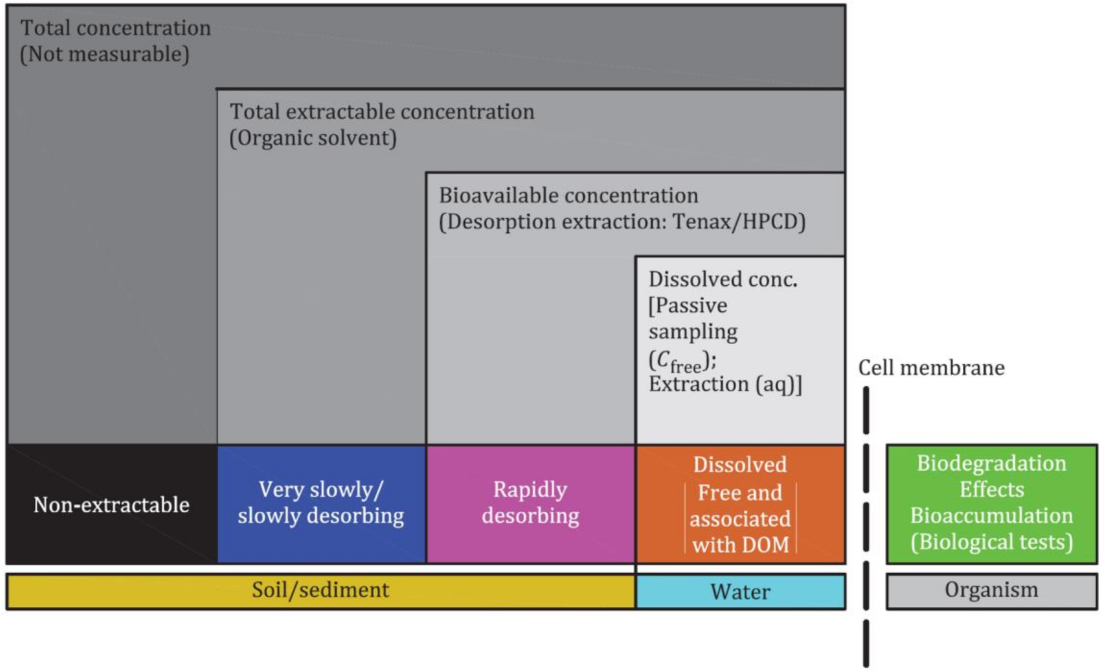
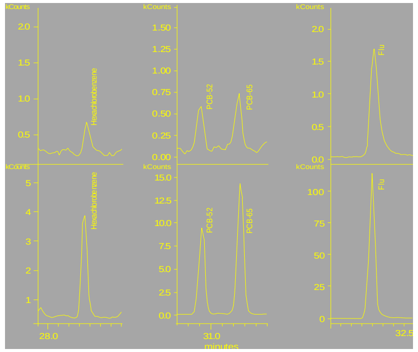


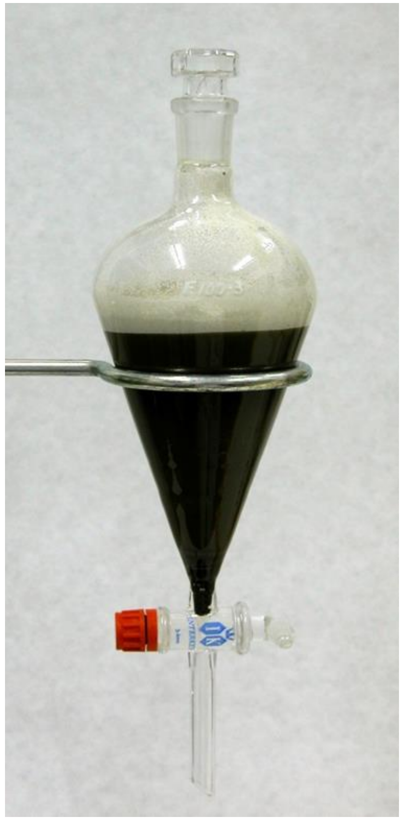
Figure 2 — Measurement of bioavailability of organic chemicals: a simplified scheme for use in regulation [Source: Ortega-Calvo et al. (2015)]



