

# Natural Abiotic Formation of Trihalomethanes in Soil: Results from Laboratory Studies and Field Samples

STEFAN G. HUBER,<sup>\*,†</sup> K. KOTTE,<sup>†,§</sup> HEINZ F. SCHÖLER,<sup>†</sup> AND J. WILLIAMS<sup>‡</sup>

*Institute of Earth Sciences, University of Heidelberg, Im Neuenheimer Feld 234-236, 69120 Heidelberg, Germany, Max-Planck-Institute for Chemistry, Mainz, Germany, and School of Physical and Chemical Sciences, North-West University, Campus Potchefstroom, Potchefstroom, South Africa*

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Trihalomethanes (THM), especially trichloromethane, play an important role in photochemical processes of the lower atmosphere, but the current knowledge of the known sources and sinks of trichloromethane is still incomplete. The trichloromethane flux through the environment is estimated at  $\sim 660$  kt year<sup>-1</sup>, and 90% of the emissions are of natural origin. Next to offshore seawater contributing  $\sim 360$  kt year<sup>-1</sup> unknown soil processes are the most prominent source ( $\sim 220$  kt year<sup>-1</sup>). This paper describes a new abiotic source of trichloromethane from the terrestrial environment induced by the oxidation of organic matter by iron(III) and hydrogen peroxide in the presence of chloride. Different organic-rich soils and a series of organic substances regarded as monomeric constituents of humus were investigated for their release of trichloromethane. The influence of iron(III), hydrogen peroxide, halide, and pH on its formation was assayed. The optimal reaction turnover for the representative compound catechol was 58.4 ng of CHCl<sub>3</sub> from 1.8 mg of carbon applying chloride and 1.55  $\mu$ g of CHBr<sub>3</sub> from 1.8 mg of carbon applying bromide; resorcin and hydroquinone displayed similar numbers. Results presented in this paper pinpoint 1,2,4,5-tetrahydroxybenzene as playing a key role as intermediate in the formation pathway of the trihalomethanes. The highest THM yields were obtained when applying the oxidized form of 1,2,4,5-tetrahydroxybenzene as THM precursor. These findings are consistent with the well-known degradation pathway starting from resorcin-like dihydroxylated compounds proceeding via further hydroxylation and after halogenation finally ending up in trihalomethanes. In conclusion, Fenton-like reaction conditions (iron(III) and hydrogen peroxide), elevated halide content, and an extended reaction time can be seen as the most important parameters required for an optimal THM formation.

## Introduction

To date more than 3800 naturally occurring organohalogens have been identified and summarized in (1), and, therefore,

it is no longer advisable to consider the formation of these halogenated hydrocarbons as being exclusively of anthropogenic origin. Of particular importance are ozone depletion in the stratosphere and the current global warming problem, where these compounds play an important role (2).

Research into global sources and sinks of volatile organohalogens as well as the understanding of mechanistical aspects are of increasing scientific importance (3–6). Trihalomethanes belong to this group of compounds with large unknown sources (7), and trichloromethane is the most prevalent one (8). In 1986 the first evidence of its natural production is provided by H. Frank and W. Frank (9) while measuring halocarbons in forests stands of the Black Forest, Germany. Moreover, Hoekstra et al. and Rhew et al. (7, 10) have provided evidence that natural soils are a probable source of trichloromethane. CHCl<sub>3</sub> is also found in emissions of savannah fires, volcanoes, hydrothermal sources, and salt mines (11) and released by algae, sea weeds, fungi, and termite mounds (12–14).

Trihalomethanes are also known as one of the most prominent groups of disinfection byproduct (DBP) in drinking water and can be detected in swimming water, cooling water, pulp and paper bleaching, and detoxification processes. Due to their high genotoxicity and carcinogenicity trihalomethanes are already the subject of a large number of studies (15).

