



Soil Pollution and EPR

Soil pollution is a direct result of industrial, agricultural, and societal growth. Many of the common pollutants can be detected with EPR leading to measures to control their distribution and aid in clean-up strategies.

Common soil pollutants are a result of:

- Industrial waste: poisonous gases, cytotoxic chemicals, radioactive materials, cancer causing agents.
- Industrial heavy metal by-products: cadmium, chromium, lead, mercury.
- Agricultural burdens: pesticides, insecticides, herbicides, fertilizers.

All these pollutants are toxic in their own right and often participate in processes resulting in the formation of surface-stabilized environmentally persistent free radicals (EPFRs). EPFRs play a role in the further generation of toxic compounds and are additionally involved in radical processes that impact the formation of humic substances, and thus carbon sequestration. It has also been found that EPFR-containing particles can generate reactive oxygen species (ROS) that induce oxidative stress.

Electron Paramagnetic Resonance (EPR) spectroscopy is the only technique for the direct and non-invasive detection

of transition metals and free radicals. By analyzing an EPR signal, one can identify, quantify and monitor long-lived EFRs in soil organic matter, short-lived ROS's and paramagnetic heavy metals.

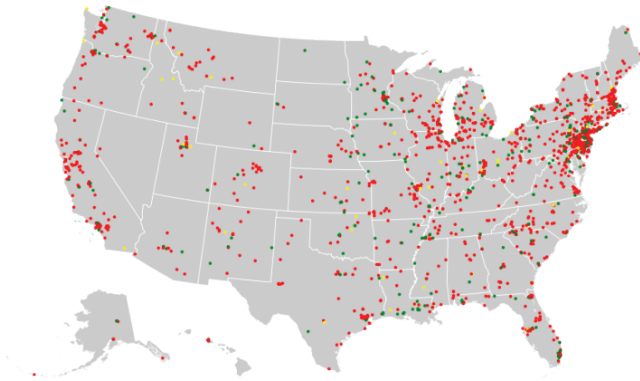
Challenge: Detailed research is required to understand the impact of pollution from industrial and agricultural sources on the soil environment. Understanding the mechanisms and roles of the inorganic, organic, and biological components of soil leads to effective strategies to neutralize toxic compounds.

Solution: The Magnettech ESR5000 benchtop EPR spectrometer package

- Detects, identifies, and quantifies EPFRs, ROS, and transition metals in contaminated soil systems
- Evaluates the health and environmental ramifications of EPFRs in soils and sediments
- Monitors radical reactions for better understanding the oxidation mechanisms and to determine the impact on human health
- Determines with high precision the g-factor using the integrated internal marker to identify the radical species.

Magnettech ESR5000 key features:

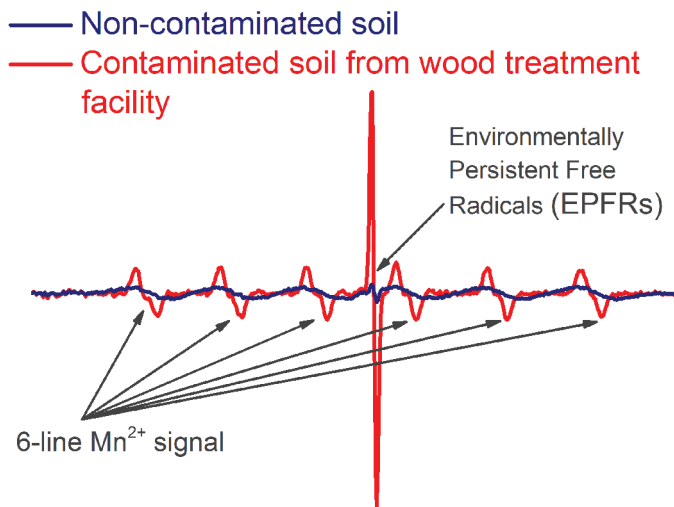
- No prior EPR experience needed
- Accurate results
- Superior sensitivity
- Ease of use
- Full workflow for measuring, analyzing and quantifying free radicals and transition metals
- Compact foot print
- Low cost of ownership



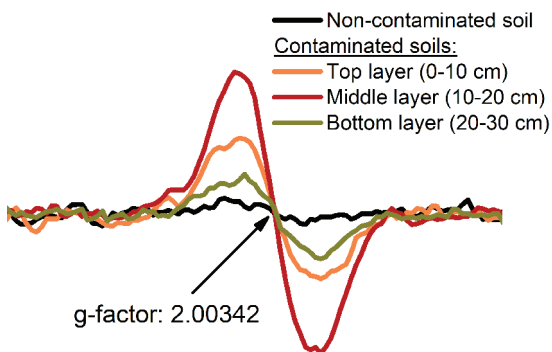
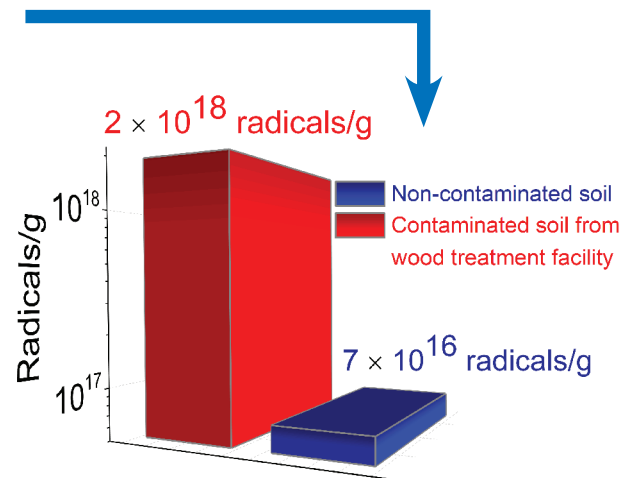
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EPR study on soil from Superfund sites in the US

