

# Novel Methods to Monitor Environmental Pollutants

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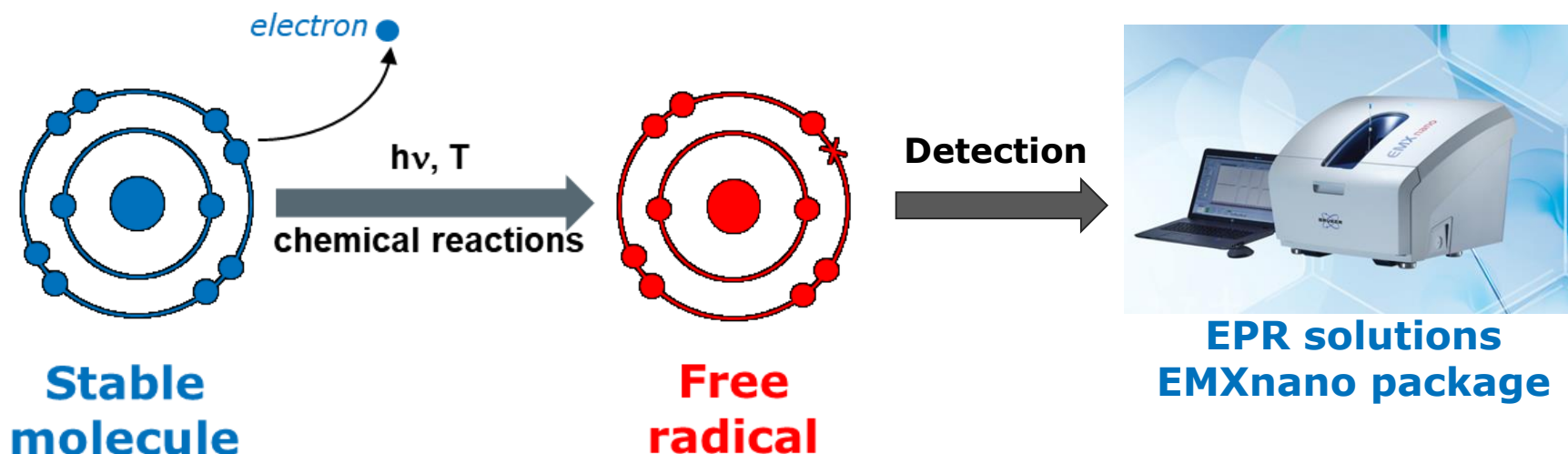
Applications Scientist, Bruker BioSpin Corp.



# What is EPR?



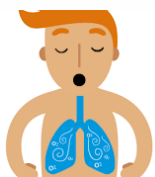
- EPR is a magnetic resonance technique that detects **unpaired electrons**
- **Unpaired electrons** occur in **free radicals** and many **transition metals**
- **Free radicals** and **transition metal ions** are often present in polluted environment (air, soil, water)



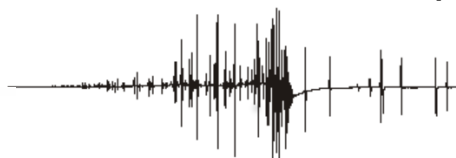
# Why are free radicals and EPR so important?



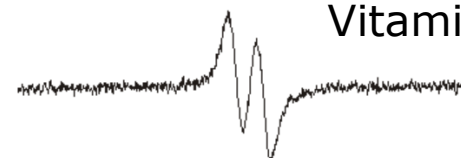
- Free radicals and transition metals are very common in everyday life



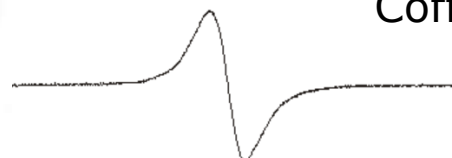
Oxygen



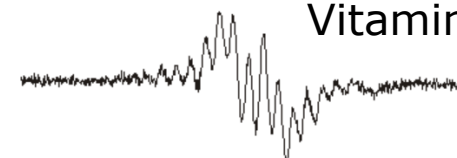
Vitamin C



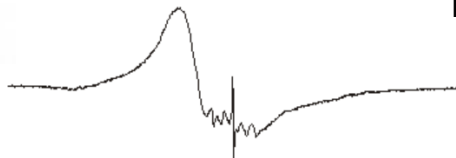
Coffee



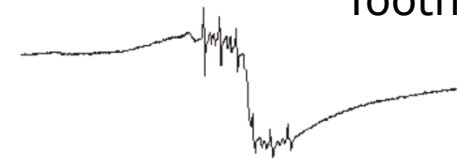
Vitamin E



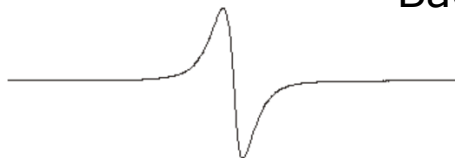
Tea



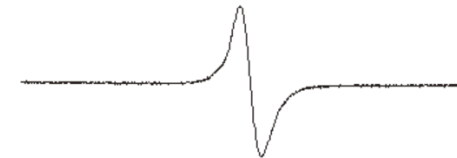
Toothpaste



Bagel



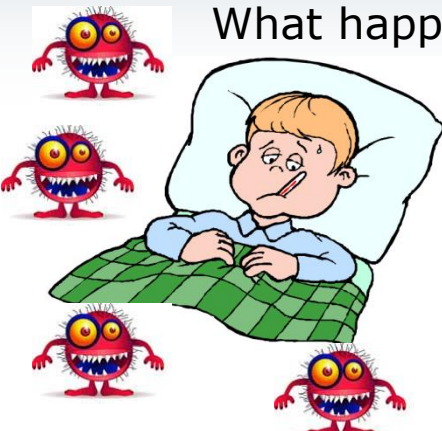
Hair



# Why are free radicals and EPR so important?



What happens when we get sick ...



Our immune system defense response

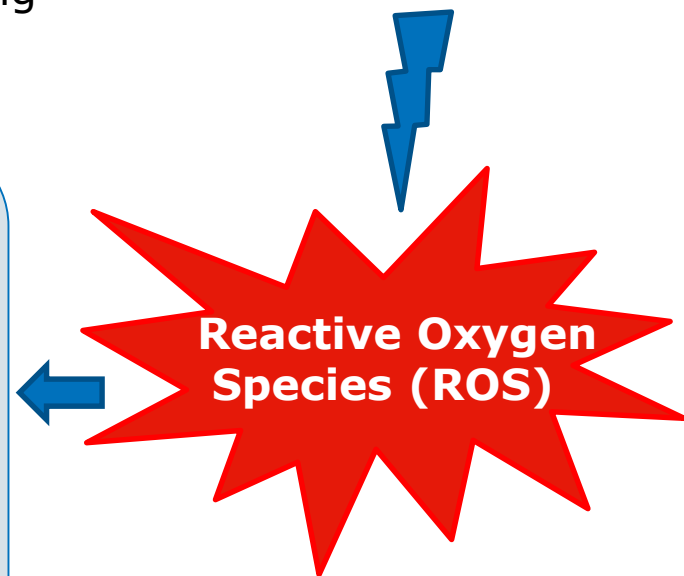


White blood cells release ROS to kill invading pathogens



Invading microbes (pathogens) attack our body => infection/disease

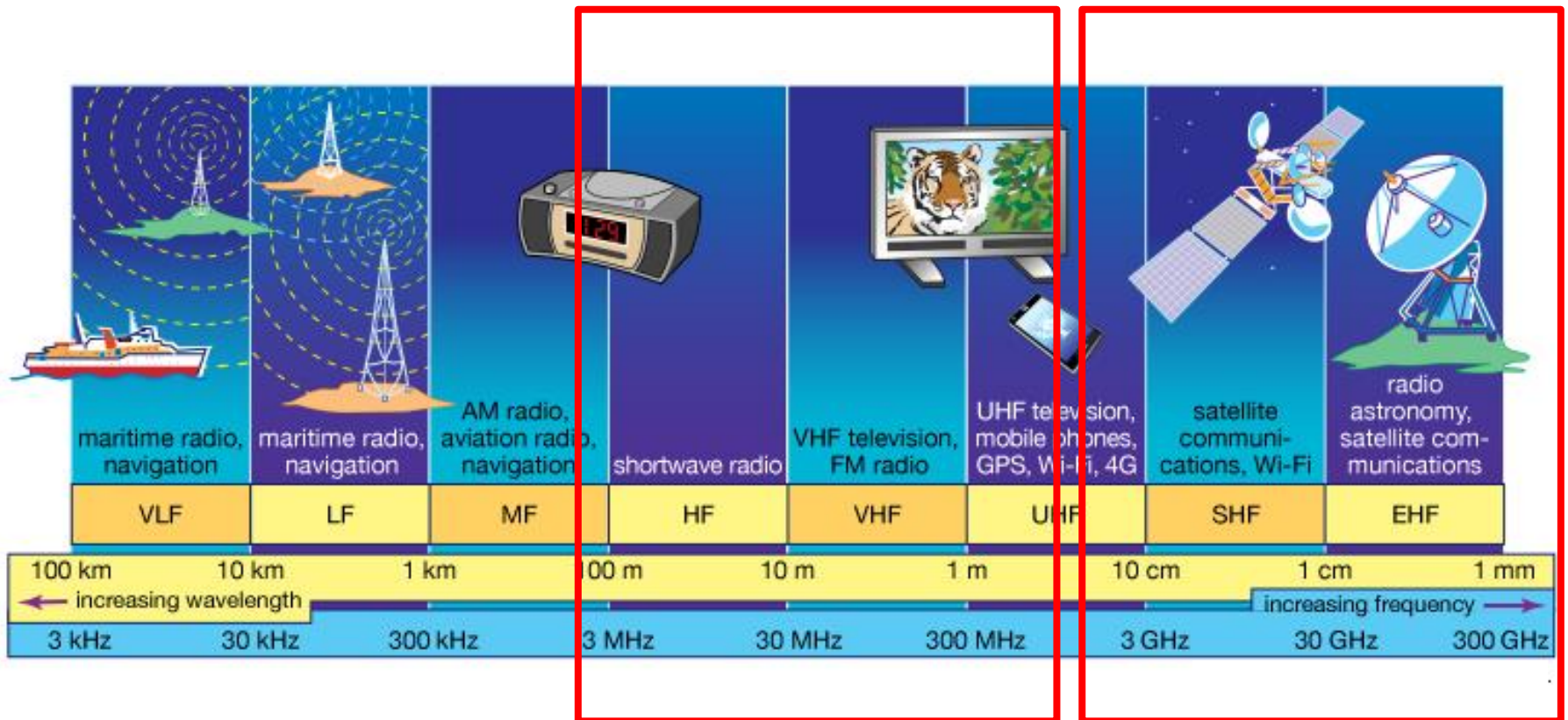
- ROS are free radicals and highly reactive!
- Their activities are beneficial but can also be toxic!
- ROS are detectable by EPR!
- EPR can tell us **HOW MUCH AND WHAT TYPE** of free radicals are detected!



