

# Declining Dioxin Concentrations in the Rhone River Basin, France, Attest to the Effectiveness of Emissions Controls

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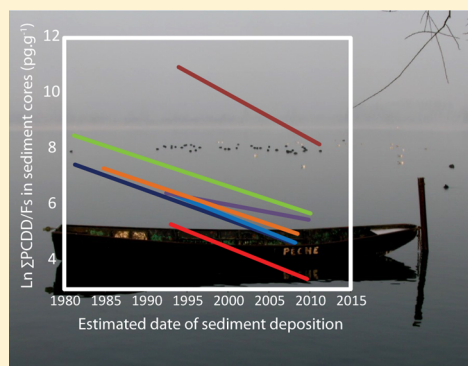
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## S Supporting Information

**ABSTRACT:** Emission-control policies have been implemented in Europe and North America since the 1990s for polychlorodibenzodioxins (PCDDs) and furans (PCDFs). To assess the effect of these policies on temporal trends and spatial patterns for these compounds in a large European river system, sediment cores were collected in seven depositional areas along the Rhone River in France, dated, and analyzed for PCDDs and PCDFs. Results show concentrations increase in the downstream direction and have decreased temporally at all sites during the last two decades, with an average decrease of 83% from 1992 to 2010. The time for a 50% decrease in concentrations ( $t_{1/2}$ ) averaged  $6.9 \pm 2.6$  and  $9.1 \pm 2.9$  years for the sum of measured PCDDs and PCDFs, respectively. Congener patterns are similar among cores and indicate dominance of regional atmospheric deposition and possibly weathered local sources. Local sources are clearly indicated at the most downstream site, where concentrations of the most toxic dioxin, TCDD, are about 2 orders of magnitude higher than at the other six sites. The relatively steep downward trends attest to the effects of the dioxin emissions reduction policy in Europe and suggest that risks posed to aquatic life in the Rhone River basin from dioxins and furans have been greatly reduced.



## INTRODUCTION

Polychlorodibenzodioxins (PCDDs) and polychlorodibenzofurans (PCDFs) are unintentional byproducts of chemical production and combustion processes.<sup>1</sup> The two most important sources are considered to be chlorinated phenols and various combustion processes.<sup>2</sup> PCDDs and PCDFs (collectively, PCDD/Fs) undergo short- and long-range transport in the atmosphere followed by deposition on soils or waters, and then transfer to bottom sediments and accumulation in food webs.<sup>3,4</sup> Direct discharges from industrial sources to aquatic systems and runoff from historical contamination sites also occur.<sup>5</sup> Anthropogenic emissions to the atmosphere increased substantially beginning in the mid-1930s, peaked in the late 1960s and early 1970s, and have since been reduced, but not completely eliminated, by various control measures.<sup>2,6–8</sup> In Europe, the fifth European Community Program of policy and action on the environment, published in 1993,<sup>9</sup> aimed to achieve a 90% reduction of dioxin emissions by 2005, compared to the 1985 level. Activities of the program were completed in 2001 with the issuing of a final strategy on dioxins,<sup>10</sup> which provided for an inventory of dioxin sources and a reduction of human exposure through food

consumption. Regulations targeting PCDD/Fs in food were adopted at the European level in 2006<sup>11,12</sup> and revised in 2011<sup>13</sup> and PCDD/Fs were added to the list of priority substances targeted by the Water Framework Directive in 2013 (WFD).<sup>14</sup>

In the United States, the U.S. Environmental Protection Agency (EPA) has worked over the past several decades to reduce dioxin emissions to air and water under the Clean Air and Clean Water Acts and in cooperation with State governments and industry.<sup>15</sup> Policies were established to control the main emission sources such as municipal waste incinerators<sup>16</sup> and chlorine-bleached pulp and paper mill effluents.<sup>17</sup> As a result, known and quantifiable total dioxin emissions in the U.S. have been reduced by about 75%, and emissions to the atmosphere have been reduced by about 85% from 1987 levels.<sup>15</sup> Dioxin emissions reductions from regulatory actions in the United States, however, have likely

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been overshadowed by the “reduction in particle emissions from large combustion systems, the elimination of chemical waste burning, and the abandonment of the chlorinated phenol business by large sectors of the chemical industry”, as noted by ref 2.

Trends in PCDDs and PCDFs were documented by several lake-sediment core studies in the 1980s and 1990s, as reviewed by ref 18. Studies of PCDD/Fs in the northeastern U.S., Germany, Netherlands, and the United Kingdom reported a general increase in concentrations from 1930–1940 to the mid-1970s or early 1980s, but a less consistent response thereafter, with a decrease in the U.S. but mixed trends in Europe.<sup>18</sup> Other European studies indicate downward trends in recent decades.<sup>19–22</sup> Recent downward trends also were observed in cores collected in the Baltic Sea, either along the Swedish coast or offshore, but peak concentrations occurred 16 years later on average in offshore cores than in near-shore cores.<sup>23</sup>

