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CHEMICAL CHANGES OF ORGANIC COMPOUNDS IN CHLORINATED WATER

XIII*. GAS CHROMATOGRAPHIC–MASS SPECTROMETRIC STUDIES OF THE REACTIONS OF IRGASAN DP 300 [5-CHLORO-2-(2,4-DICHLOROPHENOXY)PHENOL] WITH CHLORINE IN DILUTE AQUEOUS SOLUTION

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SUMMARY

The reactions of Irgasan DP 300 with chlorine in water were investigated by means of gas chromatography (GC) and GC–mass spectrometry. Irgasan DP 300 was shown to produce dichloro- and trichloro-2-(2,4-dichlorophenoxy)phenols in chlorine-treated water, followed by the decomposition of these intermediates to chlorophenols. No polychlorinated dibenzo-*p*-dioxins were detected in chlorine-treated Irgasan DP 300 solutions. The production of some of these compounds is dependent on the number of equivalents of chlorine per mol of compound and on the reaction pH.

INTRODUCTION

Polychlorinated phenoxyphenols (PCPPs) occur as the main contaminant of technical chlorophenol formulations[1–10] and are produced during chlorination of phenolic compounds with hypochlorite in dilute aqueous solutions[11–16]. Attention has been drawn to such compounds because their 2-hydroxy isomers (Cl_n-2-PPs, predioxins) have been shown to undergo both thermal and photochemical ring closure to form polychlorinated dibenzo-*p*-dioxins (PCDDs)[2,3,17–30]. In addition, the chlorophenols and chloroaromatics themselves may react thermally and photochemically to give PCDDs[31–36]. Although the discussion of the origin of PCPPs and PCDDs has been focused on the above two potential sources, recently Lamparski *et al.*[37] and Weerasinghe *et al.*[38] have demonstrated the presence of PCDDs in municipal sewage sludges.

A 5-chloro-2-(2,4-dichlorophenoxy)phenol is available as a commercial bactericide (Irgasan DP 300) and is also known as predoxin because thermal degradation

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* For Part XII, see ref. 45.

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of this compound produces 2,8-dichlorinated dioxin[23]. Through its use as a deodorant, medical soap and disinfectant soap, this compound is introduced into the water system. Chlorination is used extensively in waste-water treatment in order to disinfect and deodorize effluents prior to discharge, particularly when the water may subsequently be used for recreational purposes or as a source of potable water. It seems, therefore, that highly chlorinated compounds of Irgasan DP 300 are formed by its chlorination in water supplies and waste.

In order to provide further insight into the possible rôle of organic compounds in the formation of chlorine-substituted compounds and of chlorine-induced mutagens, this laboratory has continued the study of the aqueous chlorination chemistry of organic compounds[11–16,39–45]. The data presented here show the possible formation of higher chlorinated 2-PPs and chlorophenols as degradation products during chlorination of water contaminated with Irgasan DP 300, under the conditions utilized for water treatment.

EXPERIMENTAL

Materials

5-Chloro-2-(2,4-dichlorophenoxy)phenol (Irgasan DP 300) was commercially available (purity, >99.3%). Several chlorinated phenols and 2-phenoxyphenols, which are expected to be formed during chlorination of Irgasan DP 300 with aqueous chlorine, were also commercially available. Standard solutions of these compounds both alone and as mixtures were prepared by dissolving the compounds in methanol and subsequent dilutions. Hypochlorite solution was prepared by diluting sodium hypochlorite solution (*ca.* 10% available Cl; Nakarai Chemicals, Kyoto, Japan) in 0.1 *M* disodium hydrogenphosphate–potassium dihydrogenphosphate solution. The hypochlorite concentrations were determined by iodometric titration.

Treatment of Irgasan DP 300 solution with aqueous chlorine

A mixture of 100 ml of hypochlorite solution and Irgasan DP 300 dissolved in 1 ml of methanol was shaken in a separatory funnel at room temperature. After the desired reaction time, the residual chlorine was removed by addition of an equivalent volume of sodium thiosulphate solution. The reaction mixture was then acidified to pH 2 with 0.1 *M* hydrochloric acid before extraction with three 20-ml volumes of diethyl ether. The solvents were dried over anhydrous sodium sulphate and concentrated to suitable volumes, using a Kuderna-Danish concentrator, for gas chromatographic (GC) and GC–mass spectrometric (GC–MS) analyses.