# How it works



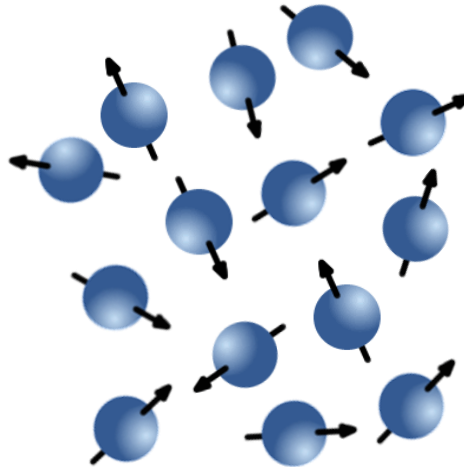
NMR Radio Frequencies EPR Microwave Frequencies



# How it works



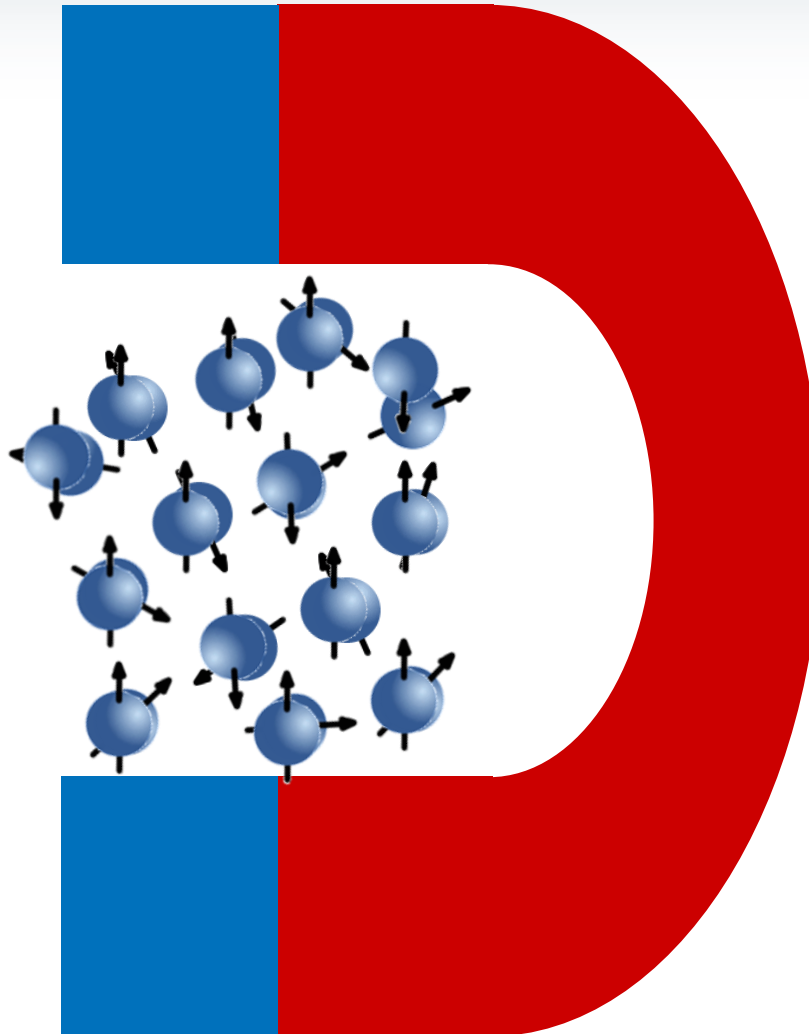
Without an external magnetic field spins are randomly oriented



# How it works

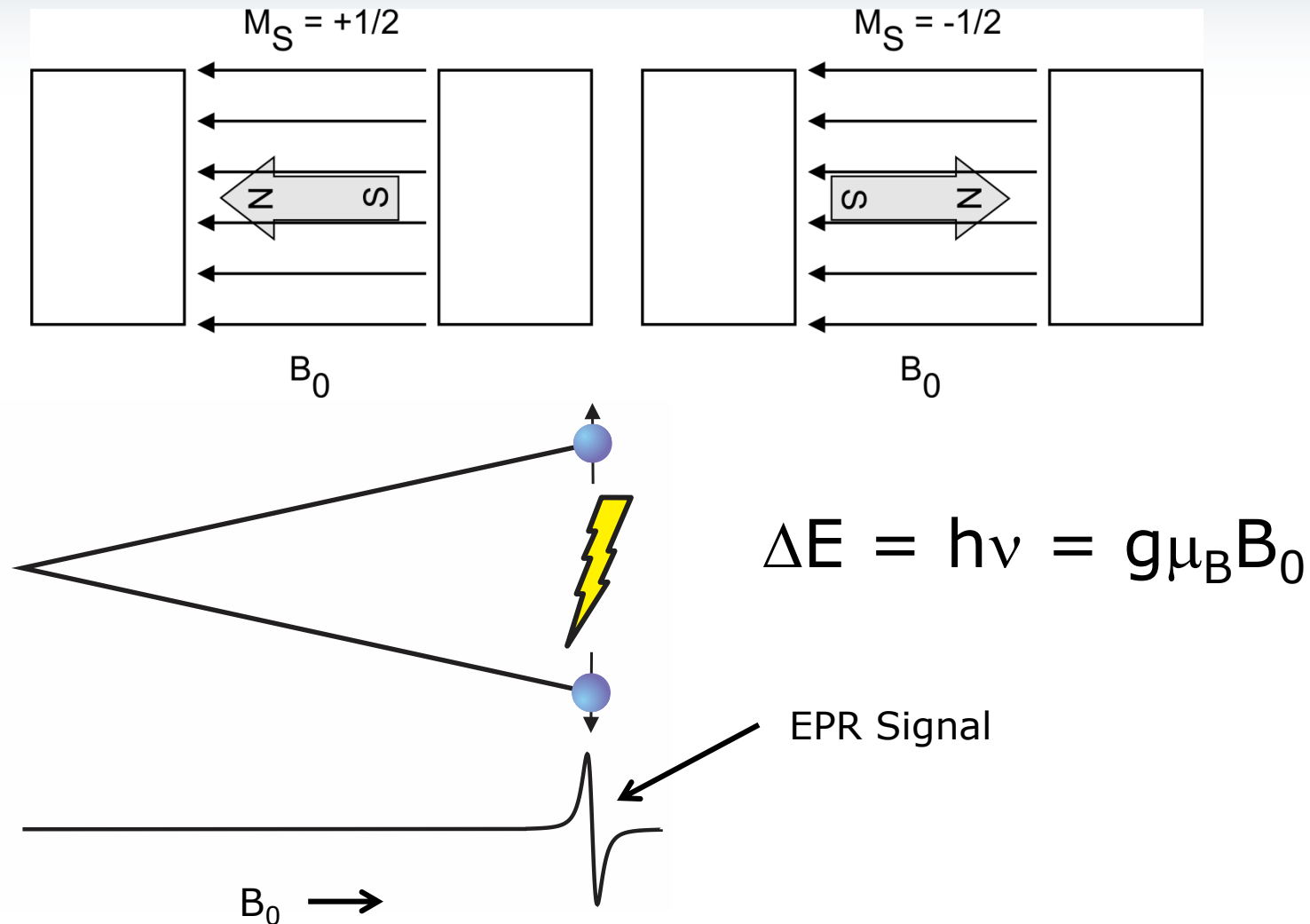
Placing the spins into a magnetic field will lead to alignment of the spins.

In reality an electron spin will assume one of two spins states with one being slightly more populated than the other.



