

Perspective

**Environmentally Persistent Free Radicals as Sources of POPs**Eric P. Vejerano <sup>1,\*</sup>, Jeonghyeon Ahn <sup>1</sup>, Junaid Latif <sup>2</sup>, Mustafa Mamun <sup>1</sup>

1. Center for Environmental Nanoscience and Risk, Department of Environmental Health Sciences, 29208, University of South Carolina, Columbia, U.S.; E-Mails: [vejerano@mailbox.sc.edu](mailto:vejerano@mailbox.sc.edu); [ja22@email.sc.edu](mailto:ja22@email.sc.edu); [msmustafa@email.sc.edu](mailto:msmustafa@email.sc.edu)
2. College of Natural Resources and Environment, Northwest Agricultural and Forestry University, Yangling, China; E-Mail: [junaid1990@nwafu.edu.cn](mailto:junaid1990@nwafu.edu.cn)

\* **Correspondence:** Eric P. Vejerano; E-Mail: [vejerano@mailbox.sc.edu](mailto:vejerano@mailbox.sc.edu)**Academic Editor:** Zed Rengel**Special Issue:** [Persistent Organic Pollutants](#)*Adv Environ Eng Res*

2021, volume 2, issue 2

doi:10.21926/aeer.2102010

**Received:** January 17, 2021**Accepted:** May 09, 2021**Published:** May 13, 2021**Abstract**

Environmentally persistent free radicals (EPFRs) are a new class organic pollutant sharing some of the attributes of persistent organic pollutants (POPs). This opinion/short review aims to describe the properties of EPFRs that merit their recognition as an additional and potentially significant source of POPs. EPFRs are ubiquitous in diverse environments because of multiple factors: (1) organic precursors from anthropogenic, biogenic, and other natural emission sources are abundant; multiple mechanisms in PM and soils form (2) EPFRs; and (3) EPFRs are stable and persist for a long time, thereby, accumulate in the environment and potentially transported long range. The hazards of EPFRs arise from their ability to induce oxidative stress and the formation of hazardous byproducts. EPFRs are ultimately deactivated by reactive processes, yielding molecular recombination byproducts that are structurally similar to those classified as POPs. It is plausible that EPFRs may form POPs *in vivo* in organisms; therefore, they are potential additional sources of exogenous POPs. Understanding the formation of EPFRs and extensive investigation of the pollutants



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generated from their recombination will add to the growing body of knowledge on their environmental and health hazards.

### **Keywords**

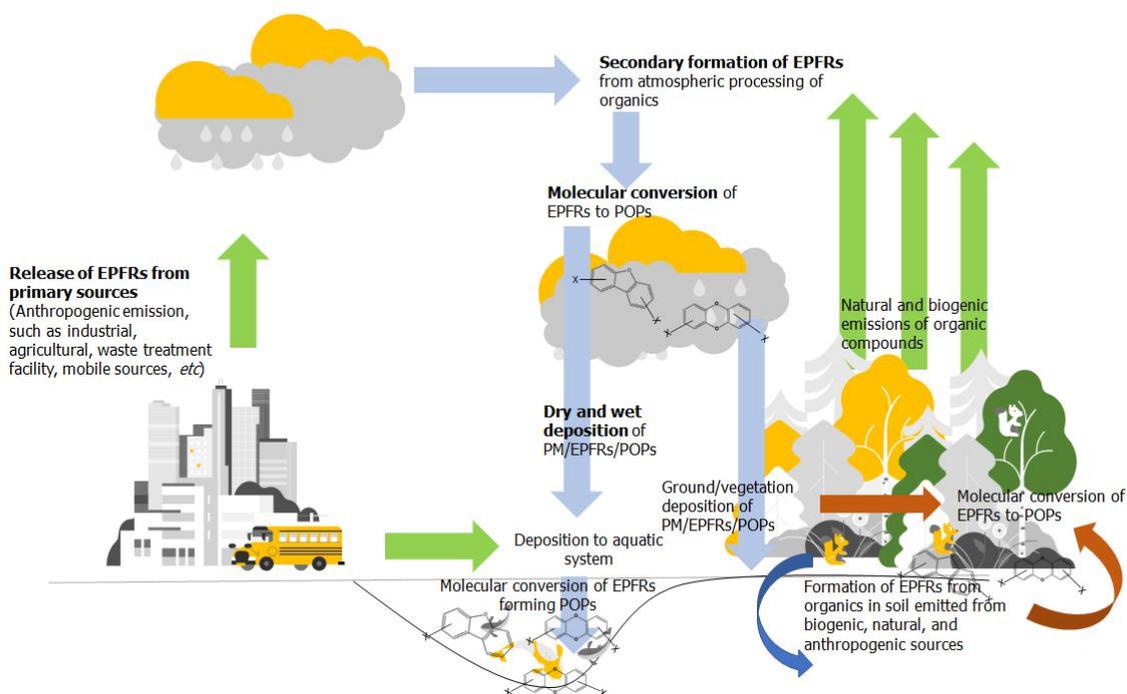
EPFRs; POPs; free radicals; dioxins; furans; persistence



