



Mécanismes naturels de dégradation abiotique des contaminants aux interfaces redox

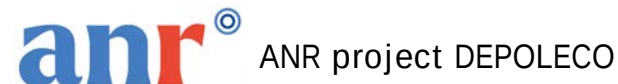
*IMPMC - **UMR 7590** - Elora Bourbon, Jessica Brest, Stéphanie Delbrel, Thierry Allard, Pierre le Pape, Guillaume Morin*

*METIS **UMR 7619** – Elodie Guigon, Fabrice Alliot, Fulvia Baratelli*

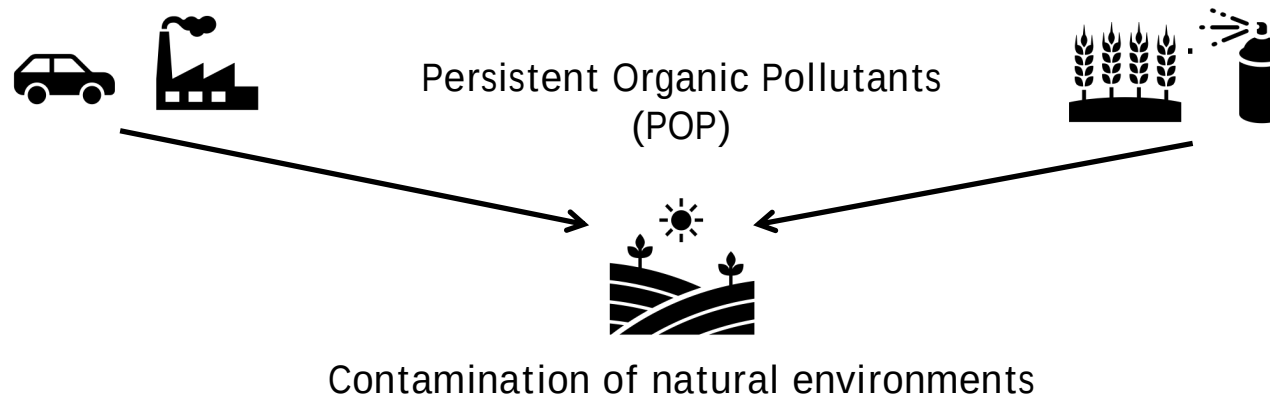
*LSCE – **UMR 8212** – Sophie Ayrault, Maeva Philippe*

*LRS – **UMR 7197** – Frédéric Averseng, Xavier Carrier*

*ECOSYS – **UMR 1402** – Sylvie Nélieu, Marjolaine Deschamp, Ghislaine Delarue,*



Introduction



Fenton reaction (Haber & Weiss, 1934): $\text{Fe}^{2+} + \text{H}_2\text{O}_2 \Rightarrow \text{Fe}^{3+} + \text{OH}^- + \text{OH}^\bullet$

Recent developments in research about advanced oxidation processes:

- **Solid substrates** such as iron-bearing minerals
- Reactive species produced by **O_2** replacing H_2O_2 and at **circumneutral pH**
Fang et al. (2013); Ardo et al. (2015); He et al. (2016); He et al. (2020)

Introduction

ENVIRONMENTAL
Science & Technology

Article

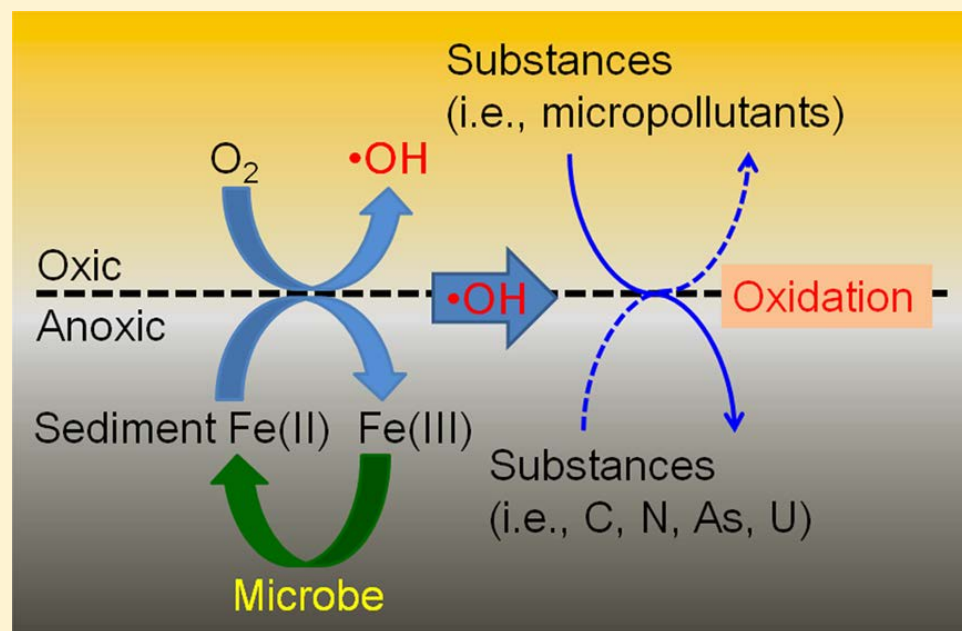
pubs.acs.org/est

Production of Abundant Hydroxyl Radicals from Oxygenation of Subsurface Sediments

Man Tong, Songhu Yuan,* Sicong Ma, Menggui Jin, Deng Liu, Dong Cheng, Xixiang Liu, Yiqun Gan, and Yanxin Wang

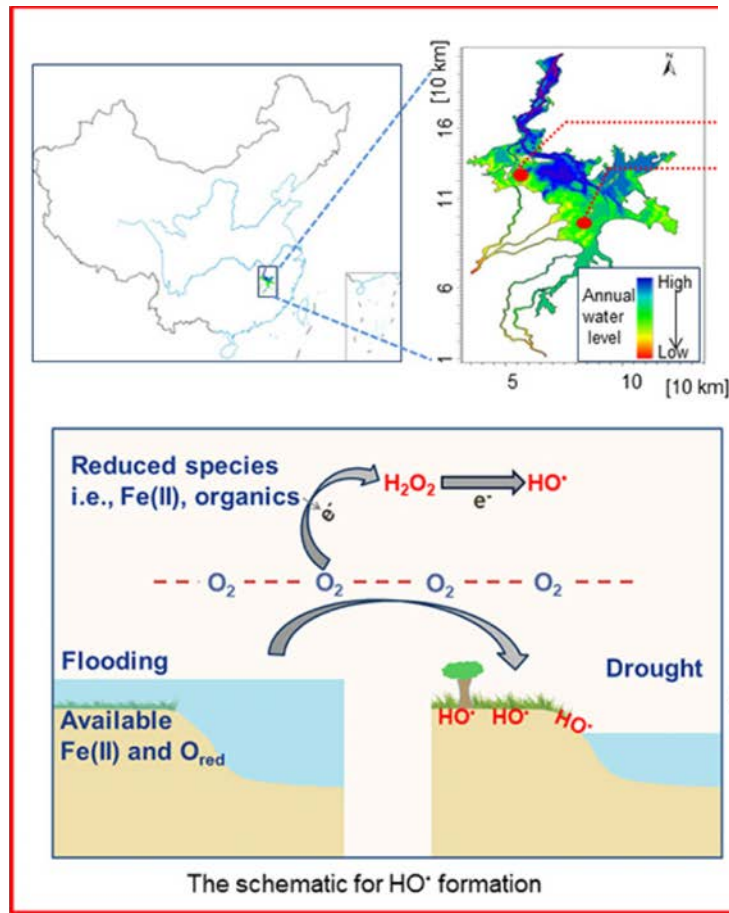
State Key Laboratory of Biogeology and Environmental Geology, China University of Geosciences, 388 Lumo Road, Wuhan 430074, P. R. China

2016



Introduction

2020



Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv



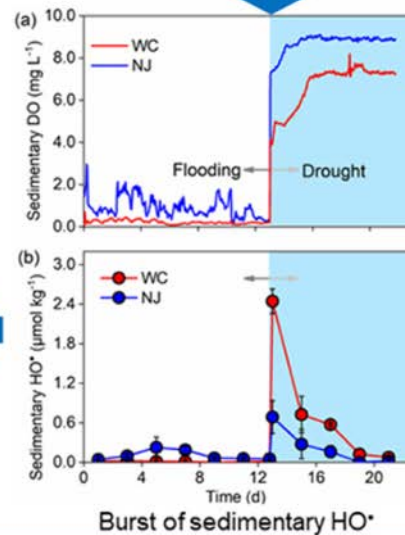
Burst of hydroxyl radicals in sediments derived by flooding/drought transformation process in Lake Poyang, China

Haiyan Du^a, Hongxia Wang^b, Zhilai Chi^c, Na Song^a, Changhui Wang^a, Huacheng Xu^{a,*}

