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Natural Abiotic Formation of Furans in Soil

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Furan and its derivatives are a potentially important, and little studied, class of volatile organic compounds of relevance to atmospheric chemistry. The emission of these reactive compounds has been attributed previously to biomass burning processes and biogenic sources. This paper investigates the natural abiotic formation of furans in soils, induced by the oxidation of organic matter by iron(III) and hydrogen peroxide. Several model compounds like catechol, substituted catechols, and phenols as well as different organic-rich soil samples were investigated for the release of furans. The measurements were performed with a purge and trap GC/MS system and the influence of hydrogen peroxide, reaction temperature, iron(III), pH, and reaction time on furan yield was determined. The optimal reaction turnover obtained with catechol was 2.33 μg of furan from 0.36 mg of carbon. Results presented in this paper show that a cleavage of catechol into a C_2 - and a C_4 -fragment occurs, in which the C_4 -fragment forms furan by integrating an oxygen atom stemming from H_2O_2 . Furthermore, phenols could be transformed into catecholic structures under these Fenton-like conditions and also display the formation of furans. In conclusion, catalytic amounts of iron(III), the presence of hydrogen peroxide, and acidic conditions can be seen as the most important parameters required for an optimized furan formation.

Introduction

Volatile organic compounds (VOC) are important trace gas components of the atmosphere and are known to be emitted from both biogenic and anthropogenic sources (1). The oxidation of VOC in the atmosphere impacts ozone and can lead to aerosol formation. Therefore VOC can influence both the oxidation capacity of the atmosphere and the Earth's radiative budget. Although many VOCs have been measured in the atmosphere, budgeting exercises performed using total reactivity measurements (2, 3) have suggested that significant fractions of the total VOC present remain unquantified.

One little-studied set of VOCs is the alkylfurans and furan. These compounds may be primary emissions (e.g., from biomass burning) (4, 5) or generated in the atmosphere from the oxidation of other precursor compounds (e.g., isoprene) (6). A selection of furanic compounds have been identified in boreal forest air (7), and vinyl furan tentatively suggested

as a component of air over the tropical rainforest (8). However, since furans have also been identified from soils, composting sites, and as microbiological products it remains unclear whether these species are mostly emitted from the plants or the underlying soil (9, 10).

Furan and its derivatives are reactive to all the main ambient air oxidants (OH , Cl , NO_3 , O_3). The major sink for furans in the atmosphere will be with the OH radical (normally reacting at position C1 adjacent to oxygen), leading to the products butenedial (11, 12), 4-oxo-2-pentendial (12), and 2-methylbutenedial from furan, 2-methylfuran, and 3-methylfuran, respectively (13). The rate of reaction of furans with OH is reasonably rapid so that their atmospheric lifetimes are of the order of hours (14). The degradation of furans with Cl radicals has also been investigated and may be significant in the marine boundary layer (15–17). If furans are uptaken to the aerosol phase they may undergo Diels–Alder type reactions there to generate semivolatile products.

Furan and its derivatives may also be formed during the photooxidation of hydrocarbon with a general structure of $\text{CH}_2=\text{CH}-\text{CR}_1=\text{CHR}_2$, such as the most important ambient VOC isoprene (8, 14, 18, 19), 1,3-butadiene (11, 19–22), and 1,3-pentadiene (21), and aromatic compounds such as toluene and *o*-xylene (17, 23, 24). Such specific oxidation products can potentially be used in conjunction with measurements of the primary emission for determining the photochemical age of air as has been done previously for isoprene, methacrolein, and methyl vinyl ketone (25, 26).

In this paper we examine the abiotic formation of furan type compounds in soil, as a potential atmospheric source. Similar to the atmosphere, oxidizing conditions also occur in soils, and through Fenton-like reactions, hydroxyl radicals can be produced in low amounts. These may react with the various organic compounds present within the soil organic matter (SOM) to form furan type compounds. To verify the assumption that furans are produced in soils, we selected catechol as a starting model compound since it has been used previously to represent the numerous complex humic substances in soil (27). The other substrates chosen to enable Fenton like conditions were iron, an abundant redox-sensitive element, and hydrogen peroxide as a strong oxidant. Furthermore, chloride was investigated as a possible halogenation agent. A series of optimization steps was performed to determine the influence of different parameters on the furan production, including hydrogen peroxide concentration, time dependence, iron(III) concentration, pH value, the dependence of temperature, and the influence of potassium chloride. After establishing these dependencies, the furan formation was studied with further catecholic and phenolic compounds to elucidate a common degradation pathway for natural aromatic soil constituents. These results and additional isotopic labeling experiments deliver an important mechanistic insight into furan formation. Finally, to confirm the results obtained with these model compounds, natural soil samples were used with and without the use of additional substitutes as iron and hydrogen peroxide.