For both natural and anthropogenic formation it is known that the halogenation of organic matter is a crucial step. In drinking water facilities elemental chlorine is responsible for THM formation, while chloride itself is likely the starting material for the natural pathway, due to its widespread availability in the terrestrial environment (16). Ballschmiter pointed to hypochlorite (ClO<sup>-</sup>) as a reactive chlorine species mediated by chloroperoxidase (CPO)-like enzymes and hydrogen peroxide (17). Analogously the formation of hypobromide (BrO<sup>-</sup>) in the presence of bromide was observed, which can result in the formation of mixed chlorinated and brominated THM.

According to the findings of Hoekstra et al. (7) that natural soils could be generally considered as a source of trihalomethanes, we investigated THM formation by applying small organic compounds as starting materials employing Fenton-like reaction conditions (18–20). The use of these model compounds is necessary for a better comprehension of the reaction mechanism (21–24). The molecules chosen were in principle polyhydroxylated benzenes (e.g., catechol, resorcin, and hydroquinone) which are representative for some structural elements of humic substances in soil. Different reaction parameters were varied and applied to catechol to obtain an overview of an optimal trihalomethane formation. After obtaining these important data, a conclusive THM reaction pathway via hydroxylated benzenes, especially 1,2,4,5-tetrahydroxybenzene, is postulated and discussed in light of the reaction schemes proposed by Boyce in 1980 (25). Hereby, 1,2,4,5-tetrahydroxybenzene could act as a similar key intermediate mentioned in the degradation pathway leading to carbon suboxide by Huber et al. (26). Finally, to confirm the results obtained by the model compounds, natural soil samples were investigated with the same optimized conditions. The use of ferrihydrite as mineral phase was investigated in this experimental section to get closer to natural soil conditions than those with the use of a soluble iron(III) salt.

\* Corresponding author phone: ++49 6221 544818; fax: ++496221 545228; e-mail: shuber@geos.uni-heidelberg.de.

<sup>†</sup> University of Heidelberg.

<sup>§</sup> North-West University.

<sup>‡</sup> Max-Planck-Institute for Chemistry.

TABLE 1. Properties of the Soils

	Rotwasser/Germany	Godschur/Russia
sampling	1996	2005
soil type	peaty sediment	sediment
geographic position	49°36'39"N 8°53'11"E	47°35'28"N 44°25'19"E
organic carbon (C <sub>org</sub> ) <sup>a</sup>	1.64%	0.3%
inorganic carbon <sup>b</sup>	<0.05%	<0.05%
Cl <sup>-</sup> -concentration <sup>c</sup>	4.5 ppm	3.6 ppm
Br-concentration <sup>d</sup>	4.7 ppm	<0.7 ppm
Fe-concentration <sup>d</sup>	1.8%	0.5%
pH value	4.0	7.3

<sup>a</sup> CS-measurement. <sup>b</sup> Via a carbonate bomb (28). <sup>c</sup> IC measurement. <sup>d</sup>  $\mu$ -XRF-measurement.

## Experimental Section

**Chemicals.** The following chemicals were used: catechol (99%; Sigma-Aldrich), ferrihydrite (27), hydroquinone (99%; Fluka), hydrogen peroxide (30%; Merck), 2,5-dihydroxy-1,4-benzoquinone (98%; Aldrich), iron(III)-sulfate (Fe 21–23%; Riedel-de-Haën), potassium bromide (99%; Aldrich), potassium chloride (99.5%; Merck), resorcin (99%; Riedel-de-Haën), sodium hydroxide (99%; Aldrich), sulfuric acid (96%; Riedel-de-Haën), and 1,2,4-trihydroxybenzene (99%; Aldrich). Doubly distilled deionized water (18 M $\Omega$  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 pH 4.0 and 7.0 buffers.

**Soils Samples.** Two different soil samples were used to verify a general, naturally occurring formation process for THM as postulated by Hoekstra et al. (7). The first one was a peaty sediment soil sampled on March 1996 from the Rotwasser nature reserve, Odenwald/Germany. The second one, a sediment soil, was sampled on June 2002 in the Godschur Valley/Russia. Following collection, the soil samples were freeze-dried and milled to fine powders (>315  $\mu$ 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.** Gas Chromatograph/Electron Capture Detector (GC/ECD) analyses were performed on a gas chromatograph (GC 8000 series Fisons Instruments) equipped with an ECD-detector (Carlo Erba, HT25). The chromatographic separation was performed using a BP624 (50 m; 0.53 mm i.d.; 3.0  $\mu$ m film thickness) capillary column. The carrier gas was N<sub>2</sub> (2 mL/min), and the ECD make up gas was Ar/CH<sub>4</sub> (95/5%, 20 mL/min). The injector temperature was 150 °C, and the GC oven temperature program was 50 °C, hold 10 min, 50 to 200 °C at 25 °C/min, hold 14 min. When sampling, aliquots of 2 mL gas phase were injected in splitless mode (1 min) into the GC.