## **1. Introduction**

Main text Research on environmental contaminants released from diverse sources has focused primarily on organic molecular pollutants, such as persistent organic pollutants (POPs). POPs are anthropogenic chemicals that persist in the environment, bioaccumulate through the food web, and pose a risk to human health and the environment. Recently, there is a growing interest in understanding molecular mechanistic processes in investigating environmental contaminants as deemed from the increasing number of papers published since 2008 from various researchers globally. One such class of pollutants is environmentally persistent free radicals (EPFRs). Over the last decade, research on this new class of pollutants has contributed to our knowledge that environmental contaminants can exist as long-lived free radicals [1-3]. EPFRs have received more attention in the last decades because of their ability to induce oxidative stress that leads to multiple health dysfunctions [4, 5]. EPFRs are well known to produce reactive oxygen species [6, 7]. A single EPFR can generate 10 hydroxyl radicals [8]; given the ability of EPFRs to cycle catalytically, renders them more hazardous than conventional environmental pollutants.

In this paper, we describe the properties of EPFRs that merit their recognition as an important contributor to POPs. We describe the ubiquity of EPFRs in the environment because of factors responsible for their formation, stability, and persistence. Figure 1 summarizes the emission sources and processes that have been known to contribute to the formation of EPFRs and the processes that convert them to POPs in different environmental compartments.



**Figure 1** Formation of EPFRs from various environmental matrices and their ultimate conversion to persistent organic pollutants (POPs). Secondary processes such as oxidation and multi-generational processing of VOCs can produce EPFRs. Degradation, conversion, and transformation of organic matter in soil produce EPFRs that will eventually recombine to form POPs. Wet and dry deposition of EPFRs in aquatic surfaces can facilitate the formation of POPs (e.g., polychlorinated dibenzo-*p*-dioxins and furans). The persistence of EPFRs depends on the matrices, but EPFRs are extremely long lived compared to other free radicals (i.e., atmospheric free radicals). A common pathway for many of these processes is the formation of EPFRs by transition metals as that are abundant in PM and in soils. These multiple sources, the abundance of precursors, and diverse pathways demonstrate the accumulation of EPFRs in the environment.

## 2. What are EPFRs?

Free radicals are unstable species or atoms carrying unpaired electrons. Conventional, small inorganic free radicals are highly reactive, transformed into molecular species within a fraction of a second. EPFRs (e.g., cyclopentadienyl, phenoxy, and semiquinone radicals), when constrained on surfaces, are long-lived existing for at least several minutes [1]. Persistent free radicals were first identified in the 1950s when Ingram and colleagues detected paramagnetic signals in carbonized coal and charcoals [9]. But only in the nearly two decades, the presence in environmental matrices and health significance of EPFRs have been extensively studied [10]. In earlier studies, EPFRs are known to form during incineration and thermal processing of organic wastes [1]; hence, EPFRs were first detected in combustion sources, e.g., particulate matter (PM) and fly ash [1, 11, 12].