Product resolution and characterization

A Shimazu GC-6A gas chromatograph equipped with a flame ionization detector and a 2 m × 3 mm I.D. glass column packed with 2% OV-1 on Uniport HP (60–80 mesh) was programmed from 120 to 240°C at 5°C/min. The injector and detector temperatures were 260°C. The helium gas flow-rate was 50 ml/min. A Shimazu Model Chromatopac-1A data system was used to determine the retention times and peak areas on the chromatograms.

An Hitachi M-80 combined mass spectrometer-gas chromatograph equipped with an Hitachi M-003 data-processing system was used for the qualitative analyses of samples under the following conditions: ion-source temperature, 250°C; trap current, 70 μA; electron energy, 70 eV. A glass column (2 m × 3 mm I.D.) packed with 2% OV-1 on Uniport HP (60–80 mesh) was used for the GC separation of the diethyl ether extracts. The oven temperature of the gas chromatograph was increased from 120 to 240°C at 5°C/min. The helium carrier gas flow-rate was 20 ml/min. The products were identified by comparison of their retention times and mass spectra with those of authentic compounds.

RESULTS AND DISCUSSION

Production of higher chlorinated 2-phenoxyphenols (2-PPs)

A typical GC–MS (total ion current) trace of a diethyl ether extract of neutral Irgasan DP 300 solution after treatment with hypochlorite (20 equiv. of chlorine per mol of compound) for 1 h is shown in Fig. 1. At least, five reaction products can be seen on the chromatogram. Some of the peaks were identified on the basis of their retention times and mass spectra as compared with those of authentic compounds. Compounds corresponding to other peaks were determined from the mass spectrum of each peak (Fig. 2).

Fig. 2A and B show the mass spectra of the peaks in scans 21 and 41, respectively, which are the GC–MS peaks having small retention times on the chromatogram of Fig. 1. The molecular ion (M^+) of the peak of scan 21 occurs at m/z 162,

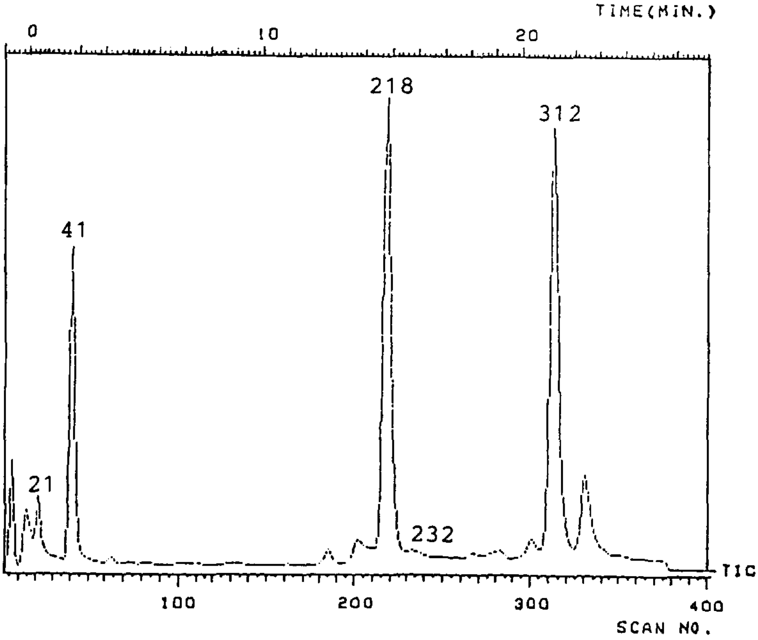


Fig. 1. Mass chromatogram (total ion current) of a diethyl ether extract of an Irgasan DP 300 solution (0.347 m*M*) after treatment with hypochlorite (20 equiv. of chlorine per mol of compound) at 20°C for 1 h. The mass spectrum for each peak is given in Fig. 2. Compounds as in Table I. The GC column temperature was increased from 120 to 240°C at 5°C/min. For other GC–MS conditions, see Experimental.