# How does EPR work?

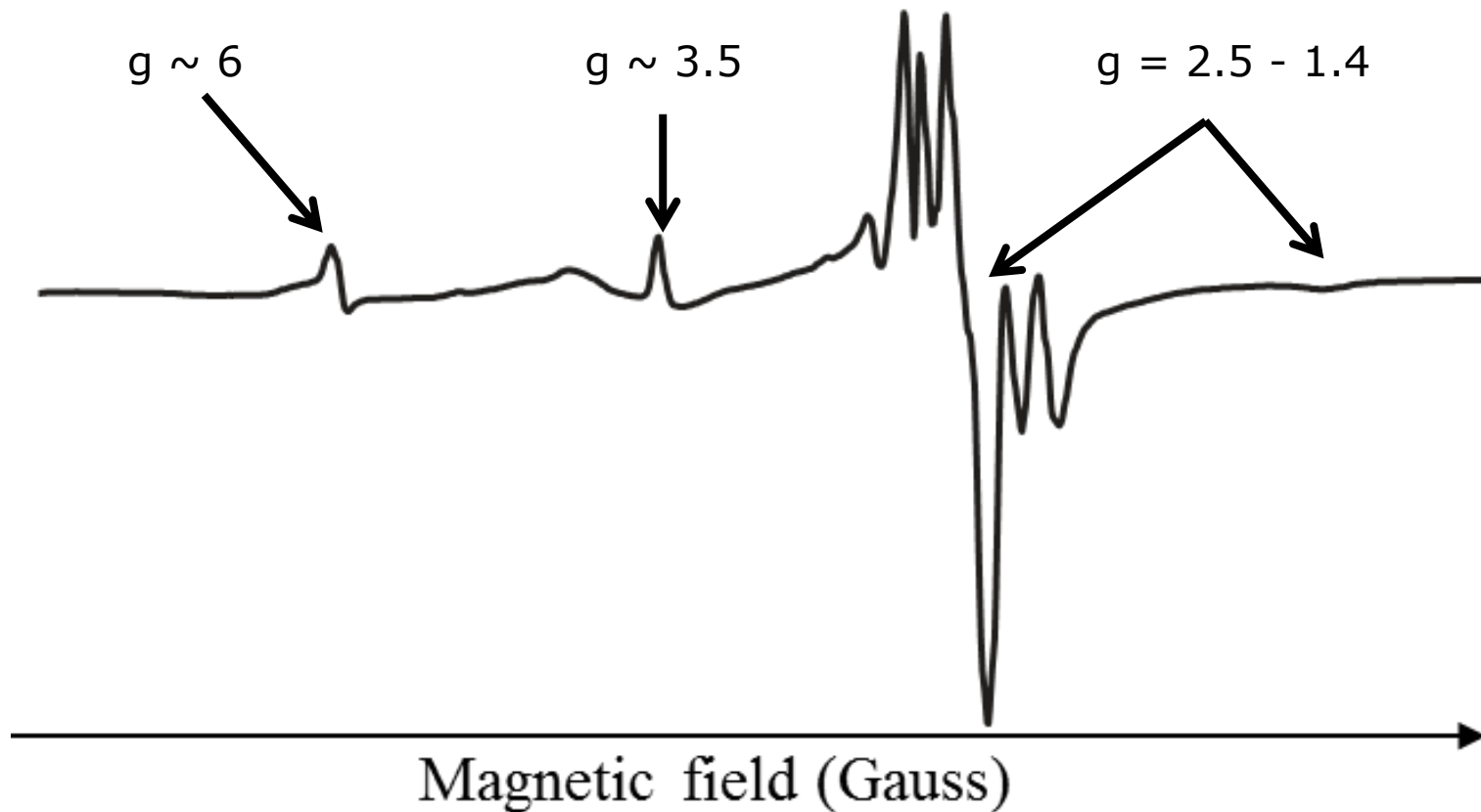
## EPR Fingerprints: the g-value





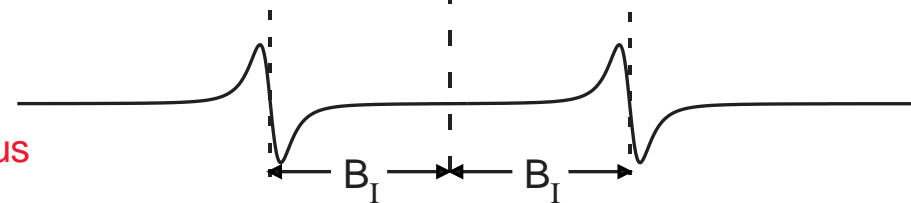
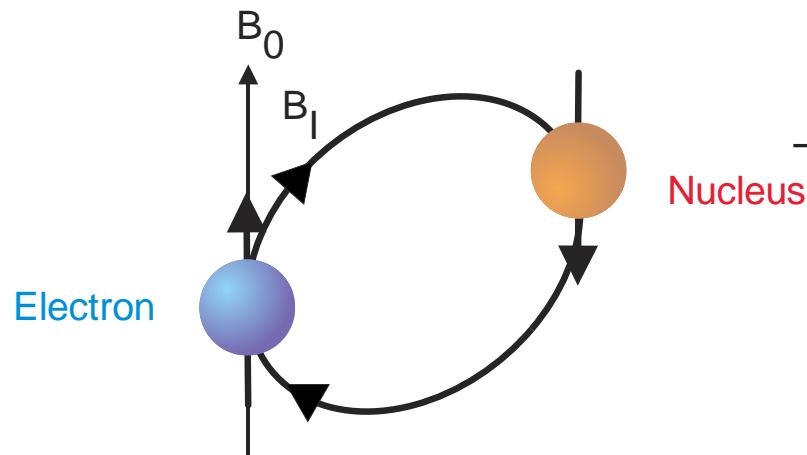
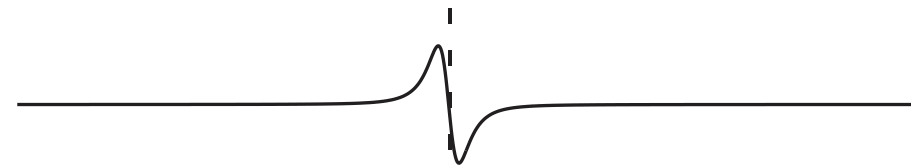
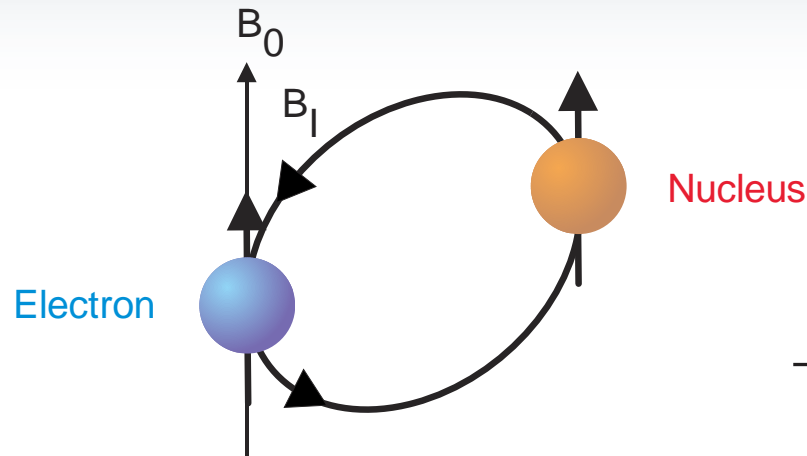
# How does EPR work?

## EPR Fingerprints: the g-value



# How does EPR work?

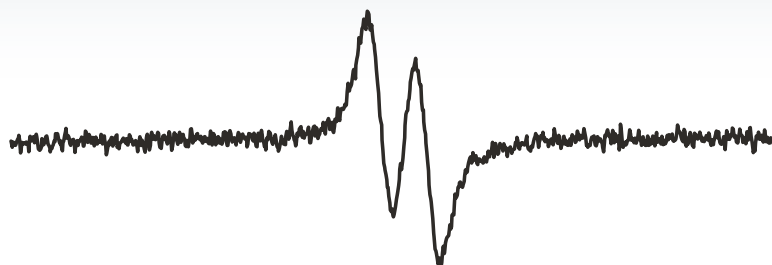
## EPR Fingerprints: Hyperfine interactions



# How does EPR work?

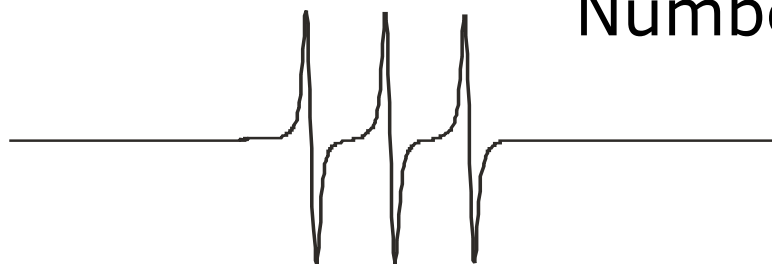
## EPR Fingerprints: Hyperfine interactions