Dellinger and colleagues defined EPFRs as stable free radicals, meaning they do not degrade after being formed and exhibit lifetimes sufficient to cause exposure and exert adverse health effects [1]. EPFRs are observable under the standard conditions for measuring paramagnetic species using a continuous-wave electron paramagnetic resonance spectrometer. Historically, the first attribution of the term EPFRs was to the free radicals generated from hydroquinone on copper oxide surface, which has a natural lifetime of 27 mins [1]. Since then, the term “EPFRs” has been used to describe persistent free radicals in diverse environments.

### 3. Mechanisms of EPFR Formation

The early hypothesis on EPFR formation mechanism has been assumed to be catalyzed by redox-active metals only [10]. As research on EPFRs progressed, EPFRs are known to form *via* multiple pathways and have been detected in other environmental matrices such as soils [13, 14]. Transition metal oxide nanoparticles/surfaces and aromatic organic species are the key components that produce EPFRs. In earlier studies, EPFRs are known to form when a resonance-stabilized molecule interacts with a transition metal oxide surface at temperatures <400 °C [1]. The current model involves three steps [1, 15]. First, an aromatic organic molecule (*e.g.*, substituted benzene) physically sorbs on a metal oxide surface. Second, a substituent is eliminated from the aromatic precursor forming a chemically bonded species on the metal surface. Third, an electron reduces the metal center (*i.e.*, Cu<sup>2+</sup> to Cu<sup>+</sup>) [1, 16] forming an EPFR. The surface-associated EPFR isomerizes, resulting in highly stable oxygen- and/or carbon-centered radicals [1, 15]. In laboratory studies, EPFRs form on various transition metal oxide nanoparticles: CuO [1], ZnO [2], NiO [17], TiO<sub>2</sub> [18], Fe<sub>2</sub>O<sub>3</sub> [19]. Organic components in soil matrix demonstrate that soil organic matter (SOM) produce organic radicals [13, 20]. Hence, there is a growing trend in studying EPFR formation in soils as deemed from the increasing number of papers published on this topic since 2008.

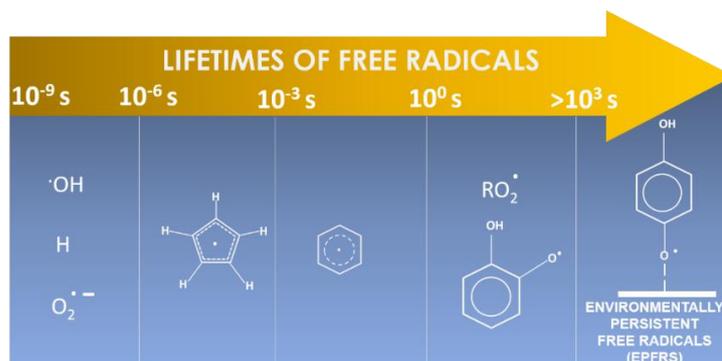
Regardless of the matrix, a common feature of these mechanisms is the formation of EPFRs *via* a metal-assisted pathway. In large macromolecules such as biochars, oxygen-functional groups interact with metals forming EPFRs, although EPFRs have been reported to form in the absence of metals [21, 22]. EPFRs also proceed *via* band bending [18, 23], which may be the mechanism for those forming on unsupported metallic or non-metallic nanoparticles (no Schottky contact). Another pathway for EPFR formation is that some soil components mediate electron transfer from organic precursors (*e.g.*, humic substances) to transition metal centers in clay minerals [24-26].

Another route for EPFR formation is homolytic cleavage of weak chemical bonds such as the C-O, C-C bonds in  $\alpha$ - and  $\beta$ -alkyl aryl ether bonds [21, 22]. This mechanism is responsible for the high EPFR yields in biochars [21, 22].

### 4. Lifetimes and Factors Affecting the Stability and Persistence of EPFRs

Perhaps, the most important attribute that EPFRs share with POPs is their long lifetimes. Their persistence is unequaled by other known radical species in the environment; EPFRs persist for several minutes to months [1, 27-31]. Figure 2 compares the lifetimes associated with different free radicals to that of EPFRs. Their extreme persistence allows them to be transported over considerable distances such as those during the Asian dust storm in 2016 [32], where they can exert their adverse effects. The stability and persistence of EPFRs depends on the type of metals

[2]. Overall, in PM and soils, EPFRs decay slowly, accumulating in significant quantities ranging from  $10^{16}$ - $10^{19}$  spins/g of PM or soils [13, 22, 33-35].