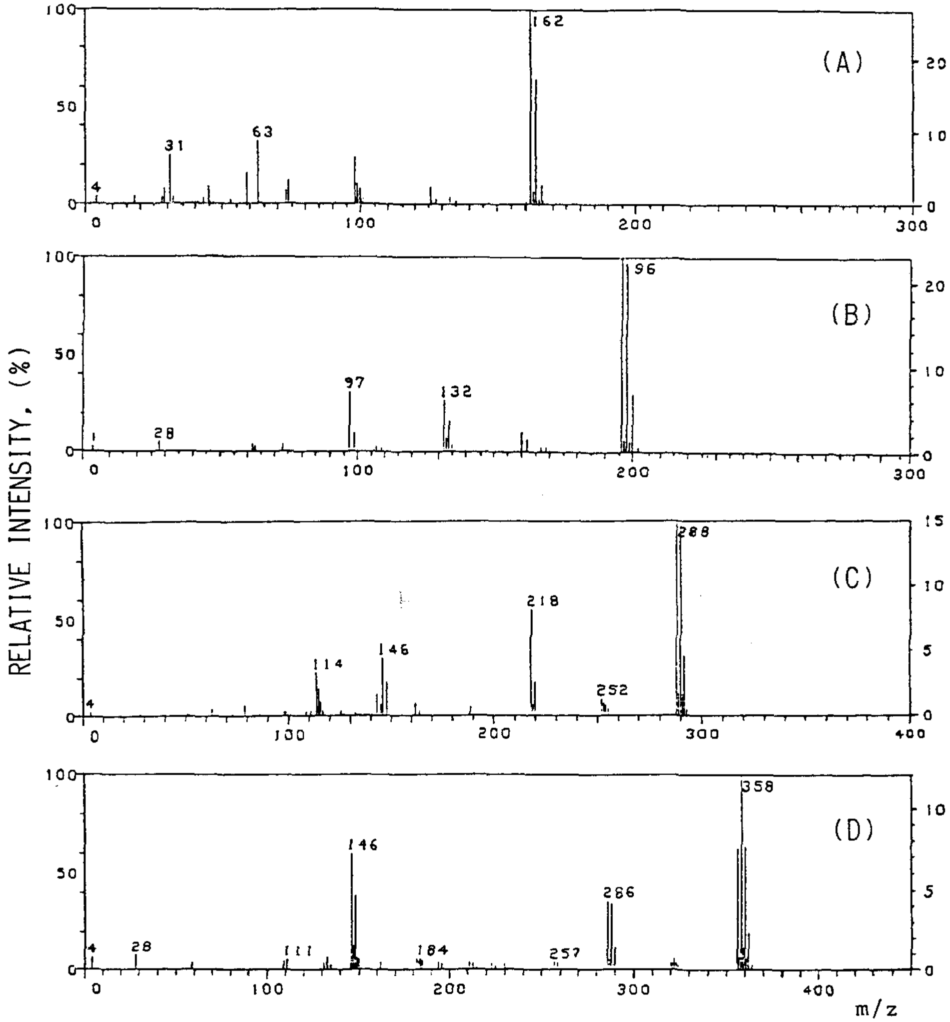


Fig. 2. Mass spectra of peaks of scans 21 (A), 41 (B), 218 (C) and 312 (D) in Fig. 1.

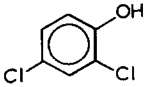
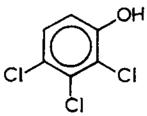
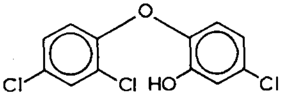
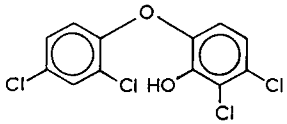
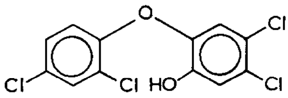
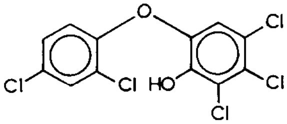
having two chlorine atoms, and four fragment ions occur at *m/z* 133 (M^+ − COH), 126 (M^+ − HCl), 98 (M^+ − Cl − COH) and 63 (M^+ − 2Cl − COH). The compound corresponding to the peak of scan 41 gave a molecular ion at *m/z* 196, having three chlorine atoms, and three fragment ions at *m/z* 160 (M^+ − HCl), 132 (M^+ − Cl − COH) and 97 (M^+ − 2Cl − COH). The mass spectra and GC retention times of these compounds were in agreement with those of 2,4-dichloro- and 2,3,4-trichlorophenol, respectively. Since these compounds corresponding to the peaks of scans 21 and 41 could not be detected when Irgasan DP 300 was chromatographed under the same conditions, it is concouded that they are produced during the reaction of Irgasan DP 300 with hypochlorite in dilute aqueous solution.