Hydrogen  
 $I = 1/2$

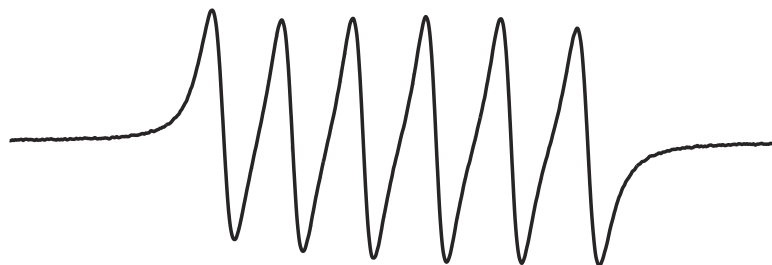


$$\text{Number of Lines} = 2I + 1$$

Nitrogen  
 $I = 1$



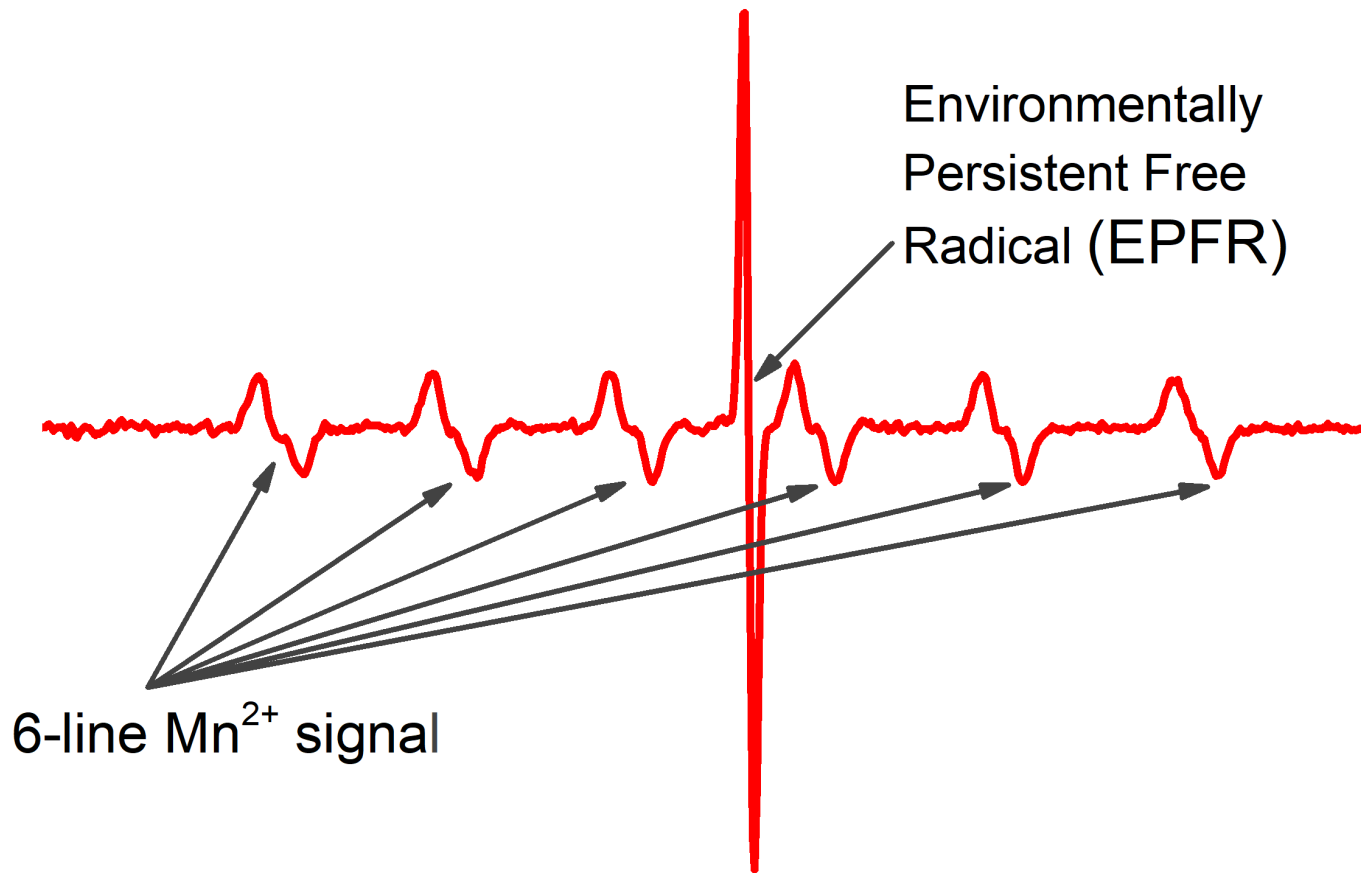
Manganese  
 $I = 5/2$



# How does EPR work?



## Contaminated soil



# Environmental applications of EPR



**Air**



**Soil**

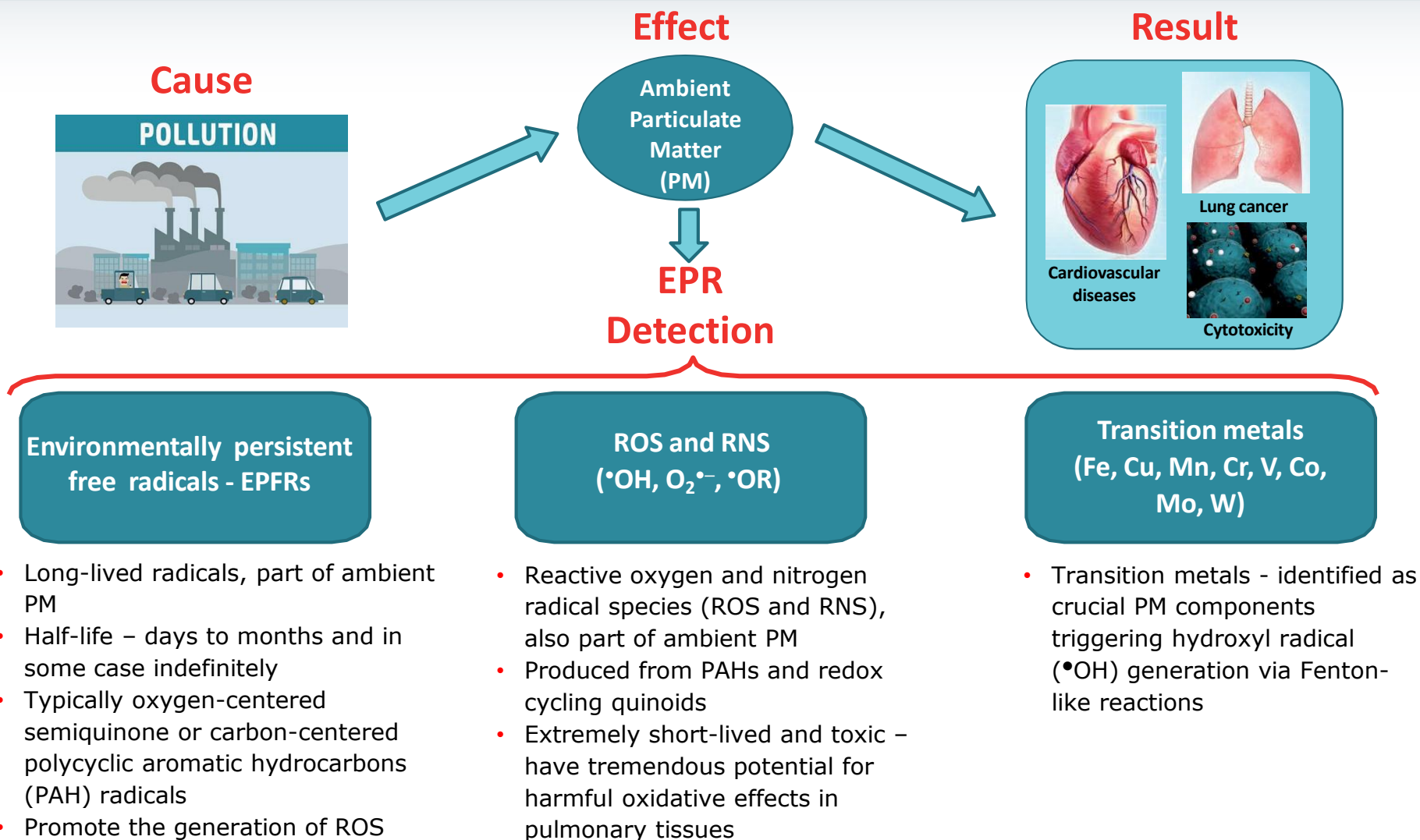


**Water**



# Environmental applications of EPR

## Air Pollution and EPR



# Environmental applications of EPR

## Air Pollution and EPR



### Challenge

- Identifying and monitoring generation of free radicals from ambient particulate matter
- Determining radicals' oxidative potential is of great concern due to adverse effects on human health



### Solution

#### EPR can:

- Detect, identify, and quantify ROS, PAHs, EPFRs, and transition metals involved in the particulate matter (PM) chemistry
- Determine the oxidative potential of PM which is an important metric to estimate potential adverse effects
- Monitor radical reactions for better understanding of the oxidation mechanisms and to determine the half-life of the radicals

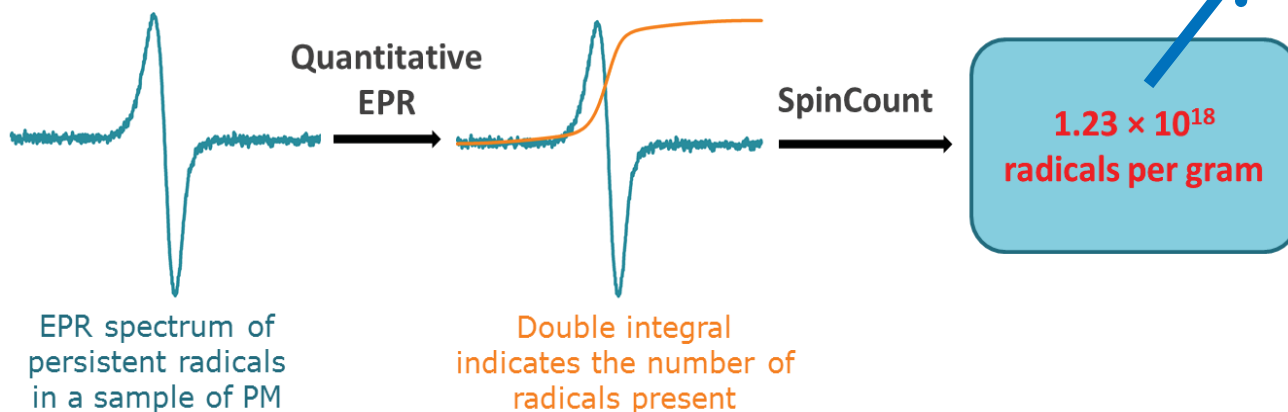
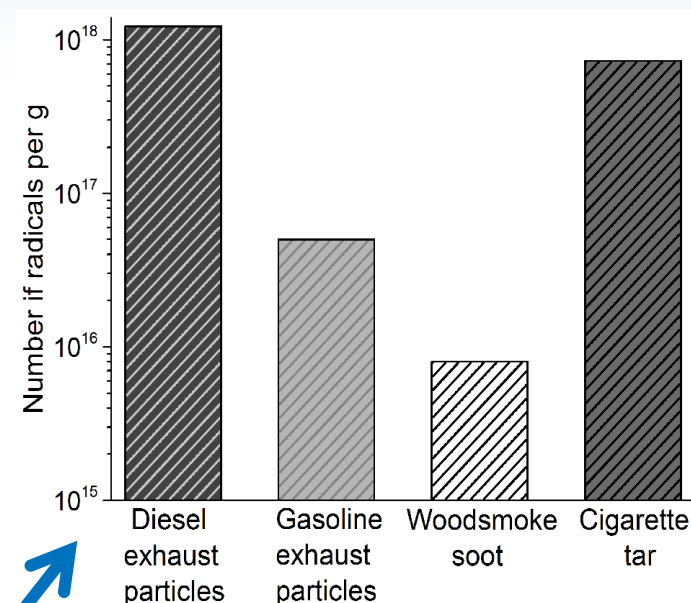
# Environmental applications of EPR