Experimental Section

Chemicals. The following chemicals were used: catechol (99%; Sigma-Aldrich), 4-chlorocatechol (97%; Aldrich), 3-chlorofuran (synthesis (28)), 4-chlorophenol (99%; Aldrich), 2,4-dichlorophenol (98%; Merck), furan (99%; Sigma-Aldrich), hydrogen peroxide (30%; Merck), ^{18}O -hydrogen peroxide (2%; 90% ^{18}O ; Icon Isotopes), iron(III)-sulfate (99%; Fe 21–23%; Riedel-de-Haën), 3-methylcatechol (98%; Aldrich), 4-meth-

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TABLE 1. Properties of the Soils

name	Sua Pan 3II	T sud 1	Rotwasser
soil type	salt pan	salt pan	peaty soil
geographic position	S 20°28'57" E 26°03'41"	N 43°39'35" E 58°30'43"	N 49°36'39" E 08°53'11"
organic carbon (C _{org}) ^a	1.3%	1.5%	29.9%
inorganic carbon ^b	1.5%	1.4%	<0.5%
Cl ⁻ -concentration ^c	2.52%	0.03%	4.58%
Fe-concentration ^d	1.68%	1.94%	17.98%
pH value	10.07	7.35	4.55

^a CS-measurement. ^b Via a carbonate bomb (15). ^c IC measurement. ^d μ -XRF-measurement.

ylcatechol (95%; Aldrich), 2-methylfuran (99%; Sigma-Aldrich), 3-methylphenol (95%; Supelco), 4-methylphenol (95%; Supelco), ¹⁸O-oxygen (97% ¹⁸O; Campro), phenol (99.5%; Fluka), potassium chloride (99.5%; Merck), sodium hydroxide (99%, Aldrich), sulfuric acid (96%, Riedel-de-Haën), and ¹⁸O-water (97% ¹⁸O; Campro). Doubly distilled deionized water (18 M Ω cm), from an ELGASTAT UHQ PS water treatment system, was employed in all experiments. All pH measurements were made using a Mettler Toledo 320 pH meter, calibrated on the free hydrogen scale with 4.0 and 7.0 buffers.

Soils Samples. Three different soil samples were used to verify a general, naturally occurring formation process for furans. The first was a salty soil sampled on June 2008 in the Sua Salt Pan/Botswana (Sua Pan 3II). The second, also a salty soil, was sampled on July 2009 and stems from the Aral Sea/Uzbekistan (T sud 1). The third soil, a peaty sediment soil, was sampled on October 2008 from the Rotwasser nature reserve, Odenwald/Germany (Rotwasser). Soil samples were freeze-dried for storage and milled to fine powders for homogeneity (>315 μ m). The chemical characterization of the soils is shown in Table 1 along with the exact sampling location. A total of 1.0 g of the powdered soil samples was used for each experiment.

Instrumentation. GC/MS analyses were performed on a Varian STAR 3400 Cx gas chromatographic system connected to a Saturn 2000 ion trap mass spectrometer. Sampling, preconcentration, and injection of the volatile analytes were controlled by a custom-made purge and trap system. The GC was equipped with a BP624 (25 m; 0.53 mm i.d.; 3.0 μ m film thickness) and a BPX5 (60 m; 0.32 mm i.d.; 1.0 μ m film thickness) capillary column, both connected in series.

Experimental Procedure. The experiments were carried out in gas-tight 20 mL headspace glass vials, filled with 10 mL of aqueous solution and shaken for a definite time on a rotary board at 500 rpm at a known temperature. After introduction of stainless steel needles as inlet and outlet through the septum the volatile compounds were purged for 7.5 min with a helium stream at 7 mL/min — regulated with a flow controller — and retained on a cooled glass lined tubing trap (−190 °C). Moisture was removed using a magnesium perchlorate water trap from the sample stream. The loaded preconcentration GLT-trap was then purged by the GC carrier gas line (He, 2.0 mL/min) and heated to 220 °C in 45 s. The GC oven temperature program started automatically: 35 °C hold 8 min, 35 to 150 °C at 5.5 °C/min, hold 5 min, 150 to 210 °C at 30 °C/min, hold 10 min.