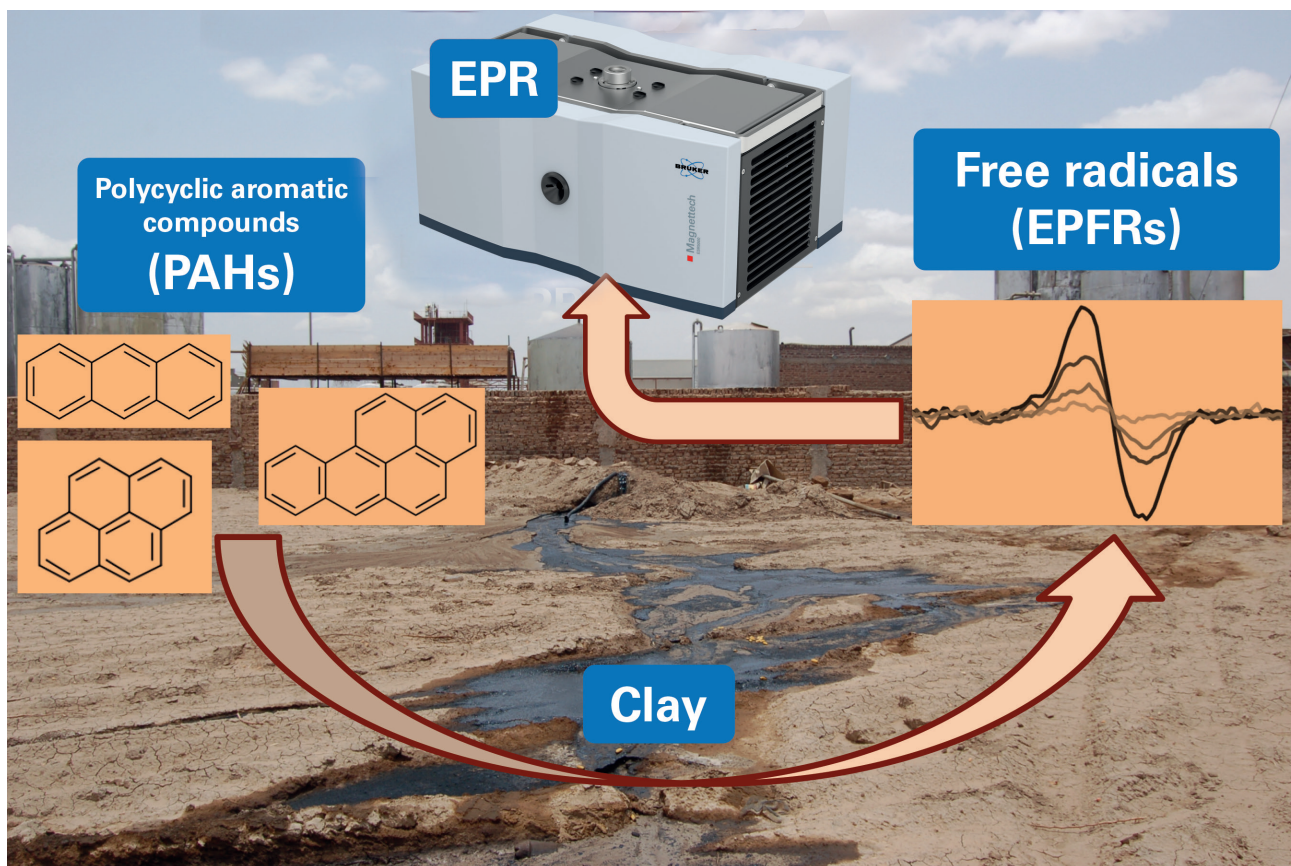
- Superfund sites are polluted locations requiring a long-term response to clean up hazardous material contaminations
- Red indicates sites currently on the National Priority List, yellow is a proposed clean-up site, and green is typically a cleaned site.