## Air Pollution and EPR



### EPR analysis of PM from various air pollution sources:

- EPR identifies and quantifies long-lived environmentally persistent free radicals (EPFRs)
- Depending on the EPR spectrum characteristics (g-factor) EPFRs are identified as O-centered semiquinone or C-centered PAH radicals





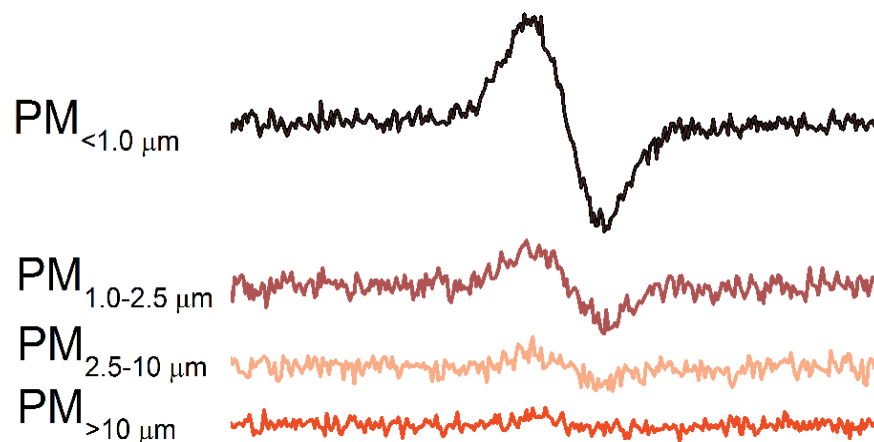
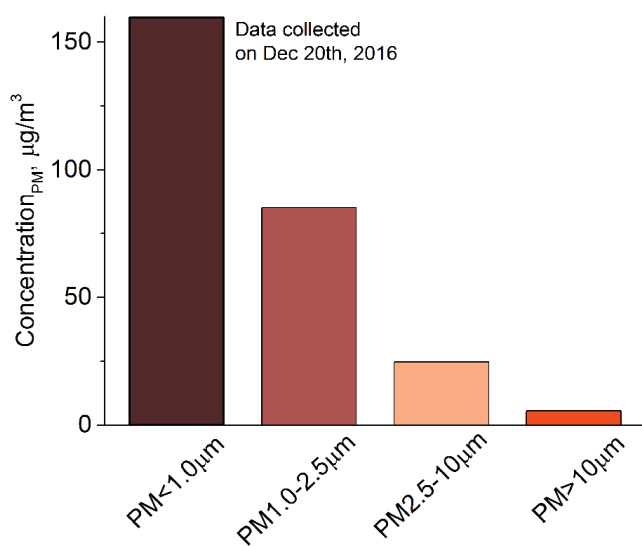
# Environmental applications of EPR

## Air Pollution and EPR



### Case study: EPR detection on airborne PM in Beijing during haze events:

- EPFRs are identified as semiquinone radicals in PM with different particle size:



- EPR shows that EPFRs are mainly persistent in the PM fraction of  $d_{ae} < 1 \mu\text{m}$  which are the most hazardous
- The daily monitoring of the EPFRs (spins/g) shows environmental changes that impact long-term effects on human health
- Such monitoring can be used to enact counter measures to reduce health risks to the public

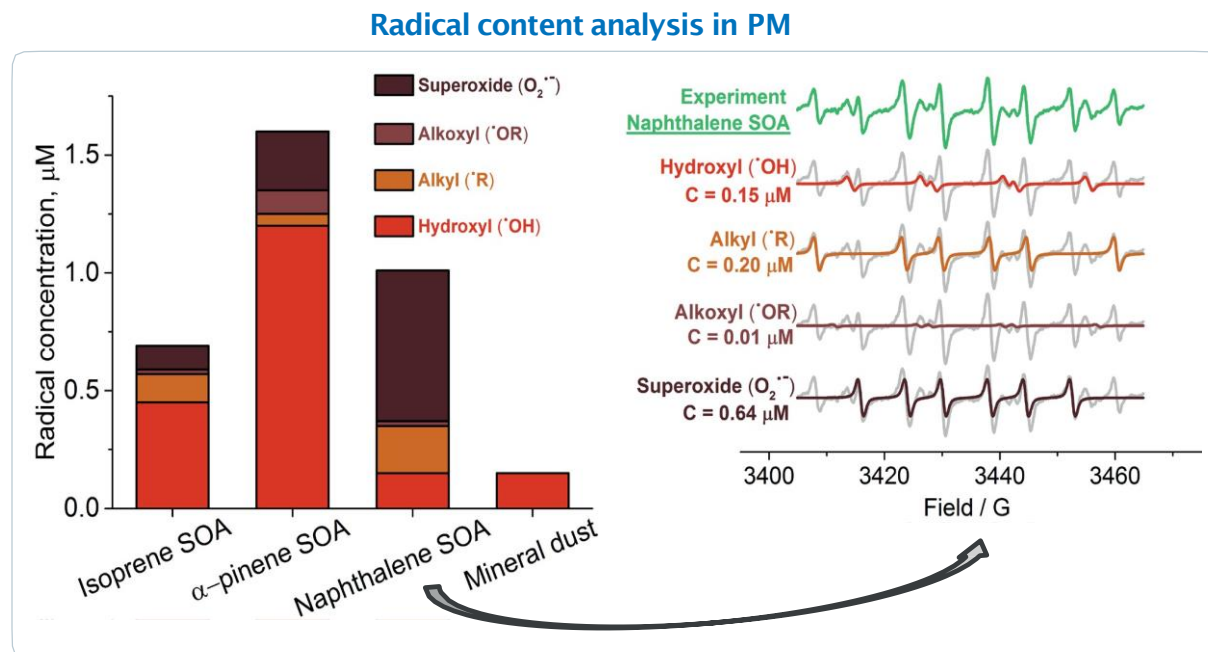
# Environmental applications of EPR

## Air Pollution and EPR



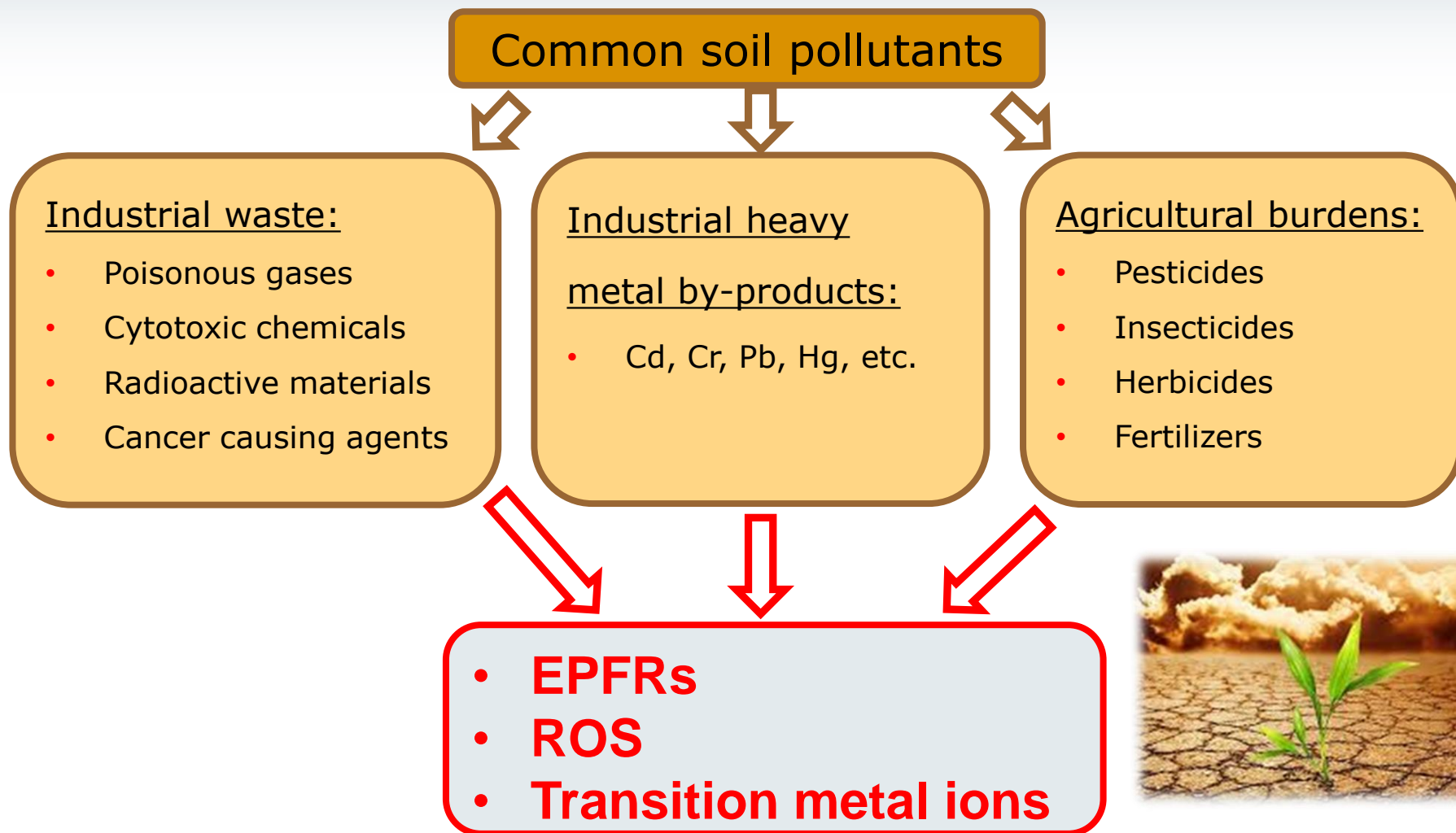
### Short-lived radicals in mineral dust and secondary organic aerosols (SOA)