PASSIVE SAMPLING UPDATE

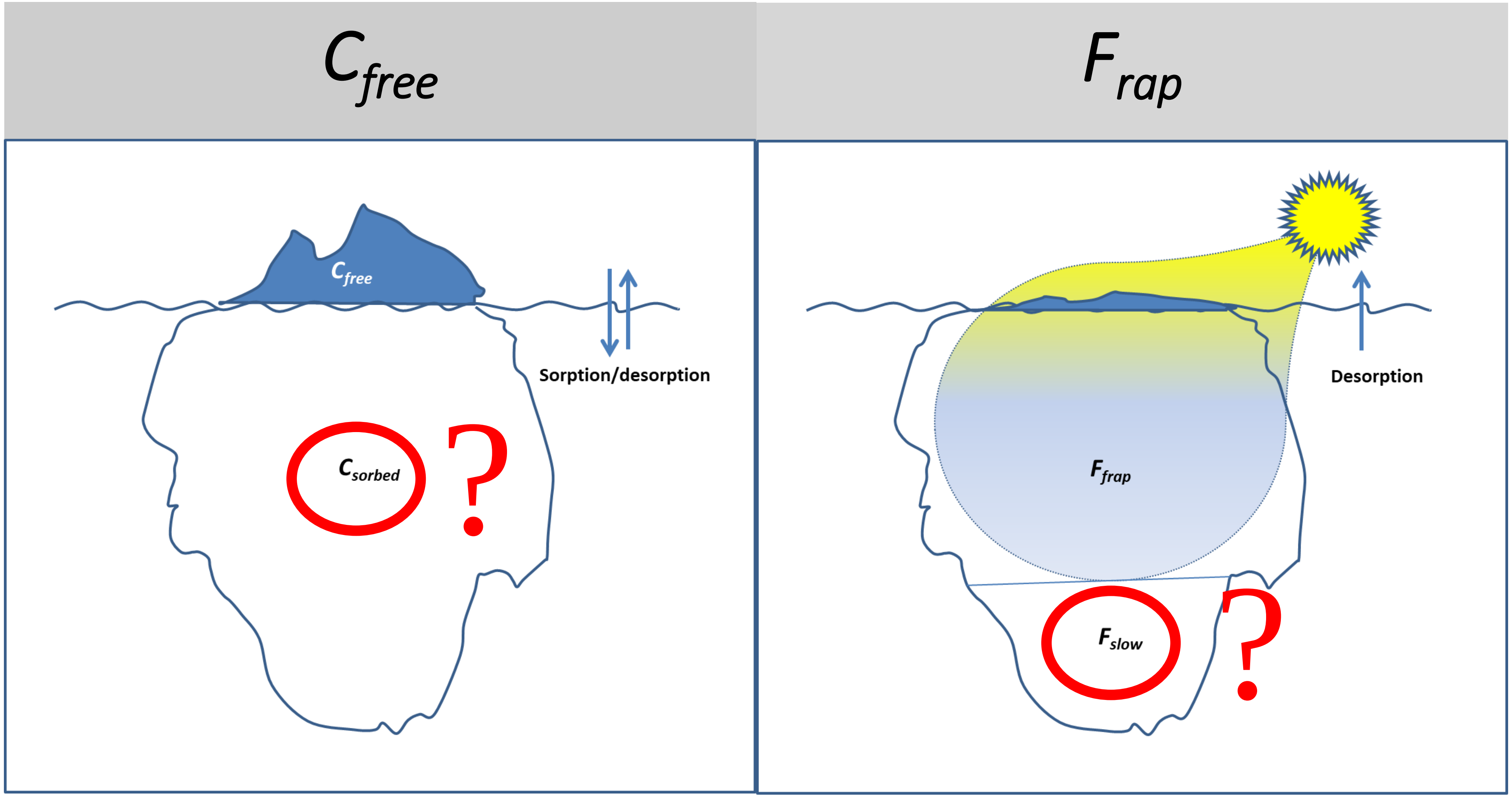
- Non-depletive, equilibrium based
- Solid polymers: polydimethylsiloxane, polyethylene, polyoxymethylene, polyacrylate, silicone rubber, as fibers or membranes
- In situ or ex situ
- Bioavailability defined as C_{free}, obtained at equilibrium (weeks), calculated from polymer-to-water partitioning coefficient
- Basis for bioaccumulation predictions based on EqP, for sediment toxicity/test exposures, and for sediment remediation goals (through K_{oc})
- No standard method available