The mass spectrum of the compound (Fig. 2C) corresponding to the peak of

TABLE I

PRODUCTS OF REACTION OF IRGASAN DP 300 WITH CHLORINE IN NEUTRAL WATER

Reaction conditions and GC–MS conditions as in Fig. 1.

Peak number	*Scan number*	*Proposed structure*	*Molecular ion (m/z)*	*m/z (relative intensity)*
1	21	2,4-Dichlorophenol  	162	166 (11), 164 (64), 162 (100), 135 (2), 133 (3), 128 (3), 126 (8), 100 (8), 98 (25), 63 (32)
2	41	2,3,4-Trichlorophenol  	196	202 (4), 200 (31), 198 (95), 196 (100), 164 (1), 162 (7), 160 (11), 136 (4), 134 (17), 132 (27), 99 (10), 97 (31)
3	218	5-Chloro-2-(2,4-dichlorophenoxy)phenol  	288	294 (4), 292 (31), 290 (97), 288 (100), 256 (1), 254 (6), 252 (9), 220 (19), 218 (55), 150 (2), 148 (18), 146 (31), 116 (18), 114 (23)
4	230	5,6-Dichloro-2-(2,4-dichlorophenoxy)phenol  	322	330 (1), 328 (10), 326 (47), 324 (100), 322 (76), 256 (5), 254 (28), 252 (43), 150 (5), 148 (31), 146 (45)
5	234	4,5-Dichloro-2-(2,4-dichlorophenoxy)phenol  	322	Same as those of compound 4
6	312	4,5,6-Trichloro-2-(2,4-dichlorophenoxy)phenol  	356	364 (3), 362 (20), 360 (64), 358 (100), 356 (63), 324 (3), 322 (6), 320 (4), 290 (12), 288 (35), 286 (35), 186 (2), 184 (6), 182 (6), 150 (6), 148 (39), 146 (60)

scan 218 in Fig. 1 gave a molecular ion at *m/z* 288, having three chlorine atoms, and three fragment ions at *m/z* 252 (M^+ − HCl), 218 (M^+ − 2Cl) and 146 (M^+ − $C_6H_3ClO_2$). The compound (Fig. 2D) corresponding to the peak of scan 312 in Fig. 1 gave a molecular ion at *m/z* 356, having five chlorine atoms, and four fragment ions at m/z 320 (M^+ − HCl), 286 (M^+ − 2Cl), 257 (M^+ − 2Cl − COH) and 146 (M^+ − $C_6HCl_3O_2$). The mass spectra and GC retention times of these compounds were in agreement with those of Irgasan DP 300 and 4,5,6-trichloro-2-(2,4-dichlorophenoxy)phenol, respectively.

The mass spectrum of the compound corresponding to the peak of scan 232 (data not snown) was interpreted as being that of a chlorinated 2-PP with four chlorine atoms. The molecular ion at m/z 322 and two fragment ions at m/z 252 (M^+ − 2Cl) and 116 (M^+ − $C_6H_2Cl_2O_2$) were observed. This small peak on the chromatogram in Fig. 1 was, however, shown by using capillary GC to overlap with two compounds. The mass spectra and GC retention times of these compounds were identical to those of 4,5- and 5,6-dichloro-2-(2,4-dichlorophenoxy)phenol, respectively. In the present work, PCDDs and other related compounds in chlorine-treated Irgasan DP 300 solutions were also tested, however, none of these compounds was detected.

A summary of the chlorination products identified or determined from their GC retention times and mass spectra is presented in Table I. According to Deinzer *et al.*[46] and Katsura *et al.*[47], certain polychlorinated 2-PPs may be as toxic as the most toxic PCDDs and polychlorinated dibenzofurans. It is, therefore, necessary to reveal the fate of these compounds reported here (Table I) in chlorinated water or an outdoor aquatic system.