- EPR detects toxic ROS and carbon-centered radical species in aqueous mixtures of SOA and mineral dust
- The radical formation is due to decomposition of organic hydroperoxides (ROOH) via homolytic cleavage or Fenton-like reactions:



# Environmental applications of EPR

## Soil Pollution and EPR



# Environmental applications of EPR

## Soil Pollution and EPR



### 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

#### EPR can:

- Detect, identify, and quantify EPFRs, ROS, and transition metals in contaminated soil systems
- Evaluate the health and environmental ramifications of EPFRs in soils and sediments
- Monitor radical reactions for better understanding the oxidation mechanisms and to determine the impact on human health

# Environmental applications of EPR

## Soil Pollution and EPR



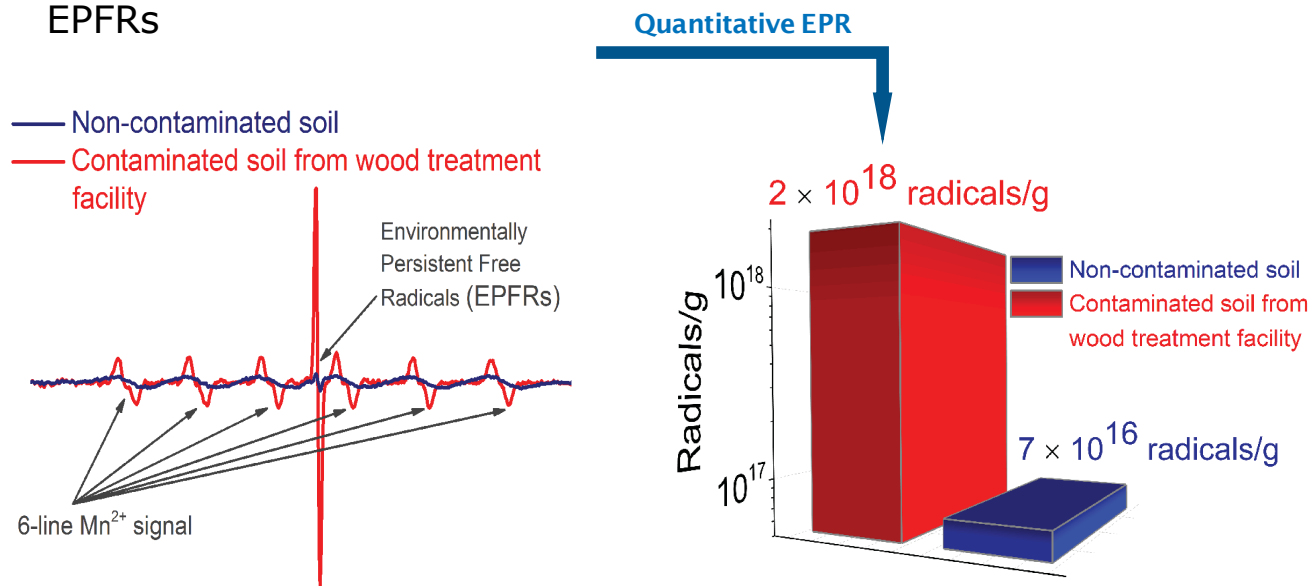
### Case study: EPR study on soil from Superfund sites in the US

- EPR detects and quantifies the formation of environmentally persistent free radicals (EPFRs) in contaminated soils from Superfund sites
- 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



A map of Superfund sites as of October 2013 (courtesy of Wikipedia).

- 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



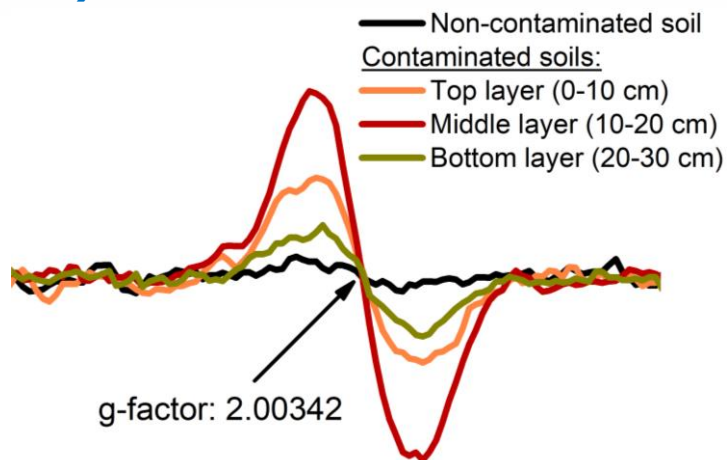
de la Cruz A. et al., *Env. Sci. Technol.* (2011) 45 6356

# Environmental applications of EPR

## Soil Pollution and EPR



### EPR study on soil from Superfund sites in the US (cont'd)



A map of Superfund sites as of October 2013 (courtesy of Wikipedia).

- The g-factor of the radical signal was used to identify this EFPR 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.

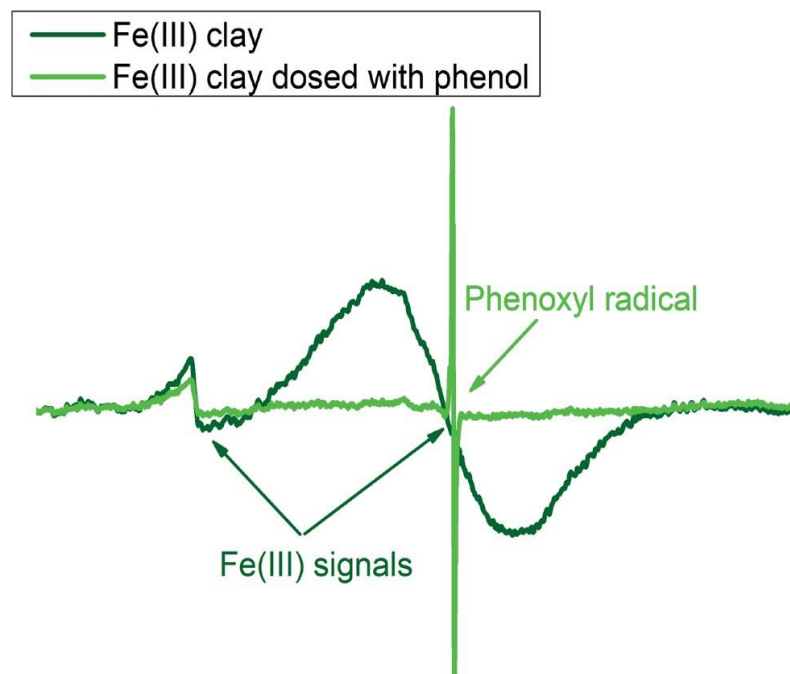
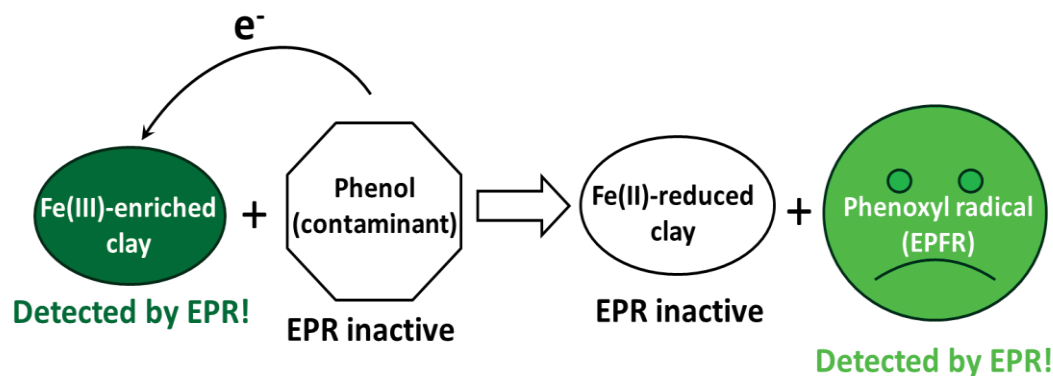
# Environmental applications of EPR