DESORPTION EXTRACTION UPDATE



- **ISO method (ISO/TS 16751) with Tenax and cyclodextrin available for non-polar OCs since 2018, soon as a full standard**
- **Bioavailable fraction as F_{rap}, obtained in a single step (20 h)**
- **Expressed in mass units: mg/kg d.m.**
- **Applicable to compounds with aqueous solubility <100 mg/L (K_{ow} > 3), theoretically applicable up to 1 000 mg/L**
- **Validated with PAHs and polychlorinated aromatics (PCBs, HCB, etc.)**
- **Better support from two-site model and perfect-sink assumption for Tenax, than for cyclodextrin**

Residue



Ortega-Calvo, 2019. Environmental Toxicology, an open online textbook. Chapter 3.6.2. Assessing available concentrations of organic chemicals.
https://maken.wikiwijs.nl/147644/Environmental_Toxicology__an_open_online_textbook#!page-5496229

ARE C_{free} AND F_{rap} METHODS COMPLEMENTARY?

	C_{free}	F_{rap}
Time for performance	weeks	hours
Preferable scenario	sediment	soil (?)
Applicability	in/ex-situ	ex-situ
Output	ng/L	mg/kg
Standard	No	Yes
Included in regulation	Yes	No

Residue

BIOAVAILABILITY: REGULATION

DEVELOPING REMEDIATION TARGETS

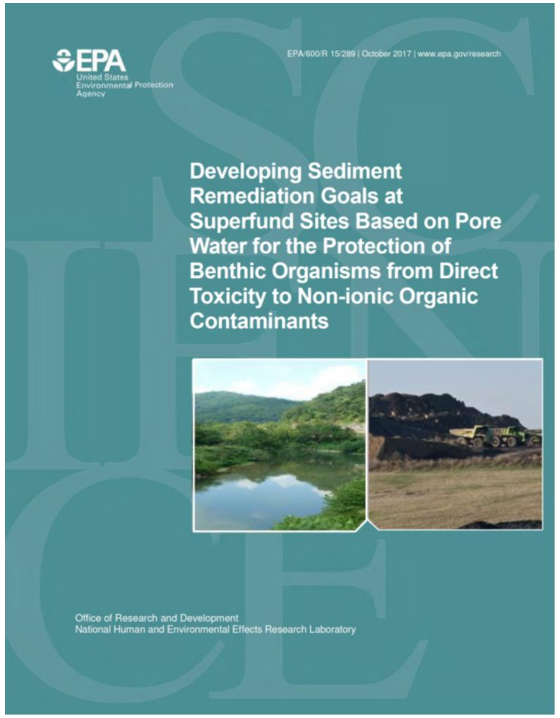
- State-of-the-art bioavailability science of passive sampling in site-specific procedures

- Refinement of sediment OC-based Cfree estimations (first tier) vs sediment toxicity testing:

$$C_{free} = \left(C_s / f_{oc}\right) / K_{oc} = C_{soc} / K_{oc}$$

- Second tier: determining actual C_{free} with PS to derive site-specific K_{oc} values

- Remediation targets for C_s based on desired C_{free} from toxicity criteria


EPA
United States Environmental Protection Agency
EPA/600/R 15/289 | October 2017 | www.epa.gov/research

Developing Sediment Remediation Goals at Superfund Sites Based on Pore Water for the Protection of Benthic Organisms from Direct Toxicity to Non-ionic Organic Contaminants

Office of Research and Development
National Human and Environmental Effects Research Laboratory

Burkhard et al. EPA/600/R 15/289 (2017)