Reactions with Catechol. To facilitate investigation of the furan formation mechanism in soils, we decided to simplify the reaction conditions by choosing catechol as starting compound. It is used in the first section of this work as a model of the many humic compounds present in soil. The influence of different reaction parameters was investigated to achieve optimal furan yield.

Concentration of Hydrogen Peroxide. The influence of the concentration of H₂O₂ on the reaction was checked first. For this purpose, solutions of 10 mL of water with initial

concentrations of 0.5 mM catechol, 2.5 mM Fe₂(SO₄)₃, and 5.0 mM KCl were prepared together with different concentrations of hydrogen peroxide and shaken for 15 min at 40 °C.

Time Dependence. A further important factor investigated was the time dependence of the furan production. Ten mL water solutions with initial concentrations of 0.5 mM catechol, 2.5 mM Fe₂(SO₄)₃, 0.35 mM H₂O₂, and 5.0 mM KCl were prepared and shaken at 40 °C for different durations.

Concentration of Iron(III). The third factor checked was the influence of iron(III) on the furan formation. For this purpose, solutions of 10 mL of water with initial concentrations of 0.5 mM catechol, 0.35 mM H₂O₂, and 5.0 mM KCl were prepared with different concentrations of Fe₂(SO₄)₃. To keep the pH value at a constant level of 2.51, NaOH or H₂SO₄ was added in appropriate amounts. The solutions were shaken at 40 °C for 15 min.

pH Value. To test a possible pH dependence on furan production, solutions of 10 mL of water with initial concentrations of 0.5 mM catechol, 0.05 mM Fe₂(SO₄)₃, 0.35 mM H₂O₂, and 5.0 mM KCl were prepared with different concentrations of sulfuric acid and shaken for 15 min at 40 °C.

Temperature Dependence. The next optimization steps consisted of varying the applied reaction temperature. Solutions of 0.5 mM catechol, 0.05 mM Fe₂(SO₄)₃, 0.35 mM H₂O₂, and 5.0 mM KCl were prepared and were shaken for 15 min at different temperatures.

Concentration of Potassium Chloride. Finally, the influence of KCl on the furan formation was investigated. For this, solutions of 10 mL of water with initial concentrations of 0.5 mM catechol, 0.05 mM Fe₂(SO₄)₃, and 0.35 mM H₂O₂ were prepared together with different amounts of potassium chloride and shaken at 40 °C for 15 min.

Reactions with Substituted Catechols. Once the optimized reaction conditions had been obtained for furan formation from catechol, the same conditions were then applied to three substituted catechols: 4-chlorocatechol, 3-methylcatechol, and 4-methylcatechol. These compounds were carefully selected to check the formation of furans from these substrates, and also to elucidate mechanistic aspects of a common formation pathway. Therefore, 10 mL aqueous solutions with initial concentrations of 0.5 mM organic compound, 0.05 mM Fe₂(SO₄)₃, and 0.35 mM H₂O₂ were prepared and shaken for 15 min at 40 °C.

Reactions with Phenols. The formation of furans was also investigated using phenols as educts. Phenols corresponding to the previously used catechols were adopted: phenol, 4-chlorophenol, 3-methylphenol, 4-methylphenol, and additionally 2,4-dichlorophenol. These were chosen specifically to enable a mechanistic comparison between both phenolic and catecholic molecule types. In particular, the possible role of the phenolic compounds as precursors of the catechols was studied. Preliminary tests already revealed the necessity of higher hydrogen peroxide concentration for the preceding hydroxylation of phenols. Therefore, 10 mL aqueous solutions with initial concentrations of 0.5