## Soil Pollution and EPR



### Free radicals in Fe(III)-enriched clay

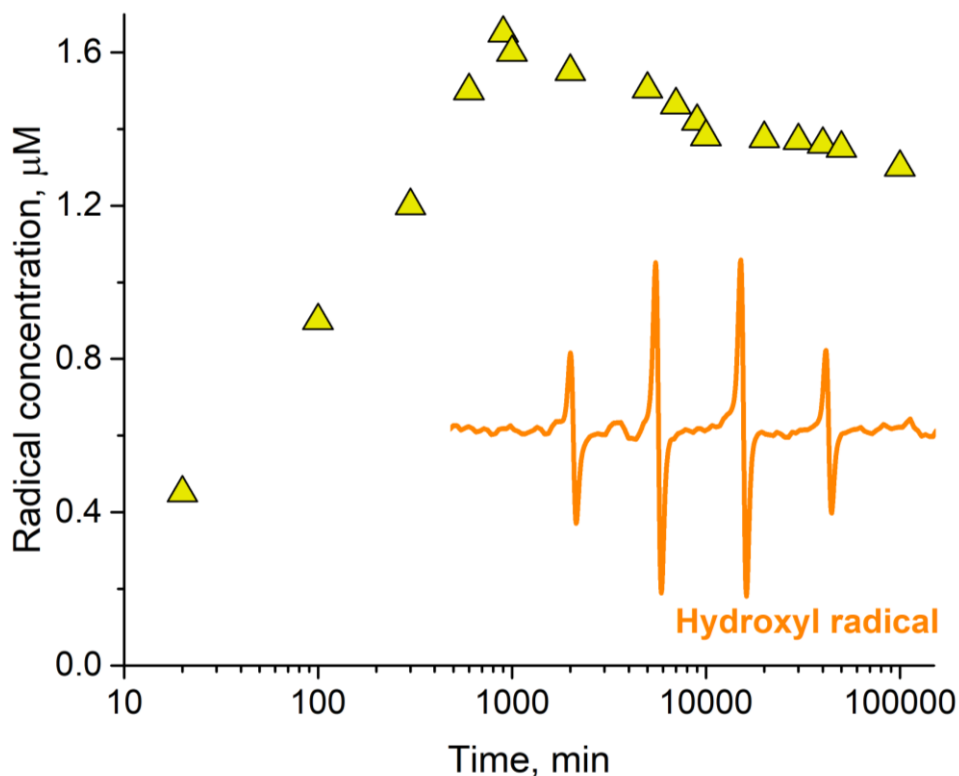
- Clay minerals act as a potential reservoir of transition metals and toxic organic pollutants
- EPR demonstrates the catalytic role of transition metal centers ( $\text{Fe}^{3+}$ ) in phenol contaminated clay minerals in the formation of EPFRs
- EPR monitors and quantifies the production of EPFRs via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



Nwosu U. et al., *Environ. Sci. Process Impacts* (2016) 18 42

# Environmental applications of EPR

## Soil Pollution and EPR



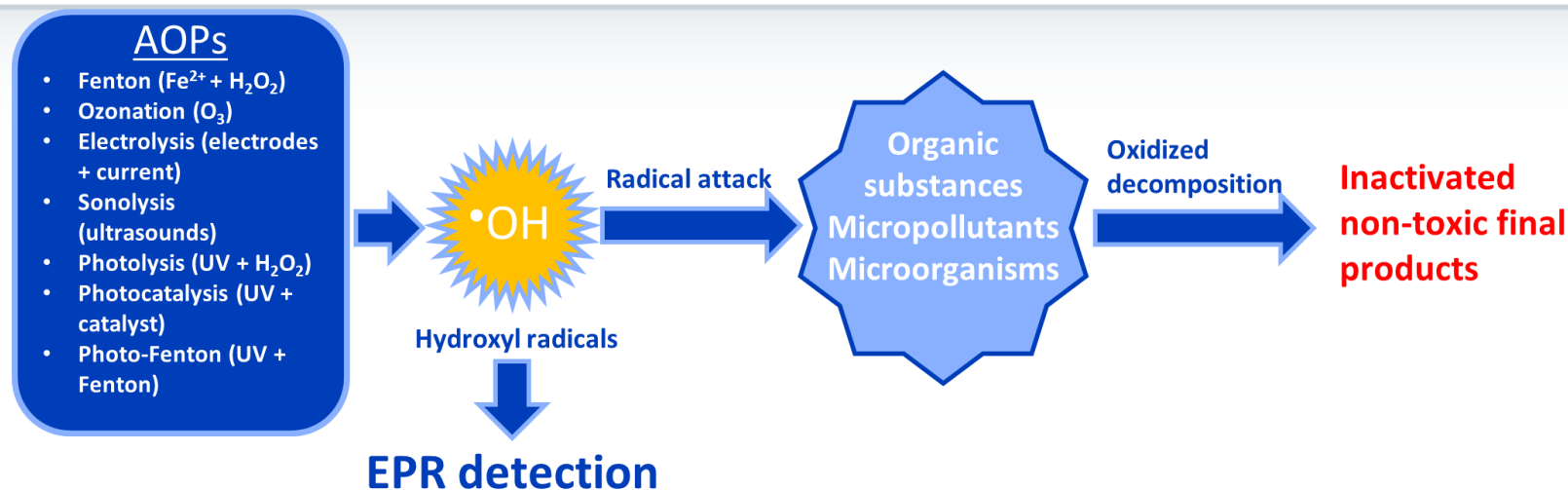
### Free radicals in biochars

- 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



# Environmental applications of EPR

## Water Pollution and EPR



### Challenge

Reduction of operating costs and optimization of the free radical yield in **Advanced Oxidation Processes** (AOPs) to improve waste and ground water treatment technology.

### Solution

EPR can:

- Detect, identify, and quantify hydroxyl radicals and other reactive oxygen species involved in AOPs
- Determine the effectiveness and help to optimize the AOPs
- Monitor radical reactions to further understand oxidation mechanisms and to determine the degradation efficiency

# Environmental applications of EPR

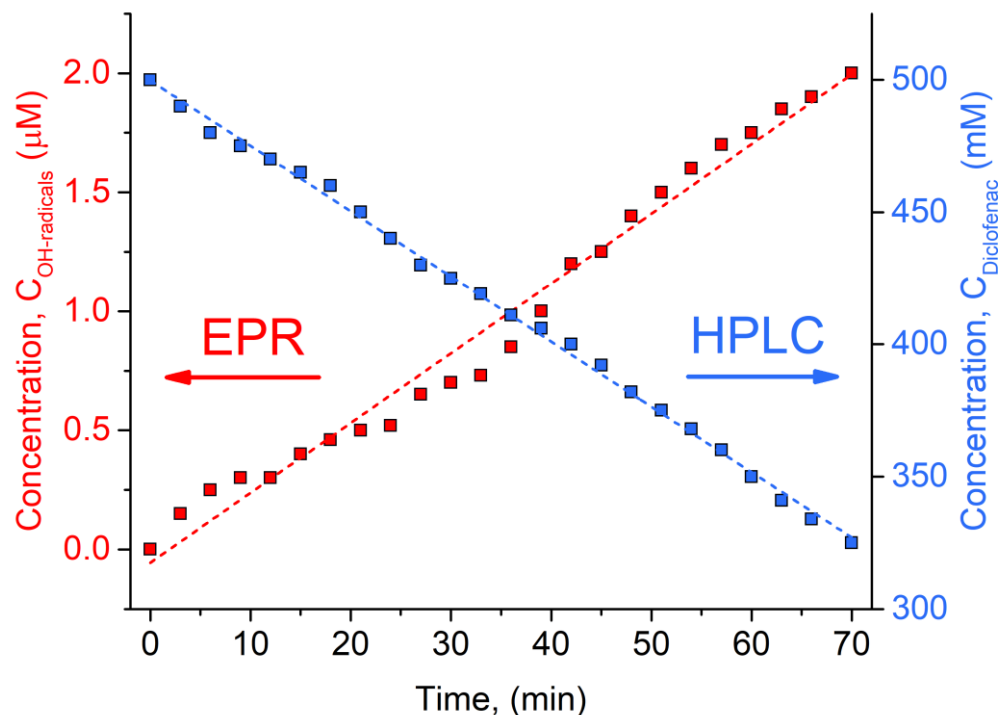
## Water Pollution and EPR



### Case study: EPR study on pharmaceutical residues

- Seven resistant pharmaceutical agents (Diclofenac, Ibuprofen, Diazepam, etc.) were decomposed by pulsed corona plasma generated in water
- The degradation of Diclofenac measured by HPLC is directly correlated to the increase in hydroxyl radical concentration over time
- Hydroxyl radicals detected by EPR are responsible for the decomposition of pharmaceutical compounds
- EPR measurement of hydroxyl radical concentration aids in optimizing the decontamination process

### AOP – pulsed corona plasma



# Environmental applications of EPR

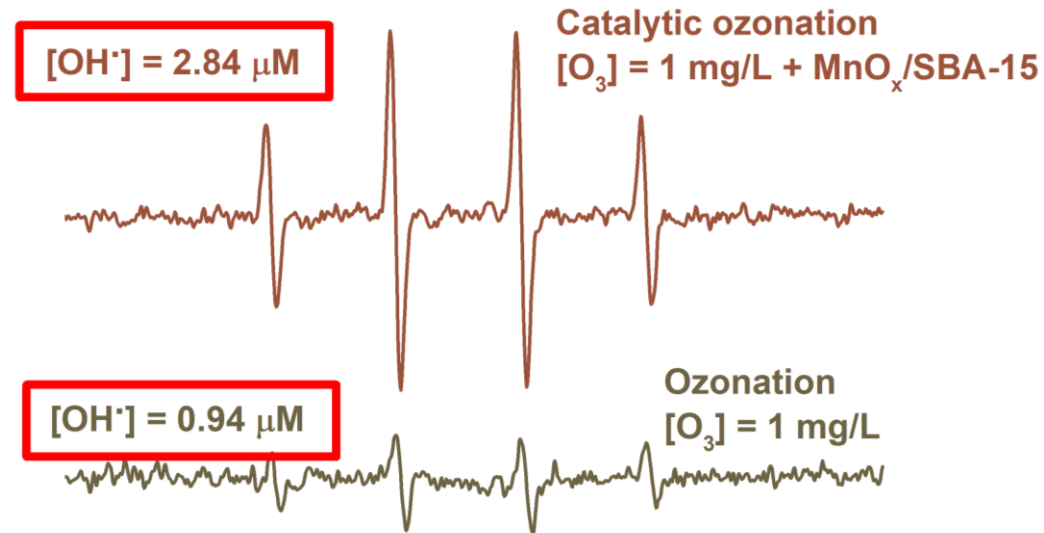
## Water Pollution and EPR



### Case study: EPR study of the heterogeneous catalytic ozonation of clofibric acid, an herbicide with an estimated lifetime of 20 years