Residue

BIOAVAILABILITY: REGULATION

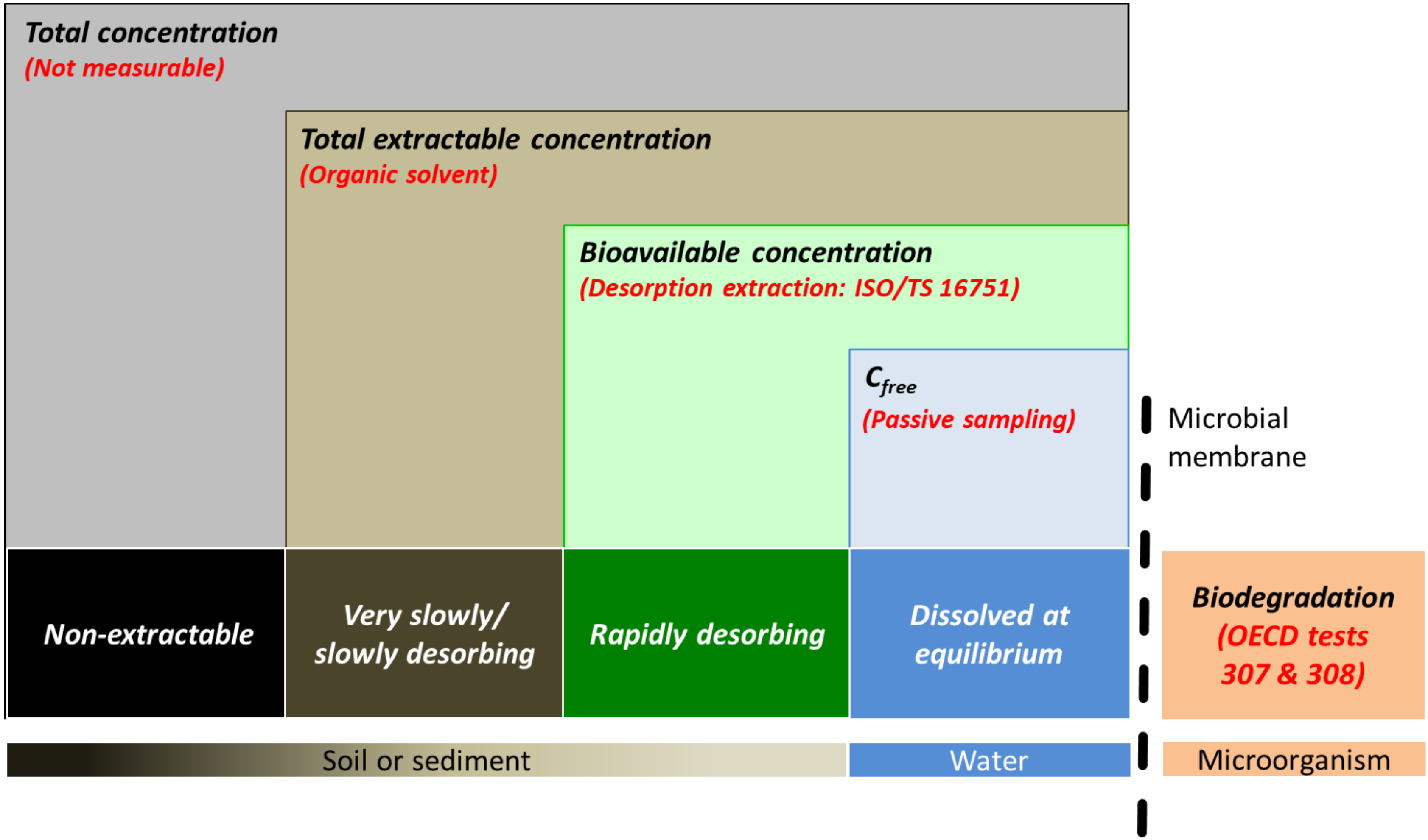
PROSPECTIVE RISK ASSESSMENT

CSIC Consejo Superior de Investigaciones Científicas

IRNAS Instituto de Recursos Naturales y Agrobiología de Sevilla

Residue

BIOAVAILABILITY-BASED IMPROVEMENTS ON pRA - PERSISTENCE



Ortega-Calvo et al. , 2020. Handbook of Environmental Chemistry, Springer

Residue

Experiments in our laboratory to the integration of bioavailability assessments in standardized procedures for monitoring the biological transformation of organic chemicals in soil: PRIMA RESIDUE PROJECT

1. Approach to study mineralization and biodegradation by OECD 307 method

NaOH trap

Agricultural soil spiked with radiolabelled and non-radiolabelled compound

Inoculation with a specific strain or use *of autoctonous microorganisms*

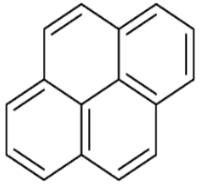
Incubation during 2 or 3 weeks

2. Bioavailability assessments at different stages of this incubation using a standardized method (ISO 16751:2020) or a adaptation of it depending on compound used in every case