Chemical and physical factors affecting the reactions of Irgasan DP 300 with chlorine in water

GC analyses of the diethyl ether extracts indicated that a rapid decrease in the amounts of the original compounds in water occurred with an increase in the molar

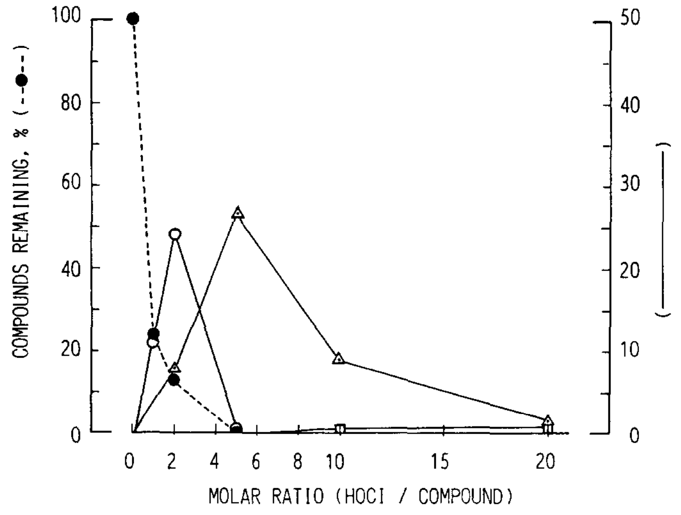


Fig. 3. Residual amounts of reaction products in aqueous Irgasan DP 300 solutions (0.347 m*M*) after treatment with hypochlorite (various equivalents of chlorine per mol of compound) at room temperature for 1 h. The yields were derived from GC peak areas, relative to the area of the starting material. ●—●, Starting material; ○—○, tetrachloro-2-phenoxyphenols; △—△, pentachloro-2-phenoxyphenol and □—□, chlorophenols.

ratios of hypochlorous acid to compound (Fig. 3). Two isomers of tetrachlorinated 2-phenoxyphenols (Cl_4-2-PPs, *m/z* 322) were the primary products from Irgasan DP 300 and hypochlorite in water. They were followed by the formation of pentachlorinated 2-phenoxyphenol (Cl_5-2-PP, *m/z* 356) and subsequent decomposition to form chlorophenols, as is seen in Fig. 3. The distribution of these Cl_4-2-PPs and Cl_5-2-PP in chlorinated water can be explained in terms of electrophilic substitution by chlorine, because the *ortho-* and *para-*positions in the phenol ring are activated by the hydroxyl substituent. Treatment at molar ratios of hypochlorous acid to the compound of >20 gave a small amount of Cl_5-2-PP and its decomposition products (chlorophenols).

The effect of the solution pH on the reactions of Irgasan DP 300 with chlorine is demonstrated in Fig. 4. A rapid formation of Cl_5-2-PP and its subsequent decomposition to 2,4-dichloro- and 2,3,4-trichlorophenol are observed in an alkaline solution. However, it seems that the Cl_5-2-PP formed in these reactions is comparatively stable under acidic conditions. This can be explained in terms of the concentrations of undissociated hypochlorous acid in the chlorinated water. Therefore, the effect of pH on the reactions of Irgasan DP 300 with chlorine in water is correlated with the titration curve of hypochlorous acid, as shown in Fig. 4.

In order to confirm whether similar reactions take place under the conditions of water treatment, different initial concentrations of Irgasan DP 300 were treated with hypochlorite compound molar ratios of 2, 5 and 20 for 1 h. The results of GC determinations of the diethyl ether extracts from the chlorinated Irgasan DP 300 solutions are shown in Fig. 5. It was found that the reactions of Irgasan DP 300 with hypochlorite in water proceed more rapidly with increasing initial concentrations of both compounds and with increasing hypochlorous acid/compound molar ratios. However, high concentrations of chlorophenols in the water were detected when 1