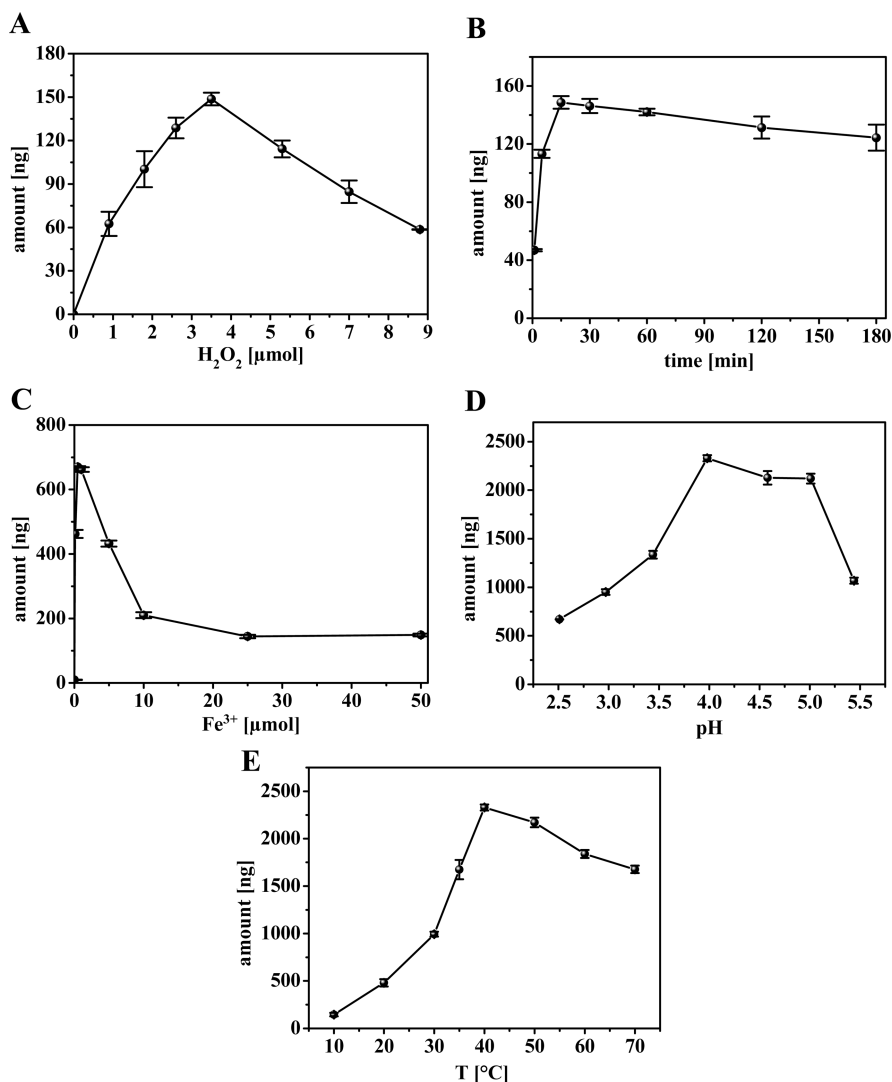


FIGURE 1. Effects of different parameters on furan formation. (A) Variation of hydrogen peroxide from 0 to 8.8 μmol : reaction of catechol, $\text{Fe}_2(\text{SO}_4)_3$, KCl, and H_2O_2 at 40 $^\circ\text{C}$ after 15 min. (B) Time dependence: reaction of catechol, $\text{Fe}_2(\text{SO}_4)_3$, H_2O_2 , and KCl at 40 $^\circ\text{C}$. (C) Variation of iron(III) from 0 to 50 μmol : reaction of catechol, H_2O_2 , KCl, and $\text{Fe}_2(\text{SO}_4)_3$ at 40 $^\circ\text{C}$ after 15 min. (D) Variation of the pH value from 2.51 to 5.44 with H_2SO_4 or NaOH: reaction of catechol, $\text{Fe}_2(\text{SO}_4)_3$, H_2O_2 , and KCl at 40 $^\circ\text{C}$ after 15 min. (E) Agitation temperature between 10 and 70 $^\circ\text{C}$: reaction of catechol, $\text{Fe}_2(\text{SO}_4)_3$, H_2O_2 , and KCl after 15 min. Symbols are average data from experiments, and error bars indicate standard deviations from triplicate measurements.

mM organic compound, 0.05 mM $\text{Fe}_2(\text{SO}_4)_3$, and 7.5 mM H_2O_2 were prepared and shaken for 15 min at 40 $^\circ\text{C}$.

Isotope Labeling Studies. ^{18}O -labeled substrates were used to obtain supporting information concerning some crucial degradation steps in the formation of furan. For this purpose, ^{18}O -labeled oxygen ($^{18}\text{O}_2$), hydrogen peroxide ($\text{H}_2^{18}\text{O}_2$), and water (H_2^{18}O) were used. These labeled compounds were each tested in one measurement. Therefore, 1 mL water solutions of catechol, $\text{Fe}_2(\text{SO}_4)_3$, and H_2O_2 were prepared in a glovebox under argon atmosphere.