<u>ISO METHOD 16751</u>

COMPOUNDS WITH LOG KOW > 3 (pyrene)

- 2 g spiked soil
- 35 mL. of Mili-Q water
- Biocide (sodium azide)
- 0,7 gr. of Tenax® (60-80 mesh) by Buchem BV

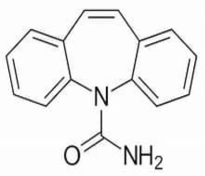


1º step: extraction at 20 h

<u>ADAPTED ISO METHOD 16751</u>

CARBAMAZEPINE **LOG K_{OW} = 2,7**

- 1 g spiked soil
- 35 mL. of Mili-Q water
- Biocide (sodium azide)
- 1,5 gr. of Tenax® (60-80 mesh) by Buchem BV

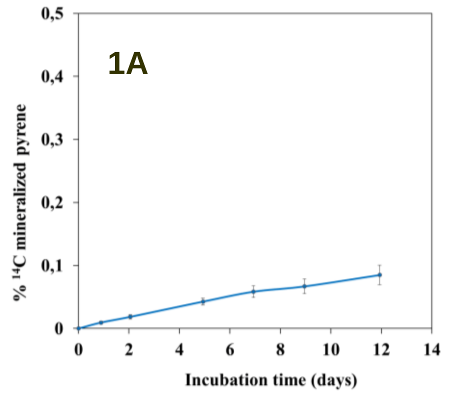


Acetone/ hexane (shaking during 24 h) ⟵ **2º step**: Extraction from receiver phase (tenax) ⟶ methanol (several sonnication and centrifugation)

3º step: after the extraction with tenax the residual soil is analysed by combustion in an oxidizer

Residue

PYRENE



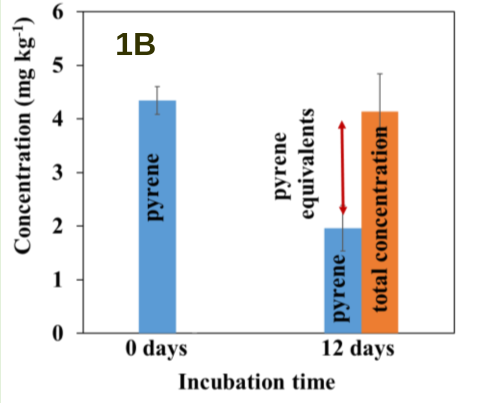
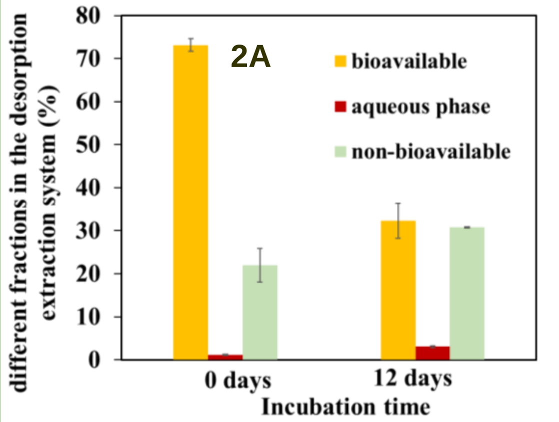


Figure 1: (**A**) Mineralization by *P. putida* G7 of ^{14}C-pyrene added to a sterelized agricultural soil. Mineralization was less than 0,2 %, indicating a cometabolic transformation. (**B**) Initial and final concentrations of pyrene and the pyrene equivalents (transformation products). The biodegradation in this experiment was 47,3 %. With the analysis of soil at final time by combustión in a oxidazer, we can asume that pyrene has been transformed to metabolites in a 52,65 %.