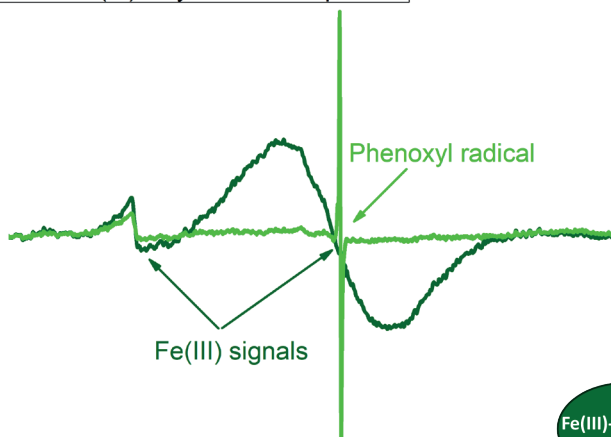
Quantitative EPR



- EPR detects and quantifies the formation of environmentally persistent free radicals (EPFRs) in contaminated soils from Superfund sites.
- The g-factor of the radical signal was used to identify this EPFR as the phenoxy radical.
- EPR monitors the radical concentration as a function of soil depth. The highest radical concentration is found in the middle depth soil layer (10-20 cm) at one of the sites which correlates with the contaminant concentration.
- The radical yield determined by quantitative EPR analysis in this site, contaminated more than 10 years ago, suggests a mechanism where the contaminant is continually producing EPFRs.

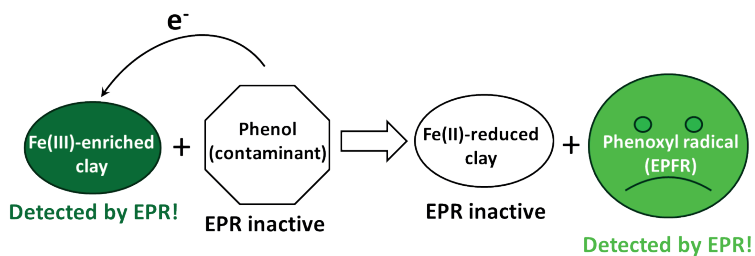


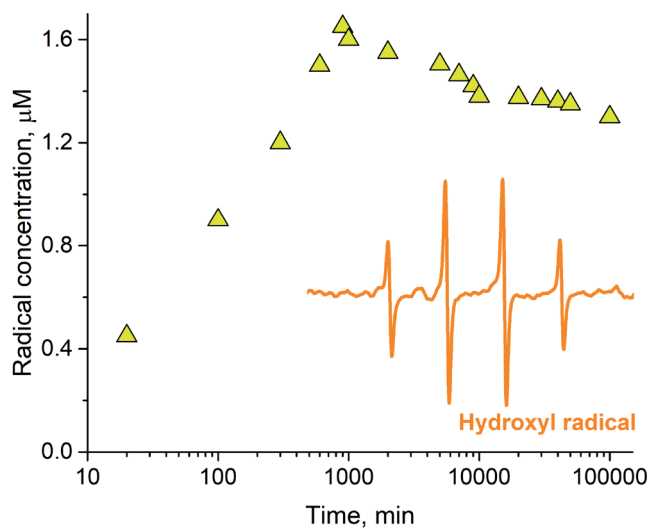
— Fe(III) clay
 — Fe(III) clay dosed with phenol



Free radicals in Fe(III)-enriched clay

- Clay minerals act as a potential reservoir of transition metals and toxic organic pollutants.
- EPR demonstrates the catalytic role of transition metal centers (Fe^{3+}) in phenol contaminated clay minerals in the formation of EPFRs.
- EPR monitors and quantifies the production of EPFRs via oxidation-reduction mechanism:





ROS in biochars (supplements added to soil to improve fertility)

- Stable O- and C-centered organic radicals are induced in biochars and detected by EPR during production (charring).
- Quantitative EPR shows an increase in the biochar-induced radical concentration during charring.
- Harmful hydroxyl radicals ($\cdot\text{OH}$) are formed that are detected by EPR.
- The time course of the ROS formation shows the stimulation of hydroxyl radical production up to 1000 minutes.

Summary:

The existence of potentially toxic EPFRs questions the long held belief that sorption of an organic pollutant into a soil matrix is a method of mitigating its environmental impact. Therefore, understanding of how EPFRs form in contaminated soils and sediments is extremely important. In addition, transition metals can act as catalysts for EPFR production and are often toxic themselves. The Magnettech ESR5000 is the solution to investigate and study this important radical chemistry and the detection of transition metals. With EPR one gains insights into the mechanisms involving generation of large amounts of EPFRs in soils which has significant impact on human health.

Furthur Reading

1. dela Cruz A. et al., Detection of environmentally persistent free radicals at a superfund wood treating site, *Env. Sci. Technol.* (2011) 45 6356
2. Liao S. et al., Detecting free radicals in biochars and determining their ability to inhibit the germination and growth of corn, wheat and rice seedlings, *Env. Sci. Technol.* (2014) 48 8581
3. dela Cruz A. et al., Assessment of environmentally persistent free radicals in soils and sediments from three superfund sites, *Environ. Sci. Process Impacts* (2014) 16 44
4. Nwosu U. et al., Formation of environmentally persistent free radical (EPFR) in iron(III) cation-excganged smectite clay, *Environ. Sci. Process Impacts* (2016) 18 42
5. Jia H. et al., Formation and stabilization of environmentally persistent free radicals induced by the interaction of anthracene with Fe(III)-modified clays, *Env. Sci. Technol.* (2016) 50 6310