In terms of discharge, the Rhone River is the largest river in France and the third largest river in Western Europe,<sup>24</sup> with a mean annual discharge just downstream from the confluence with the Saône River of 1040 m<sup>3</sup>/s (1966 to 2009) (Le Rhône à Ternay, streamflow-gaging station V3130020 (<http://www.hydro.eaufrance.fr/>)). The watershed of the Rhone River covers 97 800 km<sup>2</sup> and has marked climatic and geological heterogeneity.<sup>25</sup> The Rhone River is a complex hydrologic system with numerous tributaries, large urban areas and industrial zones, and extensive anthropogenic modification of the hydrology (Supporting Information (SI) Figure S-1). Since the Second World War, flow and sediment transport in the Rhone River have been affected by the construction of numerous dams between Lake Geneva and the Mediterranean Sea, accompanied by structures for navigation, dike construction, and channel dredging.<sup>26,27</sup> Potential sources of dioxins in the Rhone River basin include atmospheric deposition, industrial facilities, and waste-processing facilities.

An objective of the Rhone Sediment Observatory (<http://www.graie.org/osr/>) is to generate, compile, and analyze observations on sediment and associated contaminant loads and stocks in the Rhone River. In partial fulfillment of this objective, sediment cores were collected along the Rhone from 2008 to 2012 in undisturbed areas such as side channels, dated, and analyzed for PCBs and PCDD/Fs. Trends in PCB concentrations were presented previously.<sup>28,29</sup> Here we assess historical and spatial trends of PCDDs and PCDFs in Rhone sediments and discuss the results in the context of the recent addition of these compounds to the list of priority substances according to the WFD.

## MATERIALS AND METHODS

**Sampling, Analytical, and Quality Control.** Sediment cores were collected in seven side channels or other backwater areas along the main channel of the Rhone River between the outlet of Lake Geneva and the confluence with the Ardeche River (SI Figure S-1, Table S-1). The sites were chosen to evaluate the upstream-downstream distribution and temporal trends of contaminants and to assess the potential contributions of major urban and industrial areas and tributaries (e.g., the Saone, Gier, and Isere Rivers).<sup>28,29</sup> The sampling locations selected are connected to the main stream channel, in most cases by an inlet at their downstream end, and receive continuous or frequent (i.e., during high flow) sediment supply. The seven sites are referred to as ETL, MTE, CPX, TBR, BRE, ARS, and GEC, in order from upstream to downstream. Details

on sampling, site characteristics, and age dating have been given previously.<sup>28,29</sup> Dating of the cores primarily relied on <sup>137</sup>Cs activity profiles, including the 1986 peak corresponding to the Chernobyl accident, and secondarily on changes in grain-size distribution indicating important geomorphic or land-use changes in the reach of the river, the timing of major floods, or a change in the connection of the coring site to the Rhone River.<sup>28,29</sup>

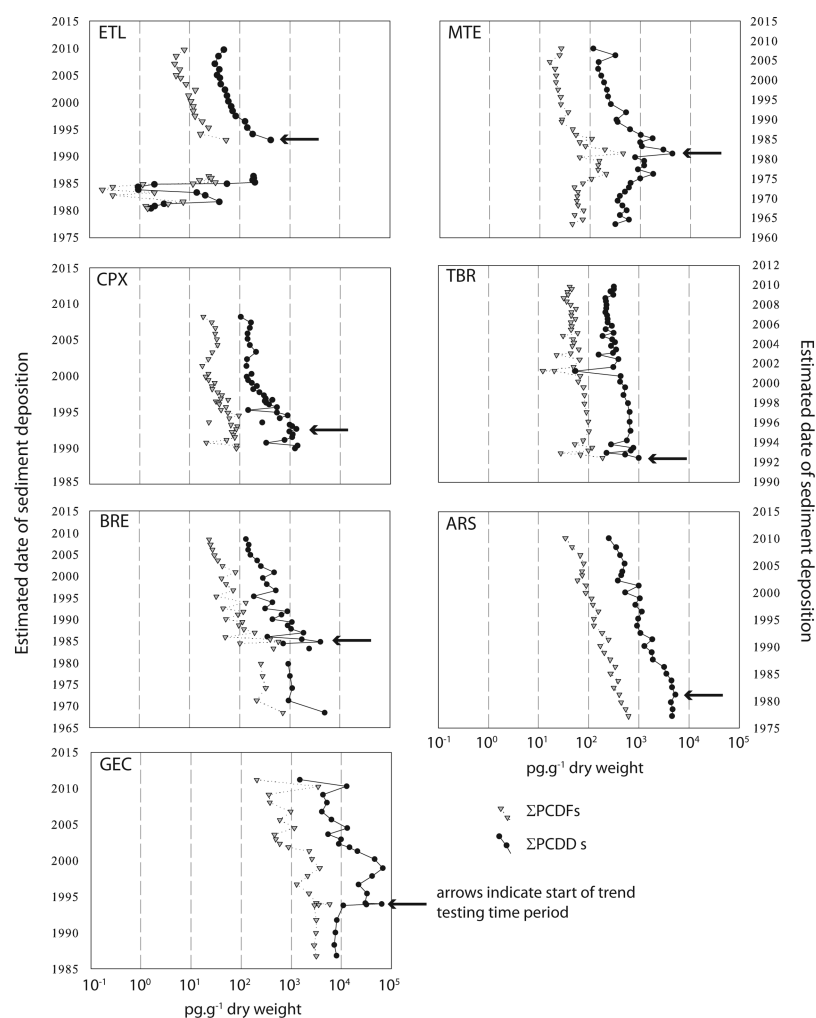
Analysis of PCDDs and PCDFs was done by the EUROFINs GfA laboratories, Hamburg, Germany, using high resolution gas chromatography-high resolution mass spectrometry. Seven PCDDs and 10 PCDFs were quantified (SI Table S-2; Table S-3). Details on extraction, purification and quantification methods, and limits of quantification are provided in the Supporting Information. Among the 75 PCDD and 135 PCDF congeners, the 17 2,3,7,8-substituted congeners were quantified and are presented here (SI Table S-2). These 17 congeners are used for the computation of the toxic equivalent concentrations (TEQs)<sup>30,31</sup> (values from ref 31 were used here) and often are the basis for regulatory actions (e.g., refs 11 and 13).