^a State Key Laboratory of Lake Science and Environment, Nanjing Institute of Geography and Limnology, Chinese Academy of Sciences, Nanjing 210008, China

^b Department of Statistics, Nanjing Audit University, Nanjing 211815, China

^c Jiangsu Provincial Key Lab for Organic Solid Waste Utilization, College of Resources & Environmental Sciences, Nanjing Agricultural University, Nanjing 210095, China



Dissolved O₂

[OH•] aqueux

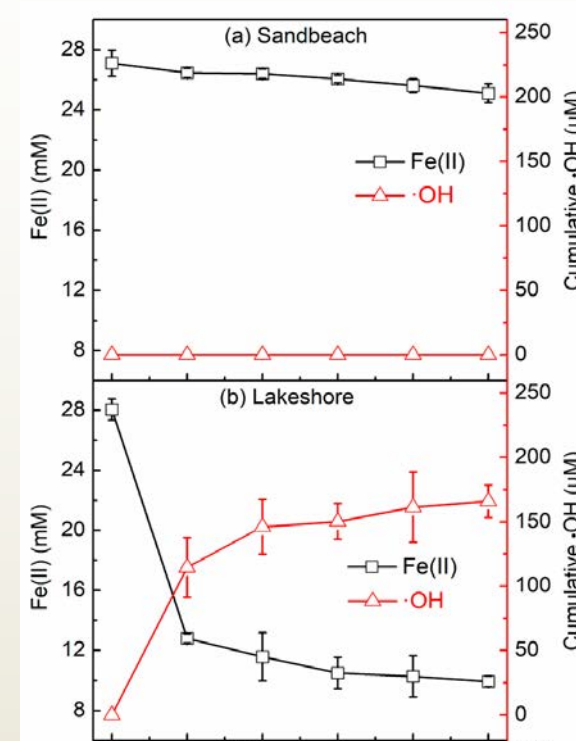
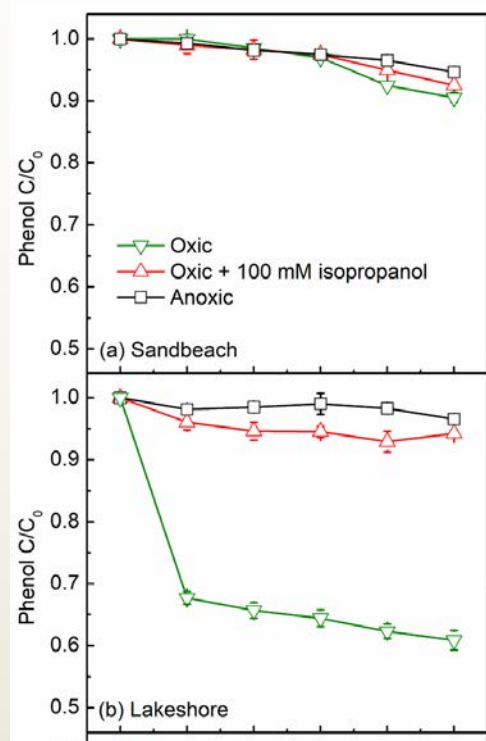
Introduction

Contaminant Degradation by $\bullet\text{OH}$ during Sediment Oxygenation: Dependence on Fe(II) Species

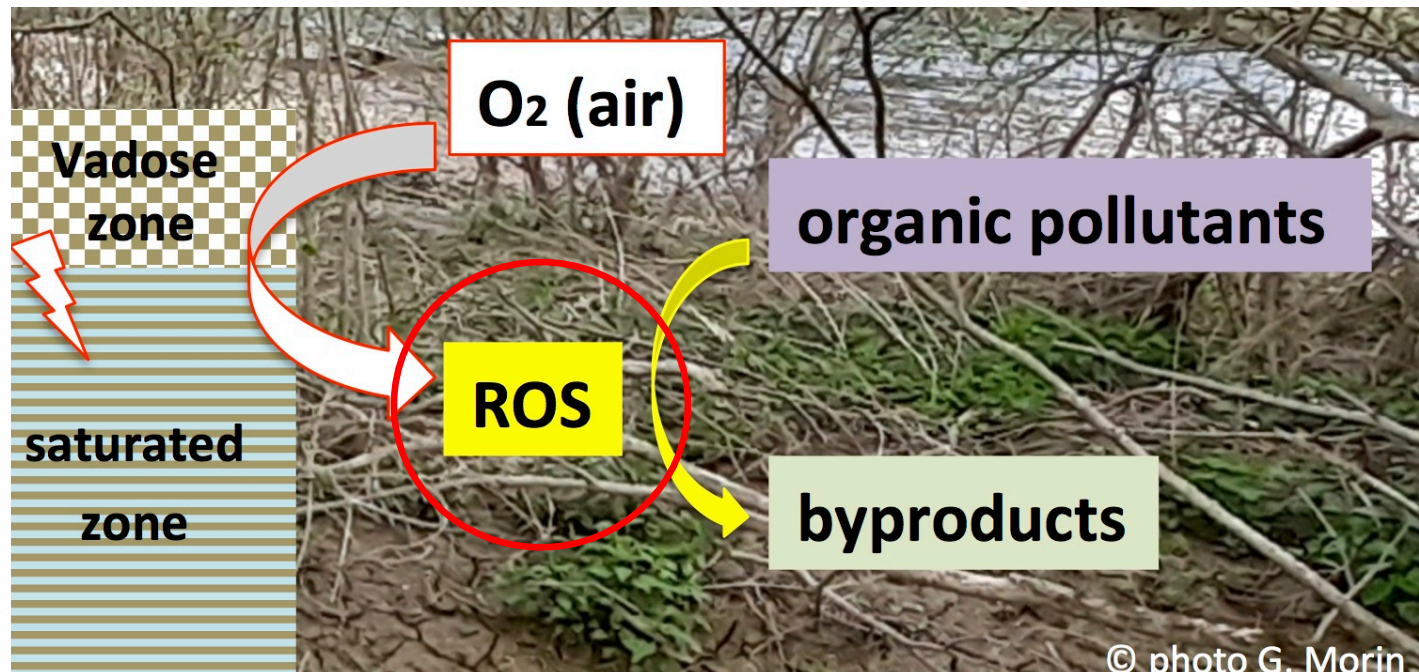
Wenjing Xie, Songhu Yuan,* Man Tong, Sicong Ma, Wenjuan Liao, Na Zhang, and Chunmei Chen

Cite This: *Environ. Sci. Technol.* 2020, 54, 2975–2984

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Fenton-like reaction with O_2 as oxidant



Tong et al. 2016
Liao et al. 2019
Zhao et al. 2023
Morin et al. 2023



Outline

- Part 1 - Natural production of Reactive Oxygen Species (ROS) in soils and sediments upon oxygenation
- Part 2 - Dégradation of Polycyclic Aromatic Hydrocarbons (PAH) upon sediment oxygenation
- Part 3 - Reductive degradation of in alluvial soils

Part 1 - Reactive Oxygen Species in soils and sediments

Ability of natural soils and sediments to produce radical species upon air-oxidation?

Experimental air-oxidation of alluvial soils/sediments naturally subjected to hydrological fluctuations

- Measure radical species using EPR spin-trapping
- Determine the identity of radical species produced using combinations of spin-trap and radical scavengers

Part 1 - Reactive Oxygen Species in soils and sediments



ACS Earth Space Chem. 2024, 8, 9, 1757–1770

<http://pubs.acs.org/journal/aescq>

Article

Non-Hydroxyl Radical Species Production during Dark Air Oxidation of Alluvial Soils

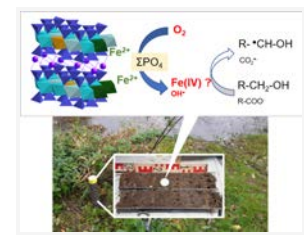
Elora Bourbon, Frédéric Averseng, Pierre Le Pape, Thierry Allard, Fulvia Baratelli, Fabrice Alliot, Alexandre Gélabert, Valentine Rollot, Elodie Guigon, Jessica Brest, Sylvie Nélieu, and Guillaume Morin*