Soil Samples. Conditions similar to those used for catechols and phenols were applied on different soil samples. Indeed, preliminary tests revealed the necessity of higher amounts of iron in the reaction than had been previously optimized. For this reason 10 mL water solutions with initial concentrations of 7.5 mM H_2O_2 and 1.0 g soil of the Sua Pan sample were prepared with different amounts of $\text{Fe}_2(\text{SO}_4)_3$ and shaken for 2 h at 40 $^\circ\text{C}$ to show this progression. Further, 3 different soils were tested with and without the addition of chemical substrates. For this procedure, on one hand 10-mL water solutions with 1 g of soil sample were prepared and shaken for 2 h at 40 $^\circ\text{C}$. On the other hand, 10 mL water solutions with initial concentration of 10.0 mM $\text{Fe}_2(\text{SO}_4)_3$,

7.5 mM H_2O_2 , and 1.0 g soil sample were prepared and shaken at 40 $^\circ\text{C}$ for 2 h.

Identification and quantitation. The furans were identified by their retention time and mass spectra were compared with those of authentic material. External calibrations of furan, 2-methylfuran, and 3-chlorofuran were made and multipoint calibration curves were used. To estimate the response factor of the non-commercial 3-methylfuran, we used the calibration of its isomer 2-methylfuran. Both compounds have similar retention times and were assumed to have an identical recovery during the different steps of the purge and trap GC/MS method. Furthermore, both isomers have comparable ionization energies: 8.56 eV for 2-methylfuran and 8.64 eV for 3-methylfuran (29).

Results and Discussion

Reactions with Catechol. The first optimization with hydrogen peroxide revealed a maximal furan yield at a H_2O_2 concentration of 3.5 μmol (Figure 1A). This is equivalent to a molar ratio of 1:1.4 compared to the concentration of catechol. No furan was detected in the absence of H_2O_2 which establishes the necessity of hydrogen peroxide for the reaction. In contrast, H_2O_2 concentrations exceeding a 1:1.4

molar ratio to catechol were found to be unfavorable for an optimal yield. Presumably, side reactions leading to higher oxidized products occur under these conditions. Therefore a hydrogen peroxide concentration of 0.35 mM was chosen for the subsequent steps.

The measurements of the second optimization revealed that the optimum time for highest furan yield was reached very quickly (Figure 1B). Approximately the same amounts of furan were found already after 15 min. Indeed, the slow decrease after 15 min indicates further degradation reactions of furan. For this reason, a reaction time of 15 min was used in the subsequent optimization steps.

The measurements with iron(III) as the variable revealed that the presence of iron in the reaction was essential for the formation of furan, but that only small concentrations were necessary (see Figure 1C). The obtained optimal ratio of 1:10 compared to catechol suggests a catalytic effect of iron(III) in the reaction. The value of 0.05 mM $\text{Fe}_2(\text{SO}_4)_3$ was chosen for the subsequent measurements.

The pH dependence of the furan formation shows the necessity of acidic conditions ranging from 4.0 to 4.5 (Figure 1D). pH values above 5.0 led to a decrease in furan concentration. It is noted, however, that increasing pH values leads to precipitation of Fe-hydroxides and thus the iron becomes unavailable for reaction. The pH of 4.0 was chosen for the final optimization step.

To obtain the temperature optimization graph, it should be noted that with increasing temperature, the vapor pressure of volatile compounds increases in the gas phase of the headspace vial. Consequently, higher concentrations were inevitably obtained with the same purging time. To determine the net formation of furan during the reaction, a calibration of furan had to be performed for each temperature. The optimization of the agitation temperature finally revealed a maximum furan production at a temperature of 40 °C (Figure 1E). The shape of the curve at lower temperatures (<40 °C) is likely explained by an appreciable activation energy necessary for the reaction. The decrease at values higher than 40 °C might be explained by side reactions such as polymerization or degradation processes of furan.

Tests with KCl revealed that starting from catechol as model compound, chloride does not appear to affect furan formation.