- EPR monitors the catalytic performance of manganese oxides ( $\text{MnO}_x$ ) in mesoporous silica as an effective catalyst for clofibric acid degradation
- EPR detects, identifies, and quantifies the formation of hydroxyl radicals to access catalytic quality
- An increased hydroxyl radical concentration after using the catalyst leads to an enhanced degradation of clofibric acid

### AOP – ozonation



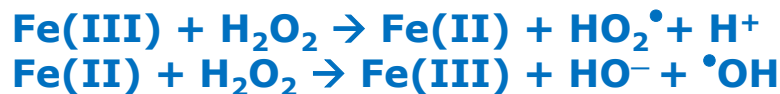
# Environmental applications of EPR

## Water Pollution and EPR



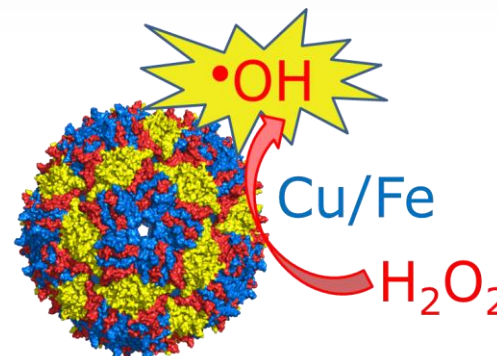
### Case study: Inactivation of bacteriophages by iron- and copper-catalyzed systems during water treatment: role of EPR

- EPR detects and quantifies the production of hydroxyl radicals that are necessary to inactivate coliphage MS2 (bacteriophage):

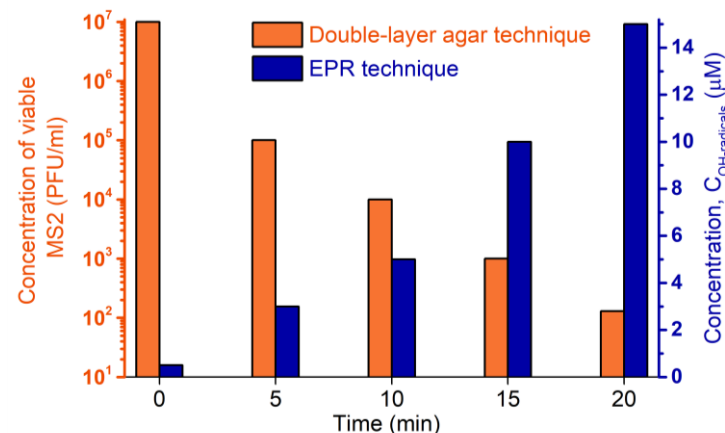


- EPR monitors and aids in the optimization of the rate of hydroxyl radical production, which strongly depends on the concentration of peroxides, transition metals, pH, light exposure
- Increasing the OH production correlates with a decrease of the virus's activity
- EPR quantification of radicals offers direct process control for optimization of the decontamination reaction

### AOP – Fenton system



Virus inactivation by Cu- or Fe-catalysis



# Environmental applications of EPR

## Water Pollution and EPR

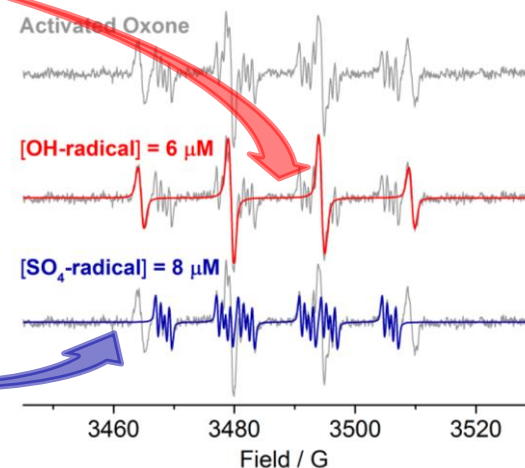


### Case study: EPR study on DDT, one of the most persistent pesticides with half-life of 2–15 years

- EPR directly detects the reactive species involved in DDT degradation catalyzed by the commercial decontaminant Oxone in the presence of transition metals
- Two radicals are identified: the sulfate radical ( $\text{SO}_4^{\bullet-}$ ) and the hydroxyl radical ( $\bullet\text{OH}$ )
- $\text{SO}_4^{\bullet-}$  is longer-lived and selectively degrades contaminants:



### AOP – Sulfate radical generation



- DDT degradation efficiency as measured by GC-MS is directly correlated with the radical concentration as measured by EPR. Control and optimization of the radical concentration results in improved degradation efficiency.

Qin W. et al., *Chemosphere* (2016) 148 68



## Summary

- Detection, characterization, and monitoring of toxic free radicals (EPFRs, ROS, PAH radicals) and transition metal ions is essential and mandatory due to their adverse health effects and environmental impact
- Understanding how these toxins form in polluted air and contaminated soil and water is extremely important
- EPR is the solution to investigate and study this important radical chemistry and neutralization of transition metals
- EPR characterizes and monitors radical formation during AOPs resulting in their improved efficacy

# EMXnano

The standard for bench-top EPR



# EMXnano

## Features at-a-Glance



- Automated tuning and measurement
- Software automated data collection, processing, and storage
- Integrated, motorized amplitude and field reference standard (marker)
- Fully-calibrated for quantitative analysis with dedicated application workflows. No need of calibration curve
  - **SpinCount**: Reference free quantification of EPR species
  - **SpinFit**: Spectrum fitting and identification of EPR species
  - Spin-trap library of EPR spectra
- Video how-to guide
- Low infrastructure requirement and low cost-of-ownership



Ease-of-use with best-in-class performance

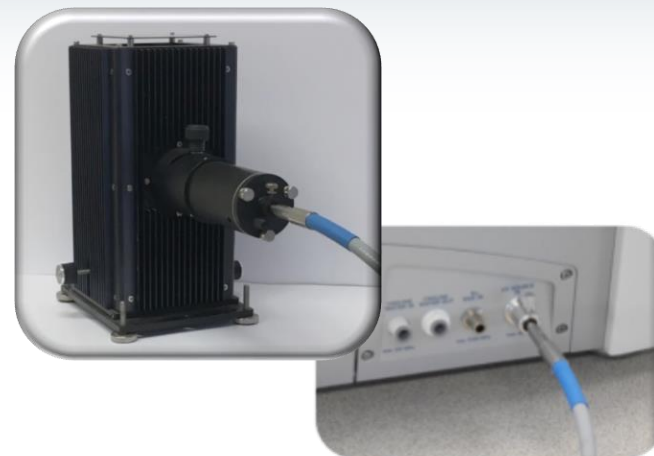


# EMXnano

## Full range of accessories



- UV irradiation system - provides in-situ irradiation of the sample in the microwave cavity with simultaneous EPR detection. A light guide is used for efficient transmission to the sample.
- Variable temperature accessory (100 – 425 K) - the digital temperature control system makes use of liquid or gaseous nitrogen for stable temperature control. Easy and quick sample exchange at any temperature offers safe operation and high measurement throughput.



# EMXnano

## Full range of accessories



- Reaction monitoring - the flow through cell is optimized to offer high sensitivity for lossy and non-lossy samples. Sample exchange is via static injection, continuous flow, or auto-sampler.
- Aqueous samples - the flat cell maximizes the usable sample volume for low concentration measures. Optical access enables irradiation with the optional UV system.
- Biological tissue samples - the tissue cell is designed for studies of plant, animal, and human tissues. Optical access enables irradiation with the optional UV system.



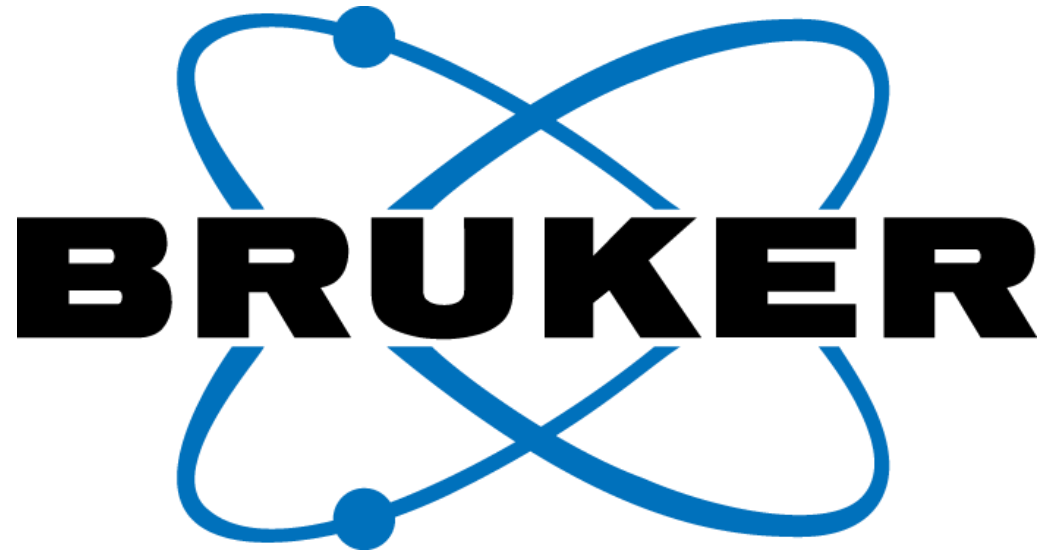
# EMXnano

## Full range of accessories



- Physiological sample conditioning - the temperature and gas controller maintains physiological or pathological conditions when studying biological samples and detecting reactive oxygen species. Software controls the temperature (+10 to +50 °C) with an accuracy of  $\pm 0.1$  °C and the gas mixtures ( $O_2$ ,  $CO_2$ , and  $N_2$ ).





**Any  
questions?**

[www.bruker.com](http://www.bruker.com)

**Thank you!**