Gas Chromatograph/Mass Spectrometer (GC/MS) analyses were done on a Varian STAR 3400 gas chromatographic system connected to a Saturn 2000 ion trap mass spectrometer. The GC/MS was equipped with a BP624 (25 m; 0.53 mm i.d.; 3.0  $\mu$ m film thickness) and a BPX5 (60 m; 0.32 mm i.d.; 1.0  $\mu$ m film thickness) capillary column, connected in series. Sampling, preconcentration, and injection of the volatile gas phase analytes from the solutions was made using a purge and trap system (Tekmar), which has been described in detail (26).

**Experimental Procedure.** The experiments were carried out in airtight closed 20 mL headspace glass vials, filled with 10 mL aqueous solution. Following mixing, samples were shaken on a rotary board at 500 rpm at 40 °C with various time periods.

To investigate the THM formation mechanism in soil we used a single surrogate compound (catechol) to represent the multitude of organic species present in soil (21). This permits mechanistic details to be examined. Chemically specific measurements of humic-like substances in soils have previously shown catechol and many species with similar chemical structures to be present.

**Reactions with Catechol.** The influence of the following parameters on the THM formation reaction was investigated with catechol.

**Concentration of Hydrogen Peroxide (H<sub>2</sub>O<sub>2</sub>).** For this purpose, solutions of 10 mL of water with initial concentrations of 2.50 mM catechol, 12.5 mM Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, 11.0 mM NaOH, and 25.0 mM KCl were prepared together with different concentrations of hydrogen peroxide and shaken for 2 h at 40 °C.

**Concentration of Potassium Chloride (KCl).** Solutions of 10 mL of water with initial concentrations of 2.50 mM catechol, 12.5 mM Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, 50.0 mM H<sub>2</sub>O<sub>2</sub>, and 11.0 mM NaOH were prepared together with different amounts of potassium chloride and shaken at 40 °C for 2 h. It should be noted that due to an impurity of the commercially available potassium chloride with 324 ppm of bromide, the use of 50  $\mu$ mol KCl (99.5%) also introduced 0.15  $\mu$ mol Br<sup>-</sup> into the system.

**Concentration of Iron(III) (Fe<sup>3+</sup>).** In order to investigate the response to varying iron concentrations, solutions of 10 mL of water with initial concentrations of 2.50 mM catechol, 50.0 mM H<sub>2</sub>O<sub>2</sub>, and 50.0 mM KCl were prepared with different concentrations of Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>. To keep the pH value at a constant level of 2.36, NaOH or H<sub>2</sub>SO<sub>4</sub> was added in appropriate amounts. The solutions were shaken at 40 °C for 2 h.

**pH Value.** To test for a possible pH dependence in trihalomethane production mechanisms, solutions of 10 mL water with initial concentrations of 2.50 mM catechol, 25.0 mM Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, 50.0 mM H<sub>2</sub>O<sub>2</sub>, and 50.0 mM KCl were prepared with different concentrations of sodium hydroxide (pH range between 2.4 and 4.1), shaken for 2 h at 40 °C.