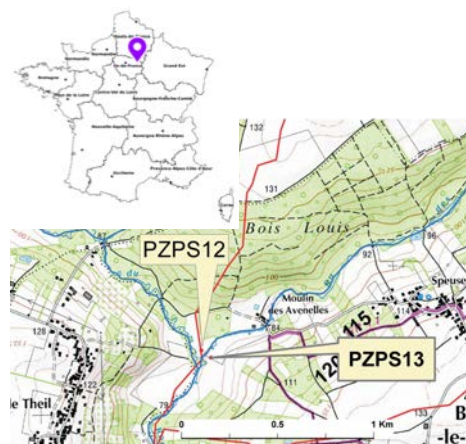
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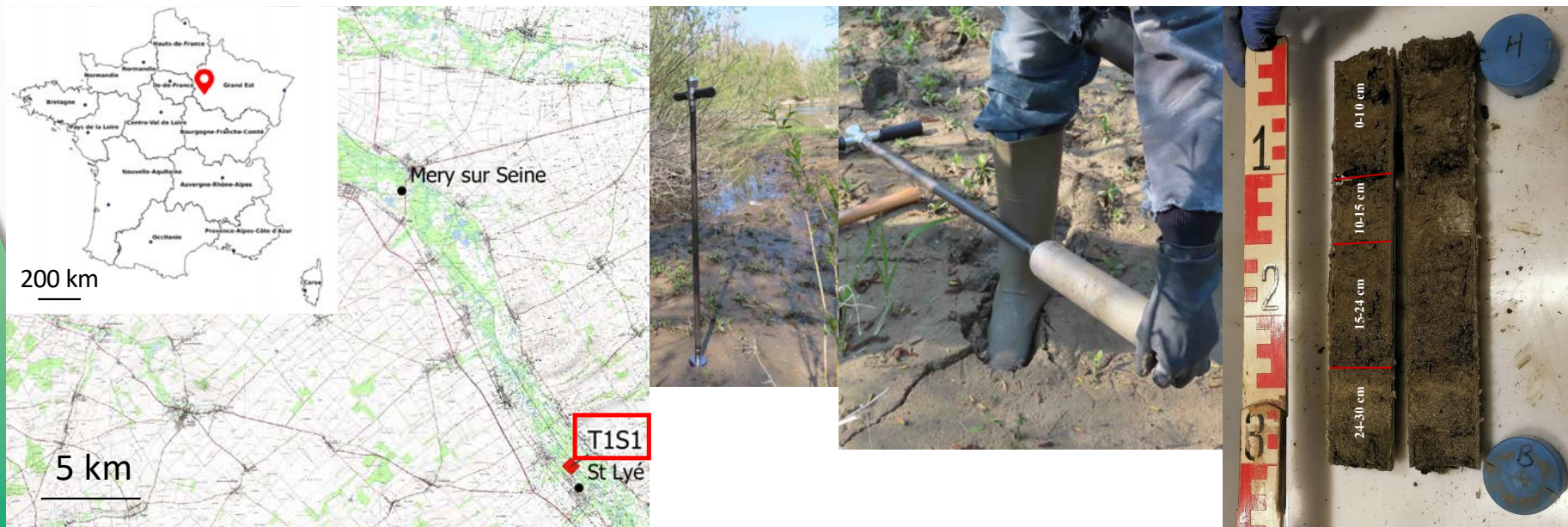
ru des Avenelles riverbank, Orgeval, France



Part 1 - Reactive Oxygen Species in soils and sediments

Alluvial sediments/soils from the Seine river basin, France (La Bassée floodplain)

4 samples from the 30cm long core T1S1

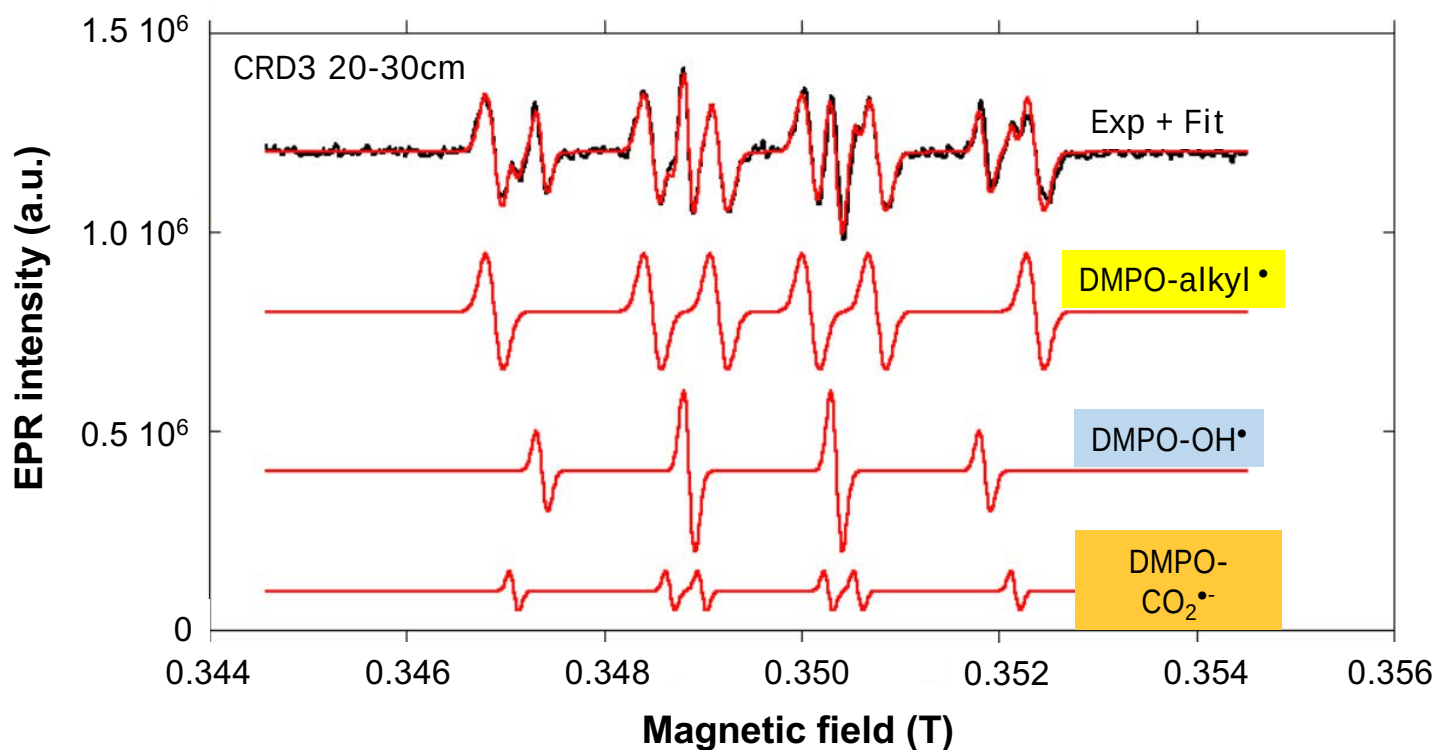


Bourbon et al. 2024

Part 1 - Reactive Oxygen Species in soils and sediments

Results - EPR spectroscopy

CRD3 20-30cm soil + phosphate buffer pH 7 + DMPO spin trap + 2min air-oxidation



Part 1 - Reactive Oxygen Species in soils and sediments

Aqueous Iron(IV)–Oxo Complex: An Emerging Powerful Reactive Oxidant Formed by Iron(II)-Based Advanced Oxidation Processes for Oxidative Water Treatment

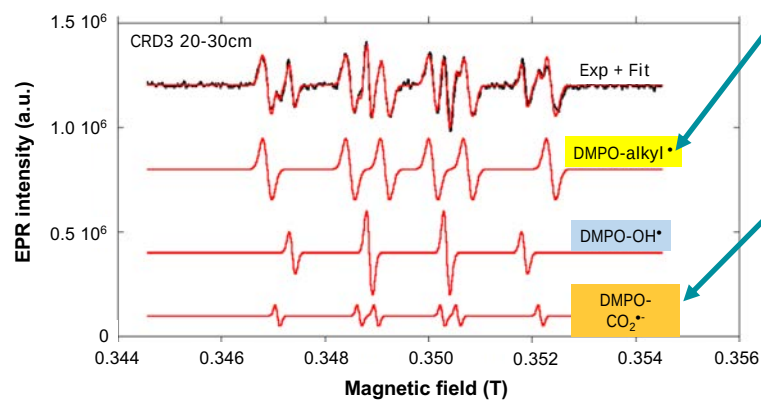
Zhen Wang, Wei Qiu, Su-yan Pang, Qin Guo, Chaoting Guan, and Jin Jiang*

Cite This: *Environ. Sci. Technol.* 2022, 56, 1492–1509

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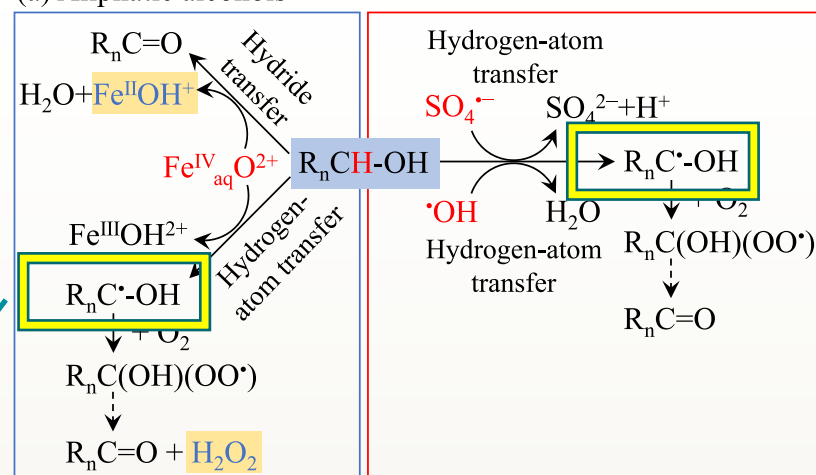
Results - EPR spectroscopy