Reactions with Substituted Catechols. The measurements with substituted catechols (a–d) indicated a similar formation of furans, dependent on the substituents and their position in the aromatic ring (Figure 2A). A chlorine atom leads to a chlorofuran and a methyl group leads to a methylfuran. The electronic effect of the ring substituent dictates the product yield. This might explain the differences obtained for 4-chlorocatechol (a) compared to catechol (b) or 4-methylcatechol (c). While 3-chlorofuran is produced only in small amounts (154 ng), furan and 3-methylfuran were produced in 15 times higher yields. Furthermore, the product yield between both methylated catechols (c and d) was almost negligible, indicating a reduced influence of the substitution position on the furan formation.

From a mechanistic viewpoint, the cleavage of the aromatic ring into a C_2 - and a C_4 -fragment as presumed in Scheme 1 step 2 explains the products obtained. The C_4 -fragment itself rearranges with the integration of an oxygen atom to furan, as shown in Scheme 1 step 3. It becomes clear that the position of the substituent on the aromatic ring is an important factor defining its position on the furan ring.

Reactions with Phenols. Compared to the experiments with catechols, preliminary tests with phenols revealed the necessity of increasing amounts of hydrogen peroxide for the formation of furans. It is assumed that hydrogen peroxide is responsible for the intermediate formation of hydroxyl radicals in the reaction. The need for higher H_2O_2 concen-

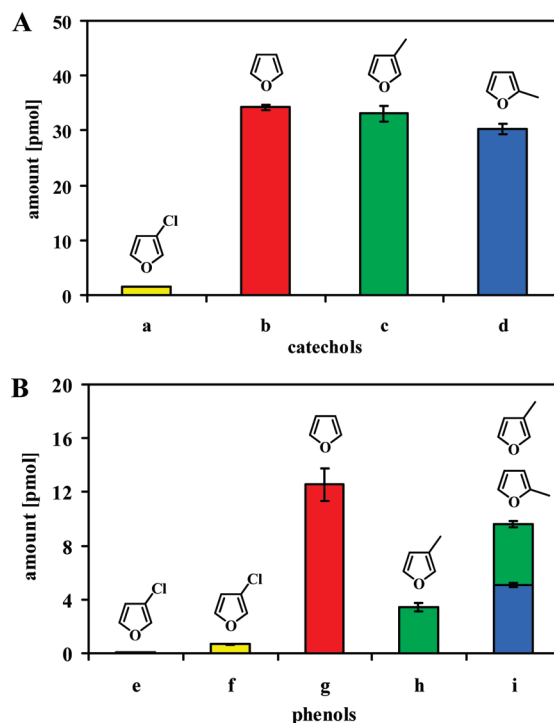
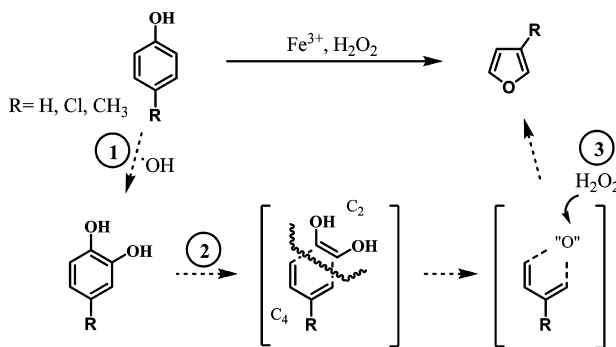


FIGURE 2. (A) Reaction of different catechols (0.50 mM), $\text{Fe}_2(\text{SO}_4)_3$ (0.05 mM), and H_2O_2 (0.35 mM) at 40 °C after 2 h: a = 4-chlorocatechol, b = catechol, c = 4-methylcatechol, d = 3-methylcatechol. (B) Reaction of different phenols (0.50 mM), $\text{Fe}_2(\text{SO}_4)_3$ (0.05 mM), and H_2O_2 (7.50 mM) at 40 °C after 2 h: e = 2,4-dichlorocatechol, f = 4-chlorophenol, g = phenol; h = 4-methylphenol, i = 3-methylphenol. Symbols are average data from experiments, and error bars indicate standard deviations from triplicate measurements.