**Figure 2** Lifetimes of different radicals. EPFRs have lifetimes ranging from several minutes to months. EPFRs' long lifetimes result from the surface-confinement of the unpaired electron.

The stability of EPFRs on surfaces has been attributed to several mechanisms: hyper-conjugation [12, 36], steric effects [37], inductive effects of electronic depletion [38, 39], hydrophobic associations, and  $\pi$ -stacking interactions [13]. The concentration and persistence of EPFRs are affected by multiple factors, primarily by molecular oxygen, relative humidity (RH), and pH. Reaction with molecular oxygen is the primary sink for the deactivation of EPFRs to molecular species [2]. The presence of water deactivates EPFR; EPFR concentration decreases 5× faster at an RH of ~75% than those exposed to less humid conditions [28, 30]. pH affects EPFR stability by shifting the type of EPFRs such as those in cigarette smoke [40]. Differences in pH affect the availability of transition metals due to redox reaction, autooxidation, and complexation [41, 42]. Overall, the accumulation of EPFRs in these matrices is because the unpaired electrons are confined on a surface, which considerably slowed down the processes that deactivate them.

## 5. Sources and Precursors of EPFRs

Many organic molecules are EPFR precursors. These classes of organic compounds have been reported to form EPFRs: aromatics [40, 43, 44] chloroaromatics [2, 45-48], polycyclic aromatic hydrocarbons (PAHs) [49, 50], complex organic polymers [31, 51], and microplastics [52]. Another abundant source of EPFR precursors is soil, which contains a vast reservoir of metals and organics [20]. There are many classes of EPFR organic precursors in soils. The yields and stability of EPFRs produced in the matrix of the organic materials are highly dependent on the complex structure of organic compounds. Processes in soils can convert or degrade large macromolecules to form similar molecular structures to known EPFR precursors. Humic substances in soils are composed of weakly associated molecular assemblies of heterogeneous polymer-like structural parts [53, 54]. Lignocelluloses are the parent compounds of biochar and the main precursors of EPFRs in soils [55, 56]. Partial decomposition of these materials produces phenol, catechol, and hydroquinone, which are established EPFR precursors [22]. Sewage sludge offers abundant biomass containing high concentrations of organic compounds [57].

## 6. EPFRs Accumulate in Diverse Environmental Matrices

Based on the above discussion, EPFRs are prevalent in the environment for three reasons. First, EPFR precursors emitted from anthropogenic, biogenic, and other natural emission sources are abundant in multiple environmental compartments. Additionally, environmental organic contaminants can be converted to EPFR precursors by secondary processes. Second, EPFRs are formed by multiple mechanisms in the presence or absence of metals. For metal-assisted formation, metals are abundant in PM and soils. Third, EPFRs are stable and persist for a long time, enhancing their potential for long-range transport.

PM and soils are two of the major environmental matrices in which EPFRs have been well known to form. In PM, the concentration of EPFRs formed over different transition metals is two orders of magnitude higher [33-35] than those on soils [13-22]. EPFRs in PM predominantly originate from combustion sources. However, laboratory studies have demonstrated that some volatile organic compounds (VOCs), *e.g.*, isoprene and naphthalene, when converted to secondary atmospheric aerosol (SOA), form EPFRs [7]. EPFRs in soils and sediments are mainly produced by secondary processes. Moreover, those in sediments and soils are formed at relatively lower temperatures and even at ambient conditions [13, 14, 21, 58, 59].