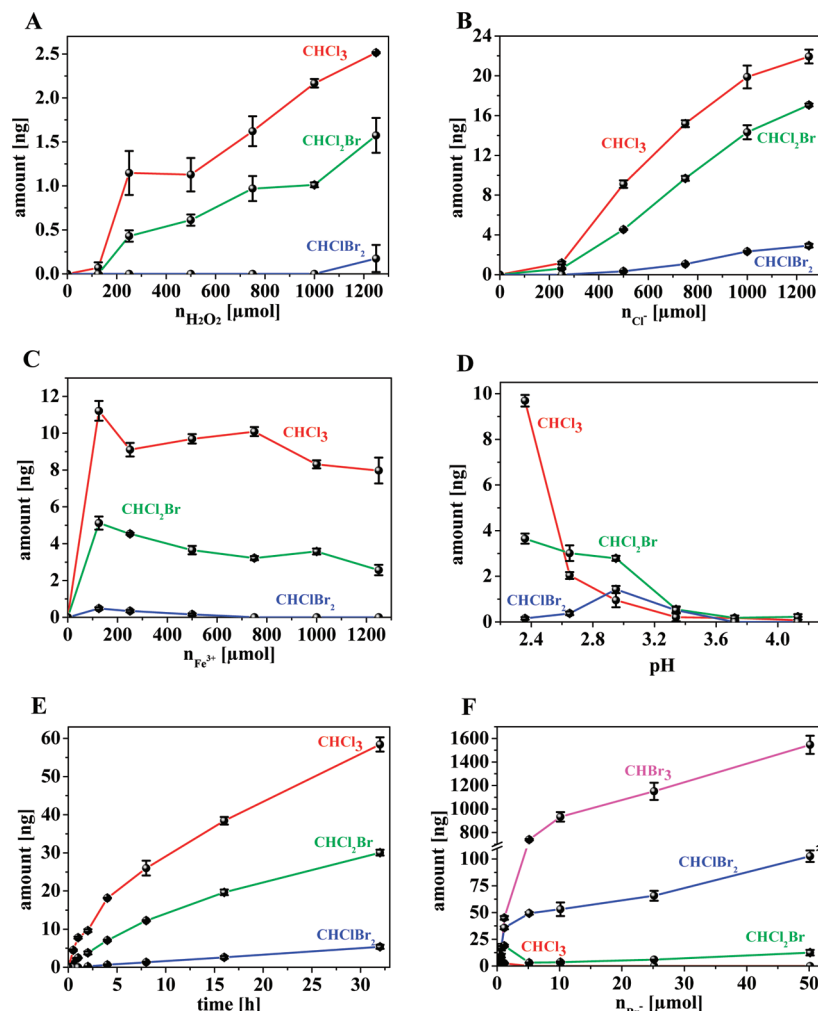
**Time Dependence.** An important factor in the amount and nature of the trihalomethanes was the reaction time. Ten mL water solutions with initial concentrations of 2.50 mM catechol, 25.0 mM Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, 50.0 mM H<sub>2</sub>O<sub>2</sub>, 50.0 mM KCl, and 23.0 mM NaOH were prepared and shaken at 40 °C for a range of times (1 min - 32 h).

**Variation of Bromide Concentration.** In order to measure the effect of KBr on the THM formation reactions, 10 mL water solutions with initial concentrations of 2.50 mM catechol, 25.0 mM Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, 50.0 mM H<sub>2</sub>O<sub>2</sub>, 50.0 mM KCl, and 23.0 mM NaOH were prepared and shaken at 40 °C for 2 h.

**Reactions with Different Hydroxylated Benzenes.** Following the determination of the optimum THM formation reaction conditions with catechol, the same conditions were then applied on its stereoisomers resorcin and hydroquinone as well as with 1,2,4-trihydroxybenzene and 2,5-dihydroxy-1,4-benzoquinone. The aim of these experiments was to examine whether a common formation pathway for trihalomethanes was operating for species with similar although chemically different structures. Therefore, 10 mL water solutions with initial concentrations of 2.50 mM of the organic compound, 25.0 mM Fe<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, 50.0 mM H<sub>2</sub>O<sub>2</sub>, 50.0 mM KCl, and 23.0 mM NaOH were prepared. These samples were shaken for 2 h at 40 °C.

**Rotwasser Soil Sample.** In preliminary experiments, 1.0 g of the Rotwasser sediment sample was shaken in 10 mL of water at 40 °C for 2 h, 24 h, and 1 week and then analyzed for THM formation using GC/ECD and GC/MS.