SCHEME 1. Presumed Degradation Pathway of Phenols and Catechols to Furans



trations points to a hydroxylation step of the phenolic moiety (see step 1 in Scheme 1) producing catechol as an intermediate product and converging to the same degradation pathway. However, the substitution pattern seems to be more selective for the furan yields (Figure 2B). The lowest values are still obtained with a chlorine atom as a substituent as with 4-chlorophenol (f). Though, the comparison between phenol (g) and 4-methylphenol (h) shows a preference for the hydrogen-atom as substituent in para-position conducting to elevated furan formation. In addition to steric effects, this could be explained by electronic effects of the methyl-group (electron donating group). If the assumption of a hydroxylation step to a catecholic structure as the initial step is correct, and the electron directive effect of a methyl-group is higher than of a hydroxyl group, 4-methylphenol (h) may induce the formation of undesired resorcinic structures.

For phenol (**g**), the hydrogen-atom is not so important, allowing the attack of the hydroxyl radical next to the pre-existing hydroxyl group, resulting in the formation of catechol. The 3-methylphenol structure (**i**) has two ortho-positions alpha to the hydroxyl group which are the most likely sites of hydroxyl attack leading to catecholic structures and thus obtaining high yields of methylfurans. Steric effects and an alternate attack position (para-position) might explain why the yield was similar to that obtained with phenol (**g**), and not higher. Additionally, starting from 3-methylphenol (**i**) both methylated furans are formed in almost equivalent amounts. A mechanistic argument for this effect is provided by the hydroxylation of the phenolic structure. A hydroxylation between the two substituents hydroxyl and methyl groups, forms 3-methylcatechol (**d**) which is known to lead to 2-methylfuran (see Substituted Catechols section). The hydroxylation on the opposite ortho-position forms 4-methylcatechol (**c**) leading to 3-methylfuran. Both pathways are plausible, supporting the theory of a C₂–C₄ cleavage of the aromatic structure as postulated in Scheme 1 step 2.

Finally, the degradation of 2,4-dichlorophenol (**e**) was investigated, revealing also the formation of 3-chlorofuran. This aspect might be of interest for research fields dealing with soils contaminated by chlorinated aromatic moieties. Chlorinated phenols, especially 2,4-dichlorophenol (**e**), are known to be degradation products of pentachlorophenol (PCP) or 2,4-dichlorophenoxyacetic acid (2,4-D) which are anthropogenic in origin and are well studied in contaminated soils due to their high toxicity. The fact that these compounds can transform to volatile compounds such as chlorofurans might bring some new insights to these studies.

Isotope Labeling Studies. These experiments provided information that there was no difference between an oxygen-containing and an oxygen-free reaction system for the yield of furan. Furthermore, no influence of ¹⁸O₂ or H₂¹⁸O was observed. Indeed, the experiment with H₂¹⁸O₂ shows the formation of ¹⁸O-furan resulted in similar yields as before, proving the integration of one ¹⁸O-atom. In conclusion, the experiments with isotopic labeled compounds established that the origin of the oxygen-atom of the furan was from hydrogen peroxide (step 3 in Scheme 1). This is in accordance with the optimization step with hydrogen peroxide mentioned above (Figure 1A), which showed the importance of H₂O₂ for furan formation.

Finally, these experiments permit us to postulate a plausible mechanistic rationale for the formation of furan-like compounds (Scheme 1). The presence of hydrogen peroxide is essential, while iron only plays a catalytic role. The reaction is really fast and proceeds under acidic conditions and at moderate temperatures. Catechols as well as phenols produced furans suggesting a common degradation pathway in which phenol is the likely precursor of catechol. The hydroxylation of the phenols is the first crucial step (step 1). It is influenced by steric and electronic effects. The ring cleavage of catechol is the second important step (step 2). The different substituted substrates used and the obtained products strongly suggest the formation of a C₂- and a C₄-fragment, in which the C₄-fragment integrates an oxygen-atom from hydrogen peroxide (step 3), culminating in the formation of furan.

Soil Samples. Preliminary tests showed that the optimization with iron(III) had a different result with soil samples than with the model compounds used. Even though 2-methylfuran and 3-methylfuran were produced with the Sua Pan soil sample (Figure 3A) at low iron concentrations, the yields of the furans were higher with increasing amounts of iron(III). The catalytic effect previously observed might be inhibited by the matrix of the soil samples. To further examine the effectiveness of previously determined optimum conditions in real soil matrices, the yields of furans were compared