CRD3 20-30cm soil + phosphate buffer pH 7 + DMPO spin trap + 2min air-oxidation



ACS Earth Space Chem. 2024, 8, 9, 1757–1770

(a) Aliphatic alcohols



(b) Aliphatic carboxylic acids

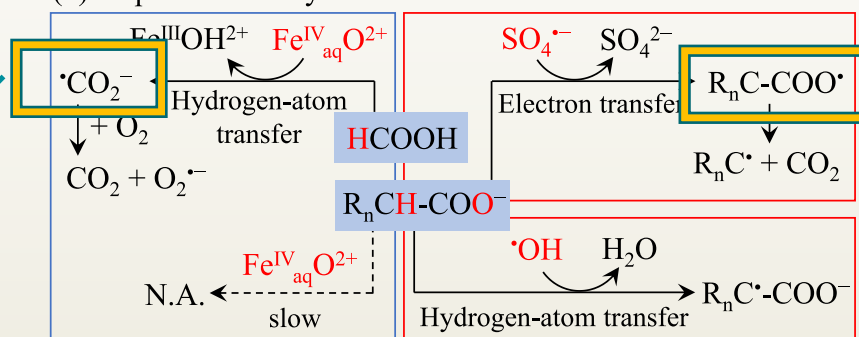
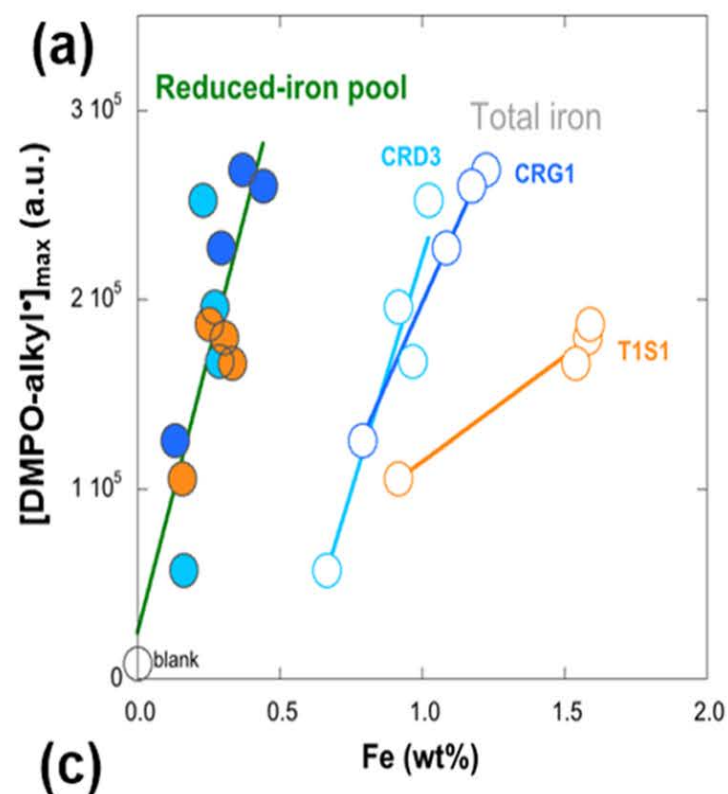


Figure 5. Comparison of the pathways for the oxidation of aliphatic alcohols and carboxylic acids by $\text{Fe}_{\text{aq}}^{\text{IV}}\text{O}_2^{2+}$, $\cdot\text{OH}$, and $\text{SO}_4^{\cdot-}$. (N.A.: The oxidation product is not available in the literature.)