**Soil Samples Supplemented by Iron Species.** Subsequently the optimized conditions derived from hydroxylated



**FIGURE 1.** Effect of different parameters on the THM formation: (A) variation of hydrogen peroxide from 0 to 1250  $\mu\text{mol}$ : reaction of catechol,  $\text{Fe}_2(\text{SO}_4)_3$ , KCl, and  $\text{H}_2\text{O}_2$  at 40  $^\circ\text{C}$  after 2 h; (B) variation of potassium chloride from 0 to 1250  $\mu\text{mol}$ : reaction of catechol,  $\text{Fe}_2(\text{SO}_4)_3$ ,  $\text{H}_2\text{O}_2$ , and KCl at 40  $^\circ\text{C}$  after 2 h; (C) variation of iron(III) from 0 to 1250  $\mu\text{mol}$ : reaction of catechol,  $\text{H}_2\text{O}_2$ , KCl, and  $\text{Fe}_2(\text{SO}_4)_3$  at 40  $^\circ\text{C}$  after 2 h; (D) variation of the pH value from 2.36 to 4.31 with NaOH: reaction of catechol,  $\text{Fe}_2(\text{SO}_4)_3$ ,  $\text{H}_2\text{O}_2$ , and KCl at 40  $^\circ\text{C}$  after 2 h; (E) time dependence: reaction of catechol,  $\text{Fe}_2(\text{SO}_4)_3$ ,  $\text{H}_2\text{O}_2$ , KCl, and NaOH at 40  $^\circ\text{C}$ ; (F) variation of potassium bromide from 0.15 to 50.2  $\mu\text{mol}$ : reaction of catechol,  $\text{Fe}_2(\text{SO}_4)_3$ ,  $\text{H}_2\text{O}_2$ , KCl, NaOH, and KBr at 40  $^\circ\text{C}$  after 2 h. Symbols are average data from experiments; error bars indicate standard deviations from triplicate measurements. Concentration details are listed in the Experimental Section.

benzenes were then applied to two soil samples (Rotwasser and Godschur Valley sediments). Ten mL water solutions with initial concentrations of 25.0 mM  $\text{Fe}_2(\text{SO}_4)_3$ , 50.0 mM  $\text{H}_2\text{O}_2$ , and 50.0 mM KCl and 1.0 g of soil were prepared and shaken for 2 h at 40  $^\circ\text{C}$ . Then we replaced the supplemented  $\text{Fe}_2(\text{SO}_4)_3$  by the mineral phase ferrihydrite. For this procedure, a 10 mL water solution with initial concentration of 5.0 mM ferrihydrite, 50.0 mM  $\text{H}_2\text{O}_2$ , and 50.0 mM KCl and 1.0 g of soil sample were prepared and shaken at 40  $^\circ\text{C}$  for 2 h.

**Identification and Quantitation.** The volatile halogenated compounds were identified by their retention time and mass spectra. An external liquid calibration standard (EPA 624 Calibration Mix) and multipoint calibration curves were used to quantify the following compounds: trichloromethane, bromodichloromethane, dibromochloromethane, and tribromomethane.

## Results and Discussion

It has been previously postulated by Hoekstra et al. (7, 8), that soil is a natural source of THM. This finding was confirmed by our initial experiments with the Rotwasser Nature Reserve soil sample. By letting the freeze-dried soil sample react with water for two hours, one day, and one

week, we observed a continuous increase in trichloromethane, bromodichloromethane, and bromodichloromethane formation with time. The amount of THM generated from the ambient soil samples were only slightly above the detection limit regarding the 2 h data but increased sharply when regarding the 168 h data. The number of potential organic precursors for THM formation in soil is enormous. To determine the key parameters influencing the formation of the THM compounds we therefore adopted a single surrogate organic precursor model compound: catechol.

**Reactions with Catechol.** The effect of varying hydrogen peroxide concentrations on the THM production reaction is shown in Figure 1A. Clear increases in trichloromethane and bromodichloromethane formation upon elevation of the  $\text{H}_2\text{O}_2$  concentration were observed. The value of 50.0 mM  $\text{H}_2\text{O}_2$  was chosen for the following experiments.