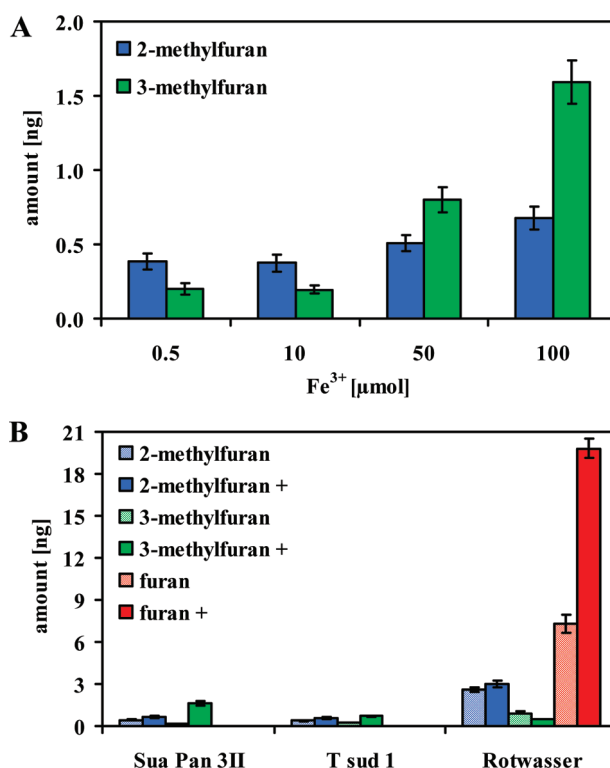


FIGURE 3. (A) Variation of iron(III) from 0.15 to 100 μmol with the Sua Pan 3II soil sample: 1 g soil, Fe₂(SO₄)₃, and H₂O₂ (75 μmol) at 40 °C after 2 h. **(B)** Soil samples with and without optimized substitutes amounts: reaction of 1 g soil, Fe₂(SO₄)₃ (100 μmol), and H₂O₂ (75 μmol) at 40 °C after 2 h. Symbols are average data from experiments, and error bars indicate standard deviations from triplicate measurements.

for soil samples without and with the addition of iron and hydrogen peroxide.

The three different soil samples revealed the formation of furans after 2 h at 40 °C without the addition of any chemical substrates. The yields and the products obtained depend on the characteristics of the samples, e.g., the organic matter (see Table 1). Furan itself is only produced in the soil sample of Rotwasser, due to its elevated organic matter content. Both methylfurans were obtained for all three soil samples. The addition of iron and hydrogen peroxide to soil samples increases the formation of furan and its derivatives. While the 2-methylfuran amounts become slightly higher, the production of 3-methylfuran is more pronounced (except for Rotwasser) and the furan formation is approximately increased by a factor of 3. Chlorofurans are not produced in these soil samples. The absence of covalently bound Cl-atoms on specific positions (phenolic moieties) within the organic matter might be the main reason for this. In conclusion, the addition of iron and hydrogen peroxide to soil samples accelerates and amplifies the formation of furans, even if their formation is already possible without the addition.

In summary, in the catechol optimizations, we obtained 2.33 μg of furan from 0.36 mg of carbon (~ 0.46%), whereas 19.8 ng (~ 4.67 ppm) of furan resulted from 299 mg of carbon in the Rotwasser soil sample with the addition of iron and hydrogen peroxide. Further conversion ratios of furans from the soil samples are summarized in Table 2. The analysis of these data shows that the high furan yields obtained from the Rotwasser soil sample (see Figure 3B) can likely be attributed to the elevated organic content. In contrast, the two salty soil samples Sua Pan 3II and T sud 1 show similar or higher conversion ratios on molar basis, pointing to distinct precursors being necessary as educts and not to the entirety

TABLE 2. Conversion Ratios of Furans (ppm) With and Without the Addition of Fe³⁺/H₂O₂

	Sua Pan 3II		T sud 1		Rotwasser	
	without	with	without	with	without	with
furan					1.73	4.67
2-methylfuran	2.31	3.85	1.87	2.73	0.63	0.73
3-methylfuran	0.92	9.15	1.00	3.40	0.23	0.12
total furans	3.23	13.00	2.87	6.13	2.59	5.52

of the organic content of soils. By assuming that these ratios were applicable on about 2000 Gt of C_{org} stored in soils (30), we should obtain yield ranges between 5 and 6 Mt of furans without the addition of Fe³⁺ and H₂O₂.

This paper adds new information and insight to the abiotic degradation of aromatic compounds in soils and contributes to the understanding of furans occurrence in the atmosphere.

Acknowledgments

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