Part 1 - Reactive Oxygen Species in soils and sediments

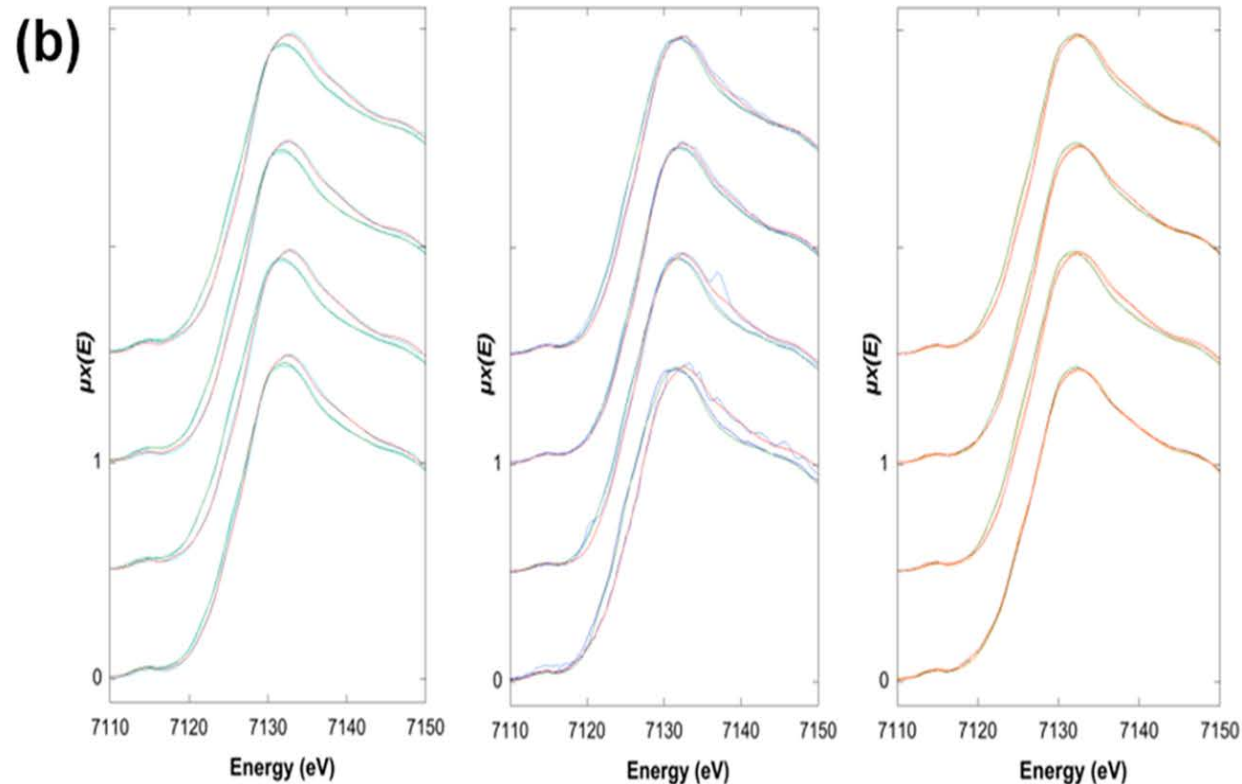
EPR spin-trapping



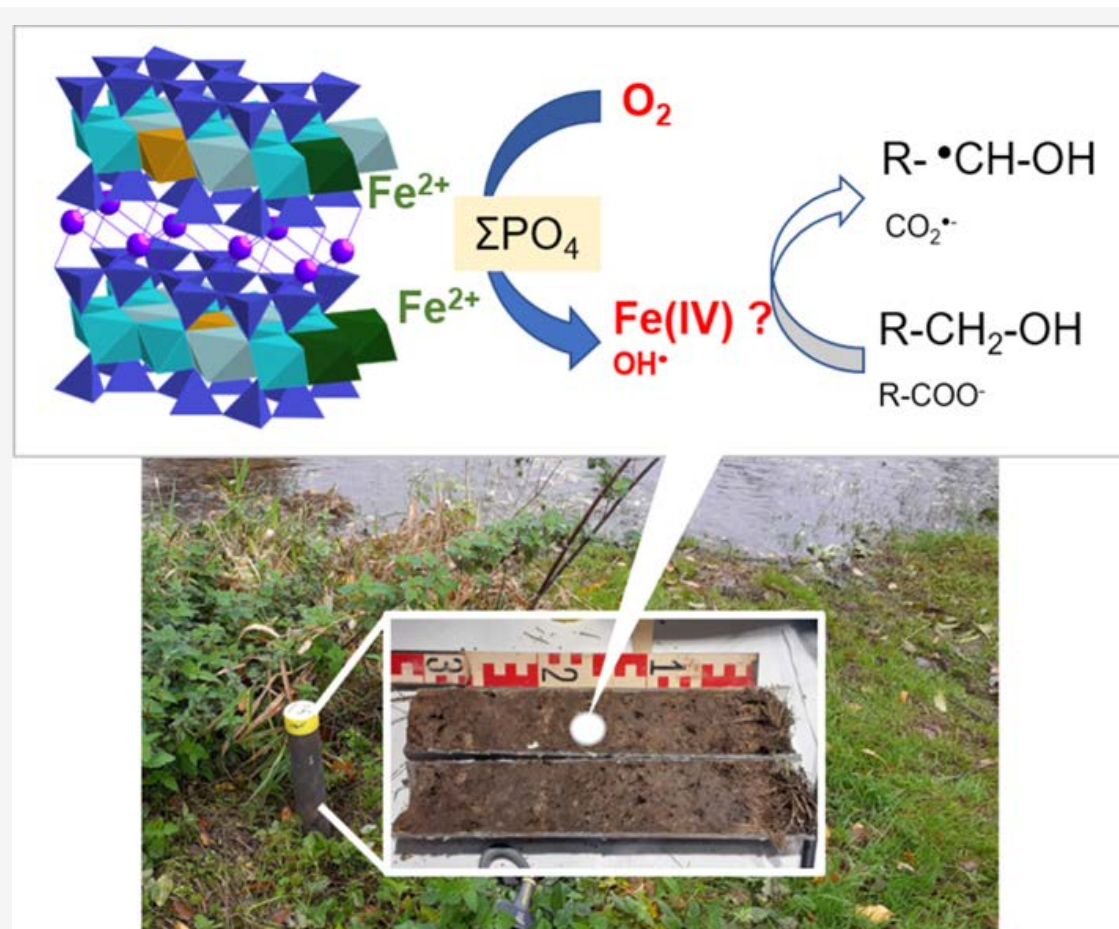
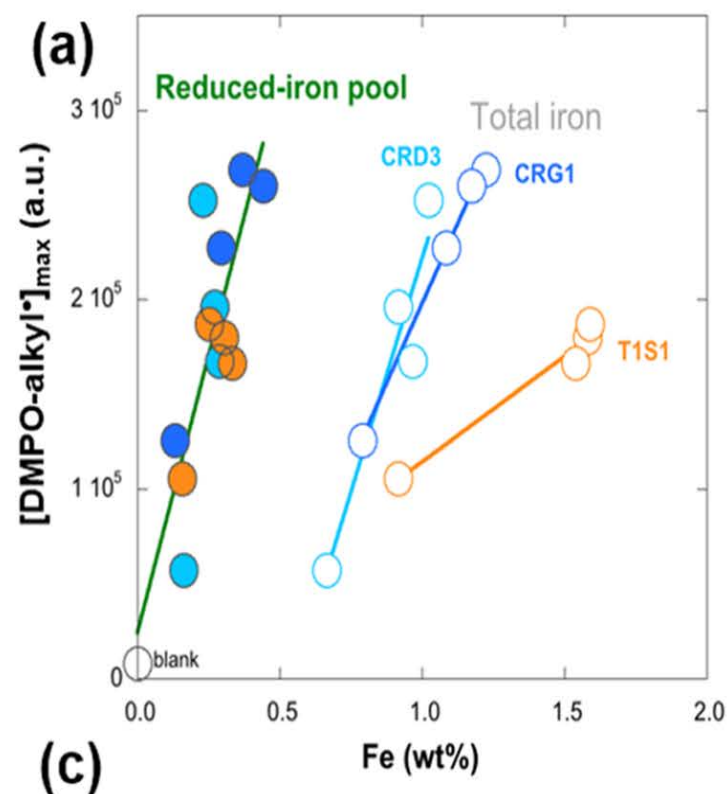
XANES Fe K-edge
CRD3

CRG1

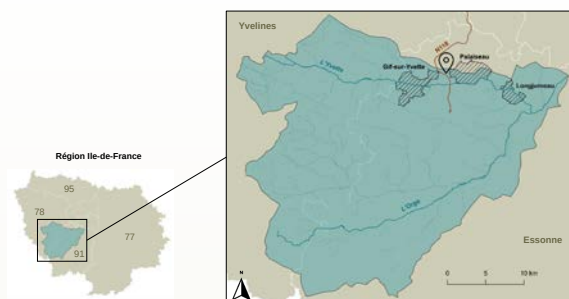
T1S1



Part 1 - Reactive Oxygen Species in soils and sediments



Part 2 – Degradation of HAP upon oxygenation of soils and sediments



sediment incubé 1 an

sediment frais

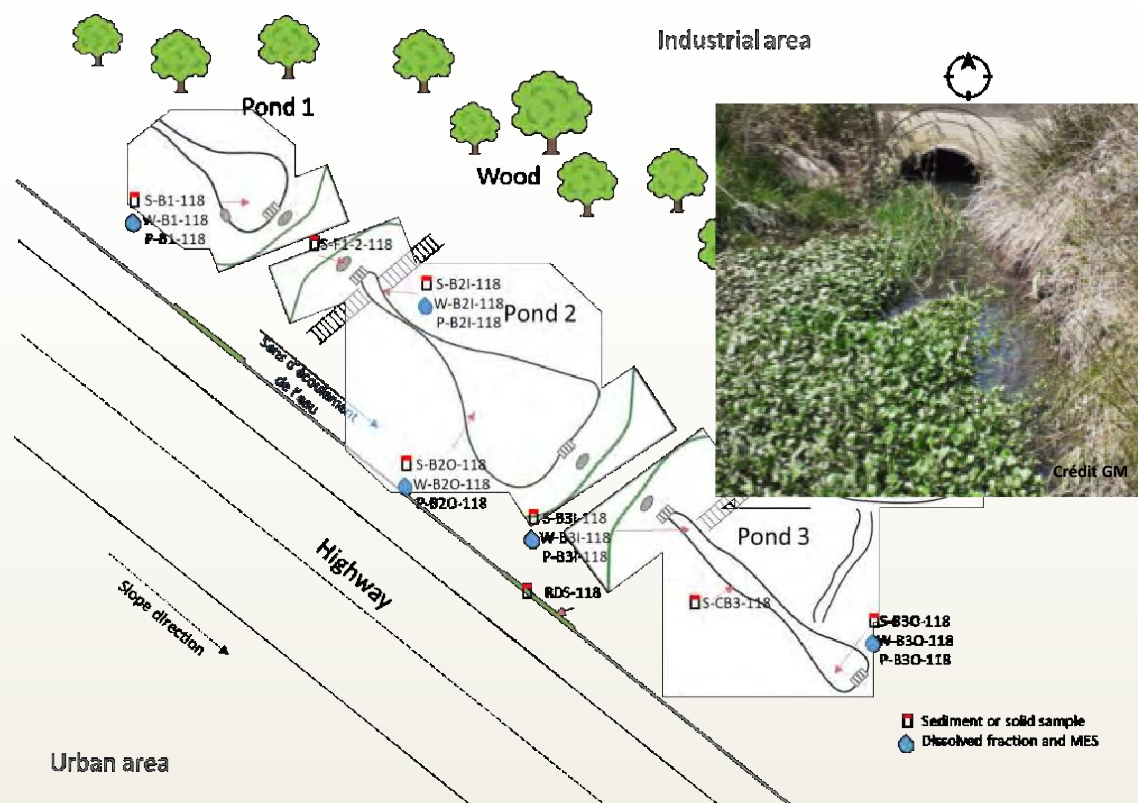
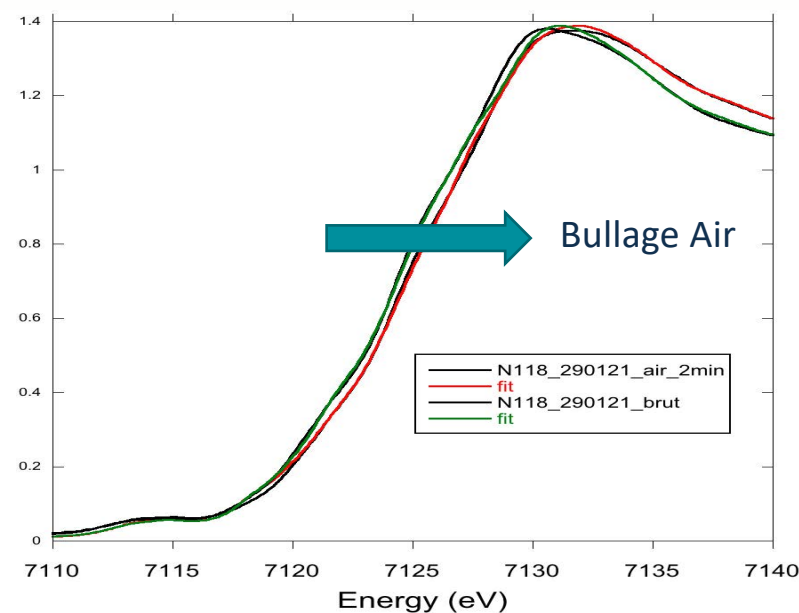
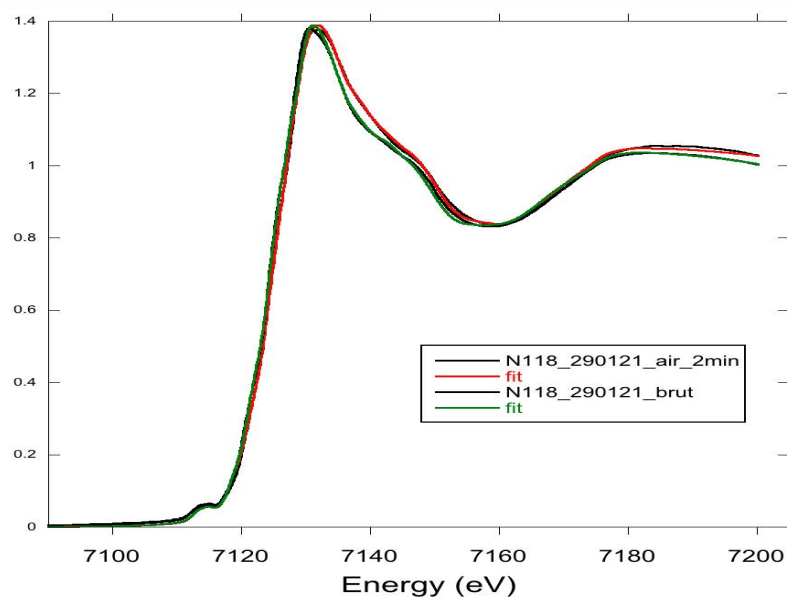