The influence of potassium chloride on the THM formation is shown in Figure 1B. An order of magnitude increase in trichloromethane is obtained when KCl is increased by a factor of 5. The dependence between the concentration of KCl and the THM appears to be linear. The value of 50.0 mM KCl was chosen for the following experiments.



The iron dependence of the reaction is shown in Figure 1C. The measurements with iron(III) revealed that the presence of iron in the reaction is essential for the formation of trihalomethanes, but that only small concentrations are necessary. For the three trihalomethanes a small decrease of the values is observed from 125  $\mu\text{mol}$  to 1250  $\mu\text{mol}$  of  $\text{Fe}^{3+}$ . The value of 125  $\mu\text{mol}$   $\text{Fe}_2(\text{SO}_4)_3$  was chosen for the next measurements, derived from the first value of the plateau shown.

The pH dependence of the THM formation showed that strongly acidic conditions are required (Figure 1D). Above a pH of 3.7, no trihalomethanes were detectable. However, with increasing pH the  $\text{Fe}^{3+}$  ions precipitated out of solution as hydroxide and thus may have become unavailable for the intended reaction. For this reason, we decided to maintain the low pH of 2.36 for the following experiments.

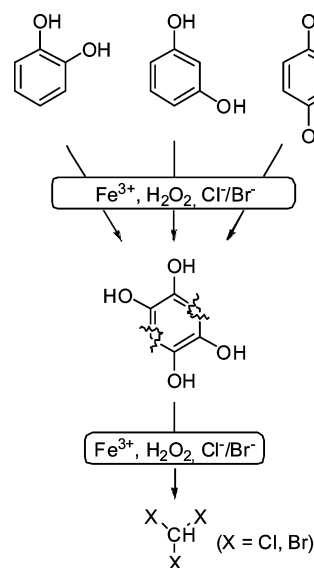
THM formation as a function of time is shown in Figure 1E. Similar to the optimization with KCl, a linear relation was observed for the three trihalomethane concentrations with time, and an order of magnitude increase was obtained within 30 h. Interestingly, although the applied chloride concentration is 3 orders of magnitude higher than that of bromide ( $\sim 1500:1$ ), the amounts of bromodichloromethane (30 ng) and dibromochloromethane (6 ng) were comparable to trichloromethane (60 ng). Under the conditions employed here,  $\text{CHCl}_3$  was most efficiently produced.  $\text{CHCl}_2\text{Br}$  was the second most abundant THM formed and  $\text{CHClBr}_2$  least, demonstrating a thermodynamically controlled reaction. A possible explanation for this distribution can be derived from the oxidation/reduction potentials of the participating substances ( $\text{H}_2\text{O}_2/\text{H}_2\text{O}$ : 1.78 V,  $\text{Cl}_2/\text{Cl}^-$ : 1.36 V,  $\text{Br}_2/\text{Br}^-$ : 1.07 V). Due to its lower redox potential, bromide is more readily oxidized to bromine by hydrogen peroxide than chloride to chlorine. Furthermore, reactive Cl-species such as chlorine or hypochlorite react with bromide to bromine or hypobromite. For this reason, the formation of brominated byproduct upon chlorination of water samples is enhanced with increasing bromide concentrations (29, 30).

The effect of potassium bromide additions to the catechol solution is shown in Figure 1F. As mentioned above, bromide was already present in the reaction mixture, because of its presence as a contaminant in the KCl. By elevating the bromide concentration, the formation of brominated THM was favored. The trichloromethane disappeared completely, while the amounts of dibromochloromethane and especially tribromomethane increased considerably. The following key information can be deduced from this optimization step: At low bromide concentrations the formation of chlorinated THM is reduced or at higher bromide concentrations even impeded. This points to an equilibrium shift to brominated THM induced by the prevalence of bromide which is more readily oxidized and polarizable than chloride. A maximal amount of 60 ng of  $\text{CHCl}_3$  was achieved with 500  $\mu\text{mol}$  of KCl in 32 h, while 1550 ng of  $\text{CHBr}_3$  was obtained with only 50  $\mu\text{mol}$  of KBr in 2 h.