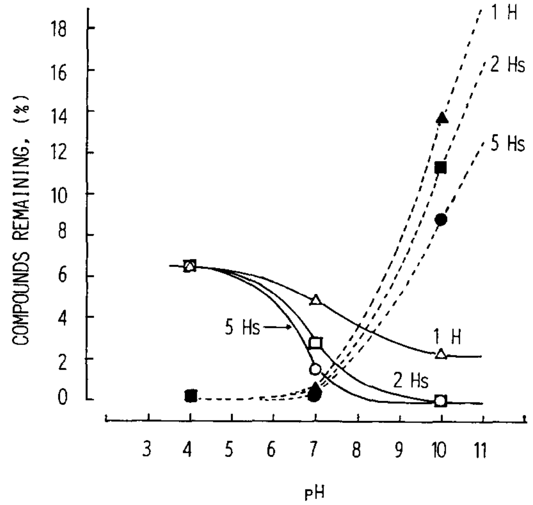


Fig. 4. Residual amounts of reaction products in aqueous Irgasan DP 300 solutions (0.347 m*M*) after treatment with an excess of hypochlorite at various pH values and room temperature for 1, 2 and 5 h. Open symbols: tetra- and pentachloro-2-phenoxyphenols. Closed symbols: chlorophenols. Other details as in Fig. 3.

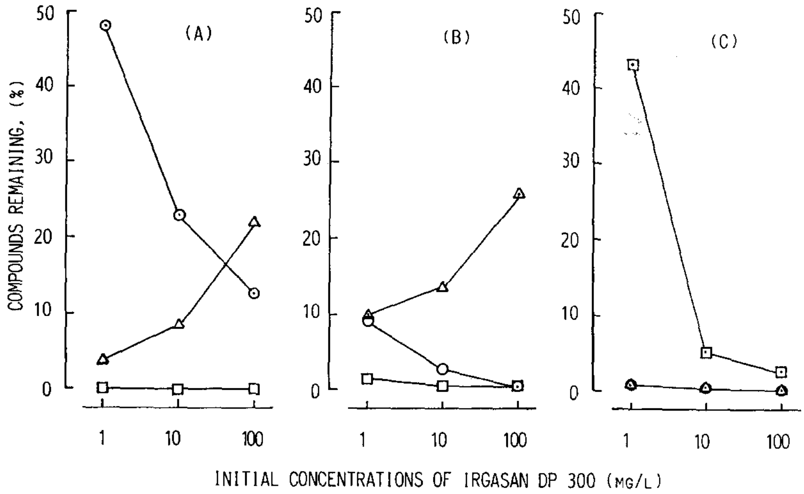


Fig. 5. Effect of the initial concentrations of compounds on the residual amounts of reaction products of aqueous Irgasan DP 300 solutions after treatment with 2 (A), 5 (B) and 20 equivalents (C) of chlorine per mol of compound for 1 h at pH 7. ○—○, Starting material; △—△, sum of tetra- and pentachloro-2-phenoxyphenols and □—□, chlorophenols. Other details as in Fig. 3.

ppm of Irgasan DP 300 was treated with an excess of hypochlorous acid (Fig. 5C). High persistences of chlorophenols in water has also been observed for phenol–chlorine reactions[40], under the conditions utilized for drinking-water treatment. Since the ultimate reaction products of phenol with hypochlorite in water have been identified as trichloroacetic acid and chloromaleic acid[43], the Irgasan DP 300–chlorine reactions may take place in a similar manner to that of the phenol reactions.

Aqueous chlorine is used to disinfect sewage water and raw water destined for human consumption. Irgasan DP 300 has been shown to produce several chlorinated aromatic compounds upon reactions with hypochlorite in water (Figs. 1 and 2). The production of these compounds is greatly dependent on the hypochlorous acid/compound molar ratio and the reaction pH (Figs. 3 and 4), with high concentrations of reaction products at moderate chlorine doses and under acidic or alkaline conditions. Acidic and alkaline chlorinated waters are generally adjusted to neutral conditions or diluted in water at the water-treatment stations. Therefore, most of the chlorinated aromatic compounds are destroyed and the hazard to public health may be substantially decreased. However, the higher chlorinated 2-phenoxyphenols are particularly interesting, as they are present in chlorine-treated Irgasan DP 300 solution and are also precursors of the highly toxic chlorinated dioxins. Recently Lamparski *et al.*[37] and Weerasinghe *et al.*[38] have demonstrated the presence of polychlorinated dibenzo-*p*-dioxins in sewage sludges.

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