Figure 3. Schéma de localisation du prélèvement de sédiment réalisé dans le bassin #3 de rétention des eaux de ruissellement autoroutier de la N118 à Orsay. D'après *Philippe et al. (2021)*. La photo montre la sortie de la buse et le bassin #3. Le point de prélèvement est indiqué par une étoile.

Part 2 – Degradation of HAP upon oxygenation of sediments

Bourbon PhD 2025

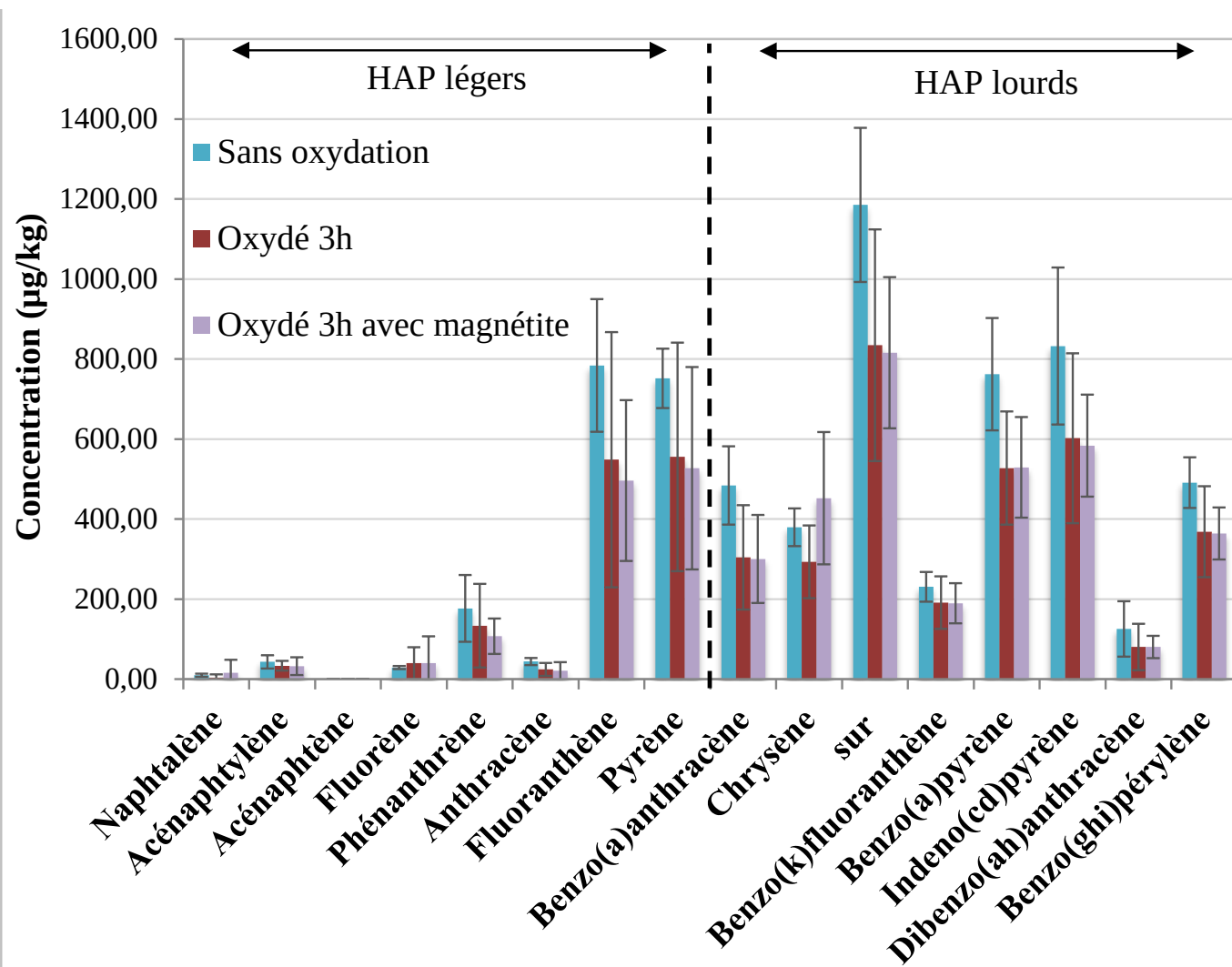
Fe K-edge XANES # sediment incubé 1 an



Echantillon	Pyrite Fe(II) %	Vivianite Fe(II) %	Biotite Fe(II,III) %	Illite Fe(III) %	Goethite Fe(III) %	Somme %	Fe(II) %	$\Delta\text{Fe(II)}$ %	Chi^2_{R} ($\times 10^4$)
N118_290121_brut	10 ± 2	13 ± 3	27 ± 6	14 ± 9	33 ± 9	98	43 ± 4	0	8,5
N118_290121_Air_2min	12 ± 2	12 ± 3	13 ± 5	19 ± 8	43 ± 8	99	33 ± 4	-10 ± 4	7,2

Part 2 – Degradation of HAP upon oxygenation of sediments

sediment
Incubated for 1 year
under anoxic conditions



Bourbon PhD 2025

Part 2 – Degradation of HAP upon oxygenation of soils and sediments



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Water Research

journal homepage: www.elsevier.com/locate/watres



(2021)

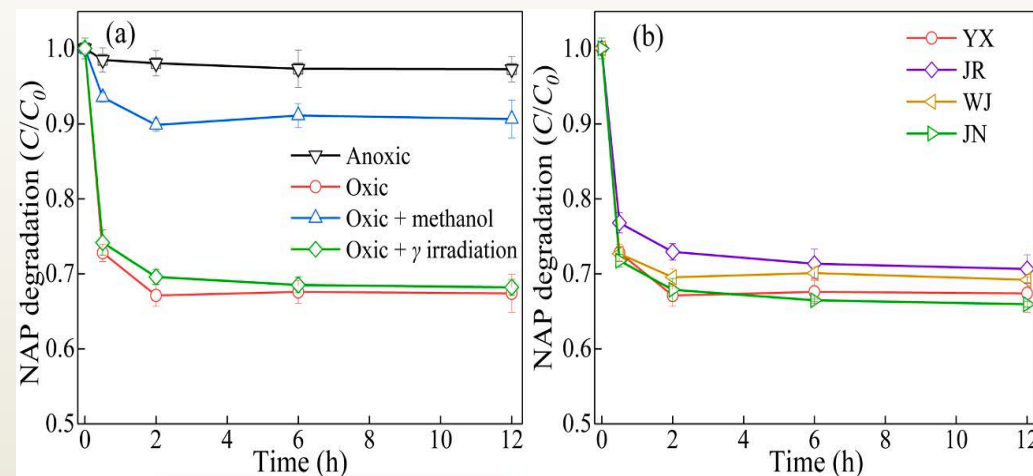
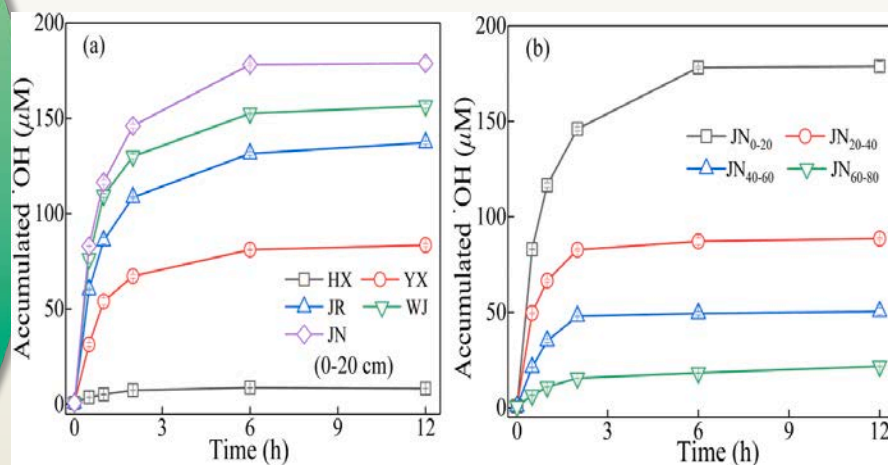