In summary linear THM increases were obtained with increasing chloride concentration and time. The addition of  $\text{H}_2\text{O}_2$  was shown to stimulate the emission of  $\text{CHCl}_3$ ,  $\text{CHCl}_2\text{Br}$ , and  $\text{CHClBr}_2$ , while the reaction was shown to proceed best at low pH.

**Reactions with Different Hydroxylated Benzenes.** The experiments performed with resorcin and hydroquinone as well as with 1,2,4-trihydroxybenzene and 2,5-dihydroxy-1,4-benzoquinone revealed a qualitatively similar formation of trihalomethanes as with catechol itself. Therefore, a common reaction pathway seems to be plausible for these substituted aromatic species. For 2,5-dihydroxy-1,4-benzoquinone, the oxidation product of 1,2,4,5-tetrahydroxybenzene produced the highest yields of trichloromethane, bromodichloro-

**SCHEME 1. Presumed Degradation Pathway of Catechol, Resorcin, and Hydroquinone to Trihalomethane**



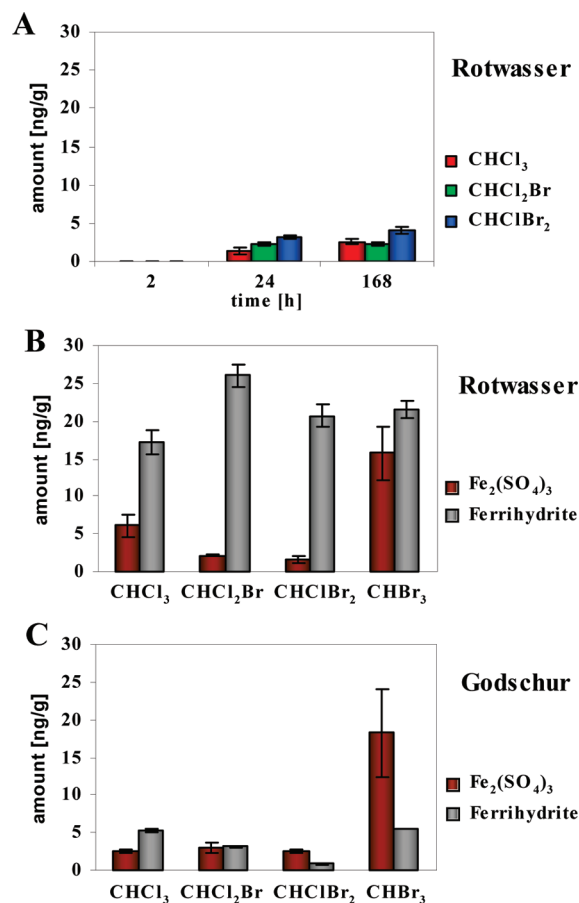
romethane, and dibromochloromethane from the five tested aromatic compounds.

THM formation from resorcin and resorcin-like compounds upon chlorination in the course of water treatment has been intensively studied over the last thirty years. One carbon of the aromatic ring in between two hydroxyl groups is polyhalogenated and finally expelled. Based on our results from the catechol and hydroquinone experiments, the picture of the degradation pathway has to be re-examined (see proposed Scheme 1). The results presented here support our assumption of a successive hydroxylation of the aromatic ring to form resorcin-like structures, two of which are present in the hypothesized key intermediate 1,2,4,5-tetrahydroxybenzene. Hydroxylation is initiated by hydroxyl radicals in the aqueous phase which are produced by the educts iron(III), redox-sensitive aromatic compound, and hydrogen peroxide (Fenton-like reaction). The next step, a combined chlorination or bromination with a ring cleavage finally leading to THM formation, is well described in many papers (25, 31, 32).

**Rotwasser Soil Sample.** We tested the time dependence of THM formation from Rotwasser sediments containing 1.64%  $\text{C}_{\text{org}}$  without any supplements (see Figure 2A). While after 2 h only qualitative evidence for a THM release was observed, the THM yield increased by a factor of 1 hundred after 7 days. In addition, these experiments revealed a strong linear relationship of the trihalomethane formation with time.