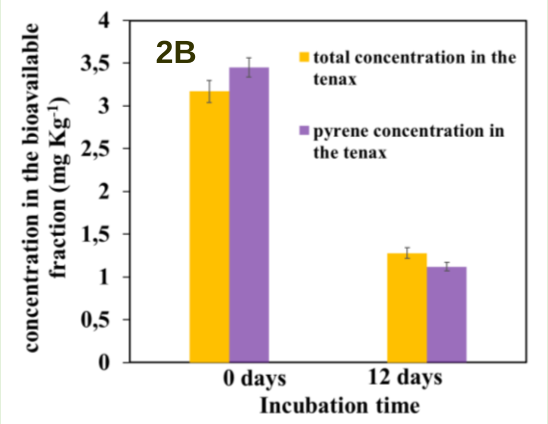
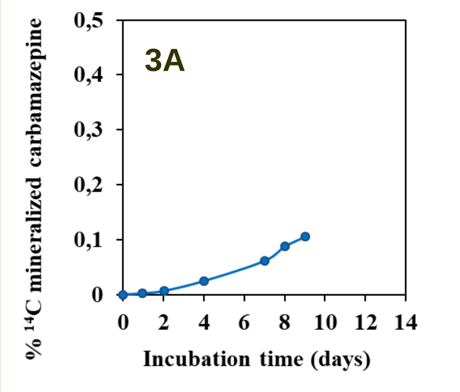


Figure 2: **(A)** Determination of the phase distribution in our system of the 14C-labelled parent compound and metabolites among soil, water and Tenax. In the case of pyrene, only 3 % were present as hydrophilic transformation products that were not trapped by Tenax but partitioned into the water. The rest remained as non-bioavailable residues. The bioavailable pyrene fraction in soil decreased as long as cometabolism proceeded, which can be also corroborated with the combined use of liquid scintillation and HPLC fractionation and we can assumed that only the pyrene is present in the tenax and not the metabolites formed in the process of cometabolism (B).

These results indicate that cometabolism decreased efficiently the risks from pyrene in the soil.

CARBAMAZEPINE



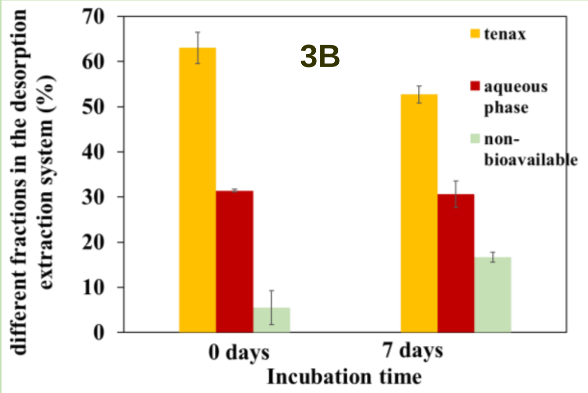
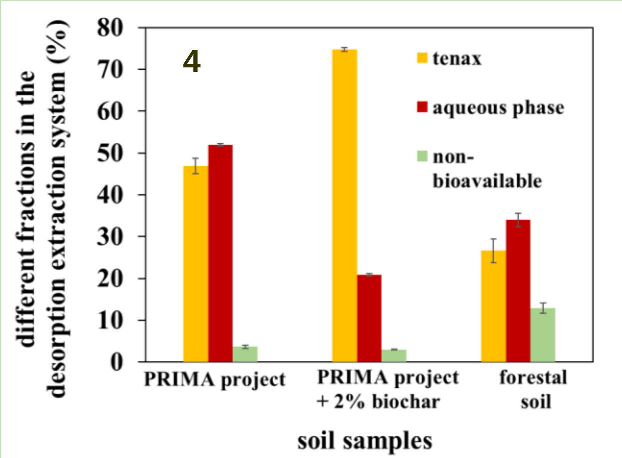


Figure 3: (**A**) Mineralization of ^{14}C-carbamazepine added to a non-sterelized and non inoculated agricultural soil.

(**B**) Determination of the phase distribution in this system of the 14C-labelled compound among soil, water and Tenax. In the case of carbamazepine the bioavailable fraction will be the sum of water fraction and tenax fraction

Figure 4: Bioavailability assessments of carbamazepine in differente soil samples using the adapted method (ISO 16751:2020)



Residue

CONCLUSIONS

- Total pollutant concentrations lead to overestimation of risk, but more realistic assessments can be done by incorporating bioavailability
- Bioavailability science is ready for use in regulation of organic chemicals
- Bioavailability can be measured through C_{free} or F_{rap}, each with pros and cons
- Proposal for integrating in pRA (OECD 307 and 308)

Residue

Many thanks for your attention

jjortega@irnase.csic.es

Instituto de Recursos Naturales y Agrobiología de Sevilla (IRNAS-CSIC)

Follow us on:

www.residueproject.it

https://twitter.com/ResidueProject