Active iron species driven hydroxyl radicals formation in oxygenation of different paddy soils: Implications to polycyclic aromatic hydrocarbons degradation

Ning Chen^a, Danyu Huang^a, Guangxia Liu^a, Longgang Chu^b, Guodong Fang^b, Changyin Zhu^a, Dongmei Zhou^{a,*}, Juan Gao^{b,*}

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^b Key Laboratory of Soil Environment and Pollution Remediation, Institute of Soil Science, Chinese Academy of Sciences, Nanjing 210008, Jiangsu Province, China

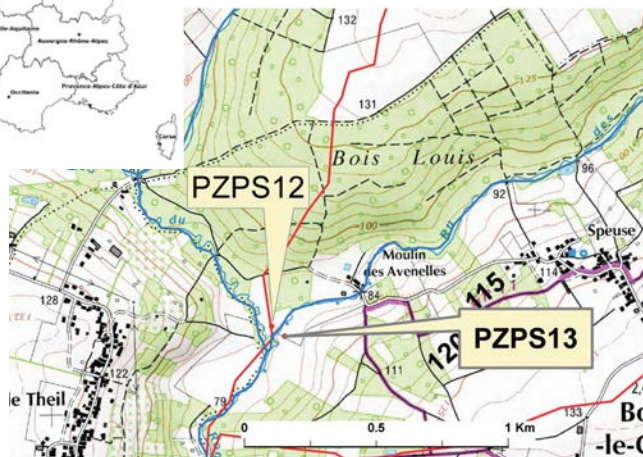


Part 3 – Reductive degradation

Samples - Orgeval site

Riverbank soils from Orgeval basin, France (Avenelles creek)

- CRD3 and CRG1 and cores, 9 samples



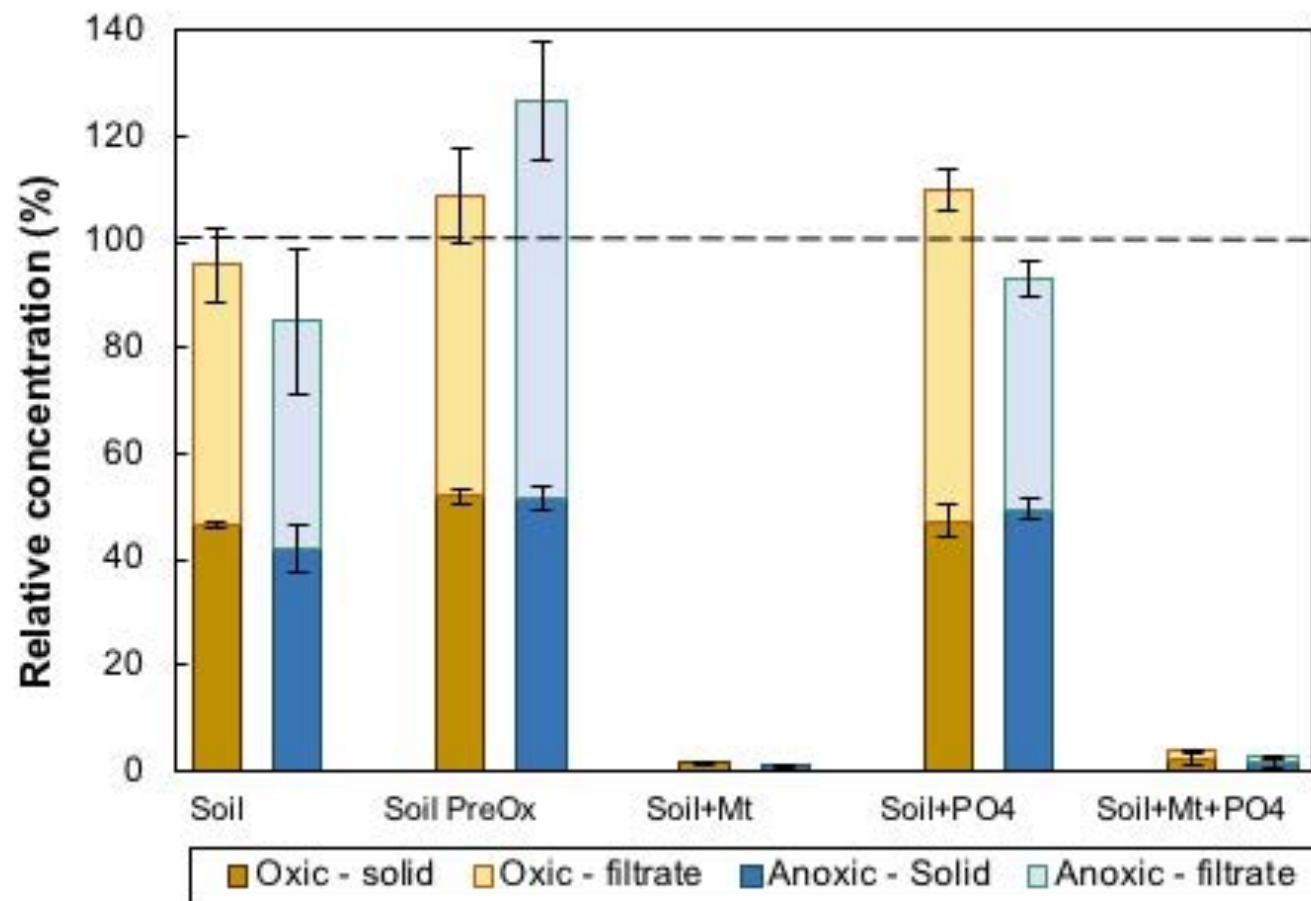
Bourbon 2025
Bourbon et al. in prep



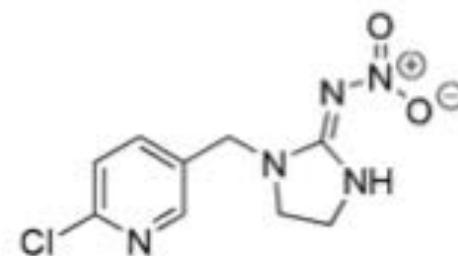
Part 3 – Reductive or oxidative degradation ?

- Fresh soils or pre-oxidized soils
- With or without nanomagnetite added
- doped with **sulfamethoxazole** and **imidacloprid**
 - impregnation period of 24 h at 4°C under anoxic conditions
 - followed by an anoxic or oxic drying procedure

Part 3 – Reductive degradation



Imidacloprid



Bourbon 2025
Bourbon et al. in prep

Reductive transformation of imidacloprid

C. Gecgel et al. / Desalination and Water Treatment 114 (2018) 341–355

351

Desalination and Water Treatment
www.deswater.com
doi: 10.5004/dwt.2018.22355

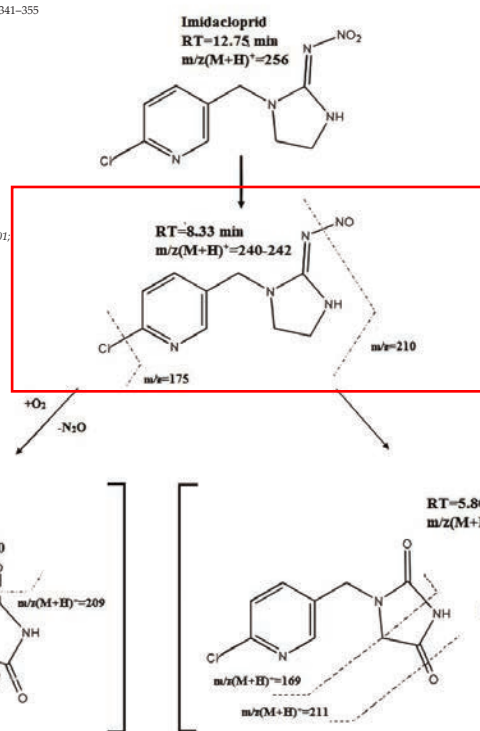
Degradation of imidacloprid in aqueous solutions by zero valent iron nanoparticles in the nitrogen medium

Cihan Gecgel^a, Utku Bulut Simsek^a, Meral Turabik^{a,b,*}

^aDepartment of Nanotechnology and Advanced Materials, Mersin University, Mersin TR-33343, Turkey, Tel.: +90 324 361 00 01; emails: mturabik@mersin.edu.tr (M. Turabik), cihangecgel@hotmail.com (C. Gecgel), utkubulutsimsek@msn.com (U.B. Simsek)
^bChemical Program, Technical Science Vocational School, Mersin University, Mersin TR-33343, Turkey