**Soil Samples Supplemented by Iron Species.** The obtained results were now applied on two soil samples. In contrast to the initial soil tests with the Rotwasser sample (Figure 2A),  $\text{Fe}_2(\text{SO}_4)_3$ ,  $\text{H}_2\text{O}_2$ , and KCl were added to the aqueous solution to enhance the reaction (Figure 2B,C).

Already after 2 h similar or higher THM amounts were detectable compared to the initial tests of one week reaction time. This suggests catechol can be representative for humic substances present in natural soils. It should be noted that in the catechol surrogate reaction an iron donor was necessary to mimic natural soil conditions. In addition we therefore examined the response of the natural soil samples to the mineral phase ferrihydrite. The results showed significantly different THM production depending both on the two soils and on the supplemented Iron-species (Figure 2B,C). For the Rotwasser sample ferrihydrite addition produced 10-fold higher THM amounts except for  $\text{CHBr}_3$  than those obtained with  $\text{Fe}_2(\text{SO}_4)_3$ . For the Godschor Valley sample the additions of both iron-species increased THM formation only



**FIGURE 2.** Time dependence and effects of  $\text{Fe}_2(\text{SO}_4)_3$  or ferrihydrite on the THM formation of soils: (A) time dependence of THM formation in Rotwasser soil samples at 40 °C; (B) application with the Rotwasser sample: reaction of the soil,  $\text{Fe}_2(\text{SO}_4)_3$  or ferrihydrite,  $\text{H}_2\text{O}_2$  and KCl at 40 °C after 2 h; (C) application with the Godschor Valley sample: reaction of the soil,  $\text{Fe}_2(\text{SO}_4)_3$  or ferrihydrite,  $\text{H}_2\text{O}_2$ , and KCl at 40 °C after 2 h. Symbols are average data from experiments; error bars indicate standard deviations from triplicate measurements. Concentration details are listed in the Experimental Section.

to a minor extent with the exception of  $\text{CHBr}_3$ . The elevated  $\text{CHBr}_3$  concentrations in both soil samples might not be attributed to bromide impurities in the applied  $\text{Fe}_2(\text{SO}_4)_3$  solution (Br concentration ca. 4 ppm).

Using catechol, as a surrogate organic compound of soil, maximum yields of 58.4 ng  $\text{CHCl}_3$  from 1.8 mg carbon ( $\sim 0.003\%$ ) were obtained in the time dependence optimization and 1.55  $\mu\text{g}$   $\text{CHBr}_3$  from 1.8 mg carbon ( $\sim 0.086\%$ ) in the bromide variation optimization. As well as Fenton-like reaction conditions (iron and hydrogen peroxide) elevated halide content and a long reaction time can be seen as the most important conditions required for optimal THM formation.

The results from a series of di- to tetrahydroxylated benzenes showed the highest THM yields when applying 2,5-dihydroxy-1,4-benzoquinone, the oxidized form of 1,2,4,5-tetrahydroxybenzene. The higher the number of OH substituents on the aromatic ring, the lower is the bonding energy of the adjacent C–C bonds. If 4 OH substituents are present, the aromaticity is lost, and an unstable quinonic intermediate is formed which after further halogenation finally degrades to trihalomethanes. For this reason 1,2,4,5-tetrahydroxybenzene seems to be a conclusive common intermediate in the course of the degradation of aromatic compounds (hydroquinone, catechol, and resorcin). It displays two

prominent carbon atoms in meta-position which is known to be necessary for the THM formation (31).

Trihalomethanes are formed from natural soils provided halide ions, organic precursors, and iron are present. When soluble iron(III) or the mineral ferrihydrite were added to natural soils, no clear THM preference for the two tested soil types was observed. While the Rotwasser soil sample produced the highest THM concentrations with ferrihydrite supplementation, the Godschor Valley sample displayed the highest THM contents with  $\text{Fe}_2(\text{SO}_4)_3$ .

This paper adds new information and insight to the abiotic degradation of aromatic compounds and helps to comprehend the occurrence of trihalomethanes in natural soils, in soil air, and in unpolluted groundwater.

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