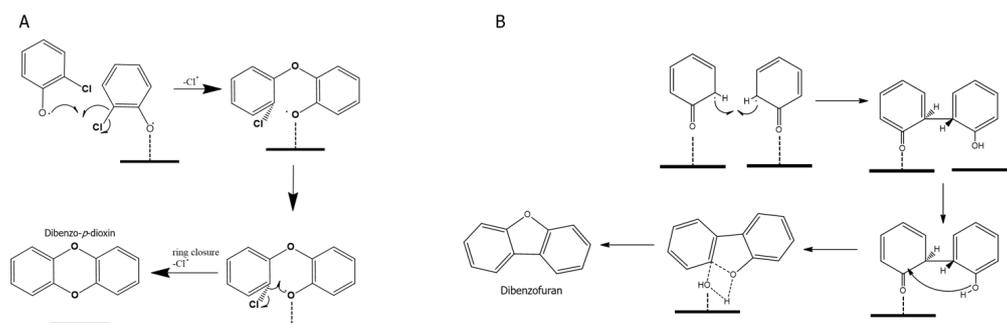
EPFRs have been detected in combustion systems [60], coal and wood-burning sites [13], residues produced by burning various plastics [11, 52], municipal and solid waste incineration [61], contaminated soils [28, 62], pyrolysis of biodiesel and biochars [63, 64], soils from Superfund wood treating sites [14, 62], decomposition of microplastics [3, 53], and fly ash produced by municipal waste incineration [61, 65, 66]. Extremely long-lived asphaltene - and semiquinone-type radicals have been detected in tar-balls collected from the Gulf of Mexico after an oil spill [67]. Thermal degradation of fossil fuels and biodiesels produces carbon-centered aromatic radicals [63], and so are bituminous coal [13]. During hydrochar processing and thermal carbonization of sewage sludge, EPFR can form even at relatively low temperatures of 120-280 °C [57]. Biochar produces oxygen- and carbon-centered EPFRs [64, 68] even in the absence of transition metals with yields as high as  $\sim 10^{18}$  spins/g [21].

Emerging pollutant such engineered nanoparticles (ENPs) is another contributing factor for the formation of EPFRs [69]. Majority of ENPs produced are metallic [70]. Although only a small fraction of ENPs will enter the atmosphere [71], emissions of pollutants catalyzed by ENPs such as EPFRs [10] and eventually POPs are reasons for concerns. Most of these ENPs will end up in landfills (>95%) [69,71]; in the presence of an abundant organic waste may easily form EPFRs. In an earlier paper, we hypothesize that because the band gap for nanoparticles exhibits size-dependence, thermally excited electrons can cross this band gap easily [72]. Some ENMs, depending on size, electronic, and chemical properties may form and stabilize aromatic species to form EPFRs [73]. ENMs can serve as charge carriers and transport electrons and holes with a high probability and efficiency [72]. This phenomenon is similar to the electron shuttling capabilities of some soil components responsible for producing EPFRs. Non-metallic ENMs can form EPFRs as long as they survive incineration and exit into the post-combustion zone intact [69].

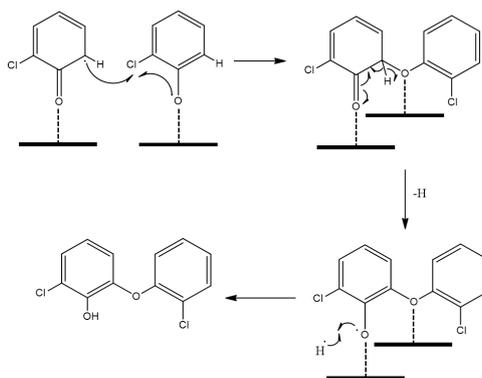
## 7. EPFRs will Recombine to Form POPs

Although relatively highly stable and persistent, oxygen- and carbon-centered EPFRs will ultimately recombine to form molecular byproducts, including those classified as POPs. Among the POPs identified by the Stockholm Convention are pentachlorobenzene, hexachlorobenzene, pentachlorophenol, polychlorinated naphthalenes, polychlorinated biphenyls (PCBs), tetrabromodiphenyl ether, hexabromodiphenyl ether, pentabromodiphenyl ether, decabromodiphenyl ether, polychlorinated dibenzo-*p*-dioxins (PCDDs), and polychlorinated dibenzofurans (PCDFs). Most of these POPs can be classified into these three classes: 1) halogenated aromatics (substituted benzene and naphthalenes), 2) halogenated biphenyl ethers, and 3) PCDD/Fs. These classes have been observed as recombination byproducts of EPFRs in liquid media [1, 73].