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114 (2018) 341–355
May



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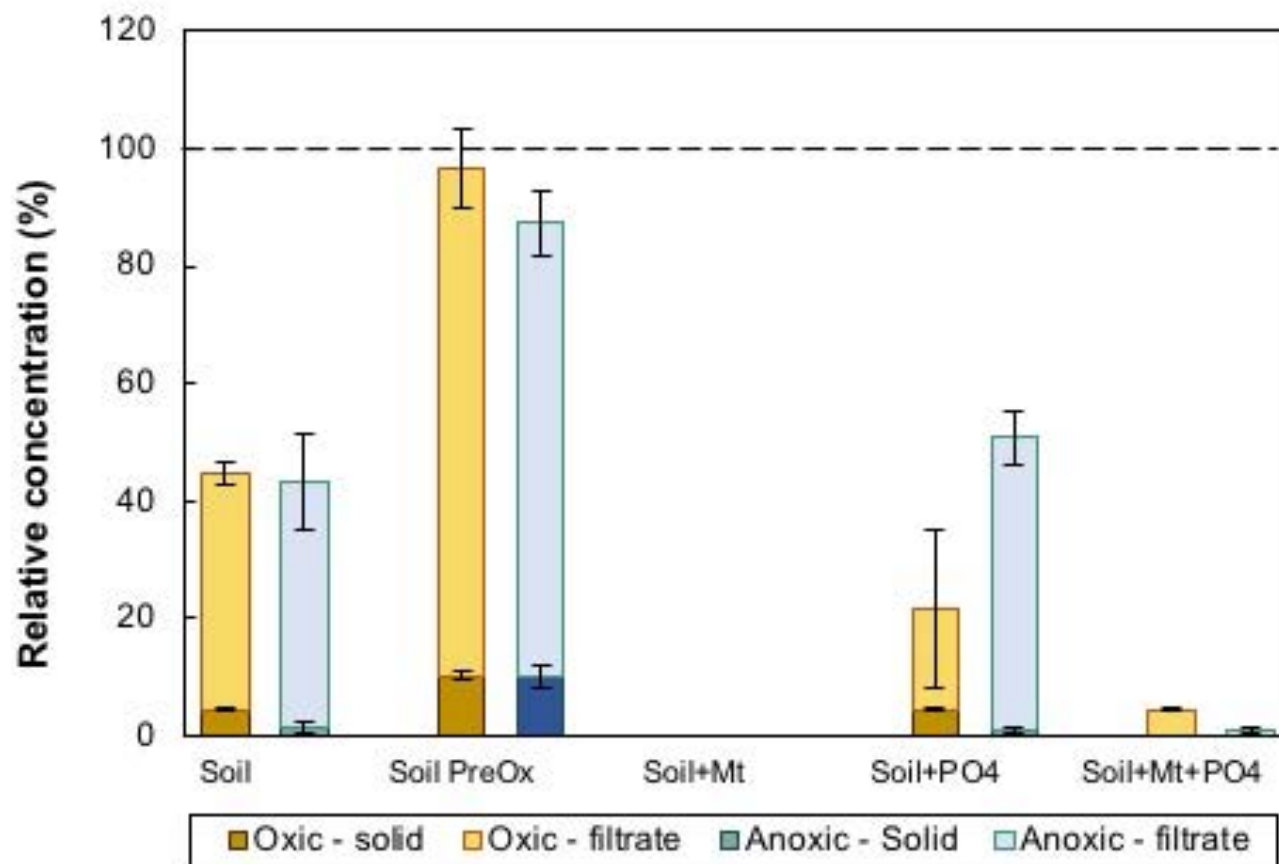
Nitroreduction of imidacloprid by the actinomycete *Gordonia alkanivorans* and the stability and acute toxicity of the nitroso metabolite

Xi Cheng, Ke-xin Chen, Neng-dang Jiang, Li Wang, Huo-yong Jiang, Yun-xiu Zhao, Zhi-ling Dai, Yi-jun Dai^{*}

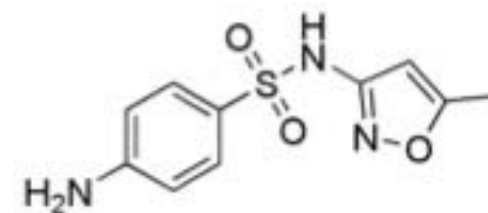
Jiangsu Key Laboratory for Microbes and Functional Genomics, Jiangsu Engineering and Technology Research Center for Industrialization of Microbial Resources, College of Life Science, Nanjing Normal University, Nanjing 210023, People's Republic of China

Fig. 10. Possible degradation pathway of imidacloprid.

Part 3 – Reductive degradation



Sulfamethoxazole



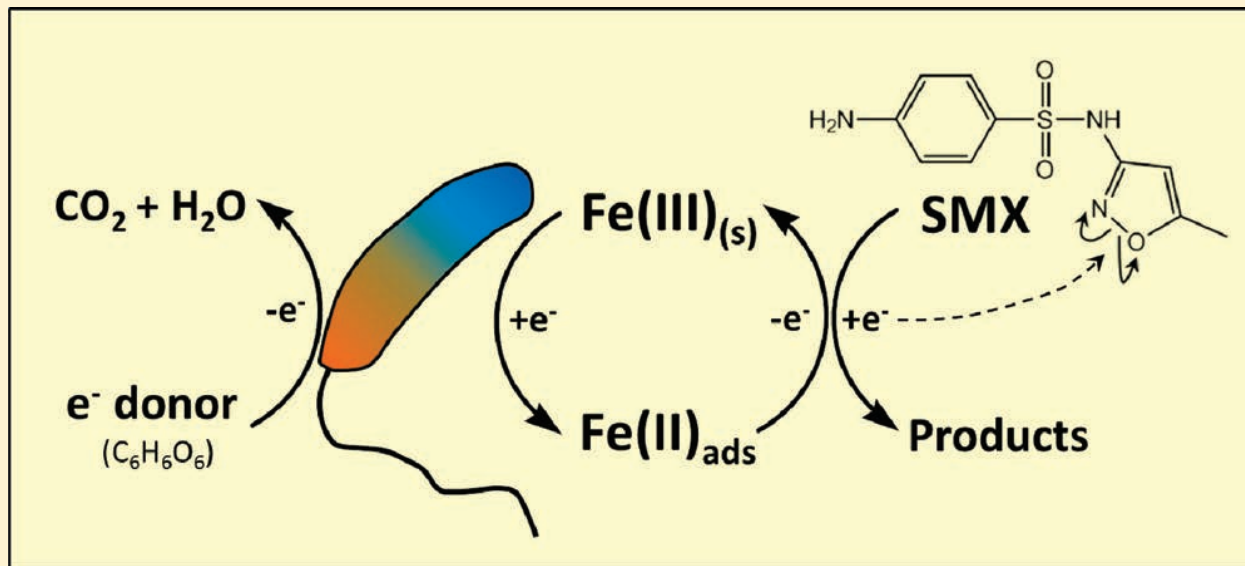
Bourbon 2025
Bourbon et al. in prep

Part 3 – Reductive degradation

Microbially Mediated Abiotic Transformation of the Antimicrobial Agent Sulfamethoxazole under Iron-Reducing Soil Conditions

Jessica L. Mohatt, Lanhua Hu, Kevin T. Finneran,[†] and Timothy J. Strathmann*

Department of Civil and Environmental Engineering, University of Illinois at Urbana—Champaign, Urbana, Illinois 61801, United States



Conclusions (1)

- ➡ Reactive Oxygen Species (ROS) are produced upon aeration of waterlogged soils and sediments
- ➡ This is explained by heterogeneous Fenton-like reactions occurring upon oxygenation of naturally occurring Fe(II)-minerals
- ➡ Fe(IV) may be dominant over OH° under such conditions when phosphate and other ligands are present



Conclusions (2)

- ▶ PAHs can be moderately degraded by O₂-based Fenton-like processes, for instance upon drying of waterlogged contaminated sediments
- ▶ Heavy PAHs appear to be more sensitive to this oxidative degradation process in the highway stormwater pond studied.



Conclusions (3)

- Iron(II)-bearing soil minerals are able to degrade organic contaminants via reductive pathways
- We observed a significant removal of sulfamethoxazole after 24h contact with a naturally reduced riparian alluvial soil
- The removal of sulfamethoxazole and imidacloprid is complete when 10 wt% nanomagnetite is added to the soil prior contact



Perspectives

- Need for direct detection of Fe(IV) in soils and sediments oxygenation experiments and for evaluating its reactivity toward pollutants
- Interest in studying the effects of multiple redox cycles on the degradation/transformations of contaminants via both oxidative and reductive pathways
- Important need for identifying the by-products of natural oxidative and reductive transformation/degradation pathways
- Further interest in evaluating the effects of natural reductive and oxidative pathways on the fate of perfluorinated compounds (PFAS)