EPFRs easily recombine when in liquid media because of the lower activation energy [48]. The most notable of the POPs from EPFRs are PCDD/Fs. Scheme 1A and 1B depict the general pathway for the formation of PCDD/Fs from EPFRs [74]. Accumulation of PCDFs is more likely to dominate as they are formed from two surface-species compared to PCDDs that require another gas-phase species [75]. EPFRs, when converted to molecular species, are capable of being halogenated [48]. Of course, the simplest molecular byproduct of an EPFR is its reconversion to its parent molecules. Pentachlorophenoxy EPFRs have been detected in soils obtained from a Superfund site [12]. Upon extraction, the EPFRs are converted back to pentachlorophenol. Condensation of phenoxy radicals will form cyclopentadienyl radicals [76], which upon recombination will produce naphthalene [76]. Whereas recombination of chloro/phenoxy EPFRs will form diphenyl ethers [48, 74]. Scheme 2 depicts the formation of 2,3'-dichloro-2'-hydroxydiphenyl ether [73].



**Scheme 1** (A) Formation of dibenzo-*p*-dioxin from reaction of 2-monochlorophenol and chlorophenoxy radical, and (B) dibenzofuran from recombination of two keto forms of phenoxy radical. For simplicity, the halogens were omitted. Black bar represents the surface. Adapted and simplified from the mechanism proposed by Lomnicki and Dellinger [74].



**Scheme 2** Formation of 2,3'-dichloro-2'-hydroxydiphenyl ether from two chlorophenoxy radicals [73]. Black bar represents the surface.

Mechanistically, the POPs listed above can form easily; their formation is subject only to the presence of precursors with the correct substituents. Given these possible mechanisms for POPs, inhalation of PM and soil particles will convert EPFRs to POPs. EPFRs extracted with protic organic solvents (those with donatable hydrogen) formed byproducts that are classified as POPs [48]. Since water is a protic solvent; it is plausible that EPFR-containing PM may form POPs in biological systems *in vivo*. Hence, this pathway may be an important exposure to POPs in humans, aside from exogenous sources.

EPFRs are non-volatile compounds because they are bound onto nanoparticle surfaces. Events such as the Asian dust storm of 2016 will transport EPFR-containing PM and/or soil particles, which have been shown to promote oxidative stress [32].

## 8. Summary and Future Research Direction

Studies on environmental pollutants have focused heavily on primary emission of organic pollutants. What is lacking a more thorough understanding of mechanistic processes that eventually produce pollutants from primary emission sources. Pollutants like EPFRs are ubiquitous in the environment, not only from direct emission from primary sources but from secondary processes in diverse environments. EPFRs are stable, persistent, prevalent in the environment, and exhibit characteristics that distinguish them from other conventional pollutants. However, EPFRs share some properties attributed to POPs, more importantly, their persistence. Unlike POPs, the hazards from EPFRs are two-fold. First, EPFRs are capable of redox cycling in biological systems, inducing adverse health effects. Second, when EPFRs ultimately recombine or deactivated by reactive processes, some of the molecular byproducts formed are hazardous POPs. These processes are additional sources of POPs.

The almost two decades of studies devoted to EPFRs have focused on their formation in different matrices, and more extensively, on their health effects. Limited studies have identified extensively the pollutants that are formed from EPFRs. Mechanistically, the formation of pollutants that are POPs or have parent structures classified as POPs is highly possible, which is limited only by the presence of precursors with the correct substituents. The potential *in vivo* formation of POPs in humans and other organisms is an additional exposure route and a concern. More investigation is needed to ascertain the type of pollutants that are formed from EPFRs.

Knowledge about them will inform on the appropriate disposal methods and management controls to lessen our risk to them.

### **Author Contributions**

EPV conceptualized, wrote, and edited the paper. JA, JL, and MM contributed to drafting and writing the paper.

### **Funding**

EPV has been supported by the National Science Foundation EPSCoR RII-Track IV grant 1738337 and grant 1834638.

### **Competing Interests**

The authors have declared that no competing interests exist.

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