**Statistical Analysis.** Trends in the sums of seven measured PCDDs ( $\sum$ PCDDs), 10 measured PCDFs ( $\sum$ PCDFs), and the 17 measured congeners ( $\sum$ PCDD/Fs), and congener distributions were evaluated statistically using the Statistica software package (StatSoft, Inc., Tulsa, OK). Sums of congener concentrations tested for trend included only detected congeners (nondetections treated as zero), as recommended in Europe for monitoring data.<sup>32</sup> The nonparametric Kendall's tau test was used and relations were considered significant for  $p$  values < 0.05. Rates of decrease in dioxin concentrations were estimated in each core by linear regression of the logarithm of  $\sum$ PCDDs,  $\sum$ PCDFs, and  $\sum$ PCDD/Fs with sample deposition dates. Times for a 50% reduction of congener concentrations ( $t_{1/2}$ ) were derived from the regression slope. Relations between median  $\sum$ PCDD/Fs concentrations for decadal time periods and downstream distance in the Rhone River were modeled using nonlinear regression, implemented as dynamic curve fitting in the SigmaPlot software package (Systat Software Inc., San Jose, CA). Dynamic curve fitting is an iterative process to find the best possible curve (equation) matching a series of data points.

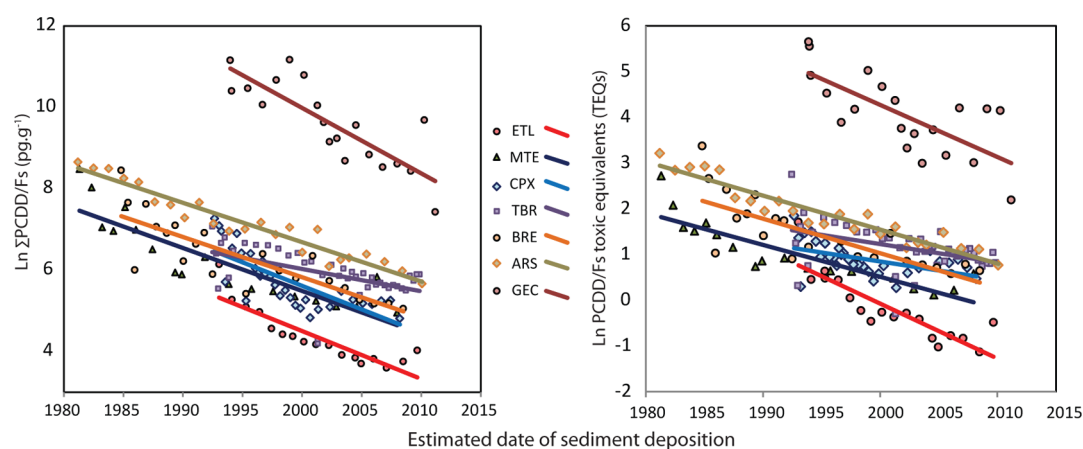
Congener patterns were evaluated using proportional concentrations of congeners. Because substitution techniques cannot denote actual values of censored data (nondetections), giving instead some distributional estimate, censored data were removed in a two-step process. First, the three most frequently censored congeners were removed: 123789-HexaCDF, 2378-TetraCDD, and 123478-HexaCDD (SI Table S-4). Second, 23 individual samples with one or more nondetections were removed, leaving 207 samples and 14 congeners. The site with the fewest remaining samples is ETL (17 samples), the most upstream site. Proportional congener concentrations were calculated and used to evaluate possible differences in congener distributions among sites and in relation to published congener profiles. Standardized proportional concentrations also were tested using principal components analysis (PCA), but the results did not add any information that could not be readily demonstrated using proportional concentrations and, thus, are not presented.

## RESULTS

Ten PCDF and seven PCDD congeners were analyzed in 230 samples. Concentrations of  $\sum$ PCDDs range over almost 5



**Figure 1.** Profiles of  $\Sigma$ PCDFs and  $\Sigma$ PCDDs in Rhone River sediment cores. Sediment coring site abbreviations are defined in SI Figure S-1.

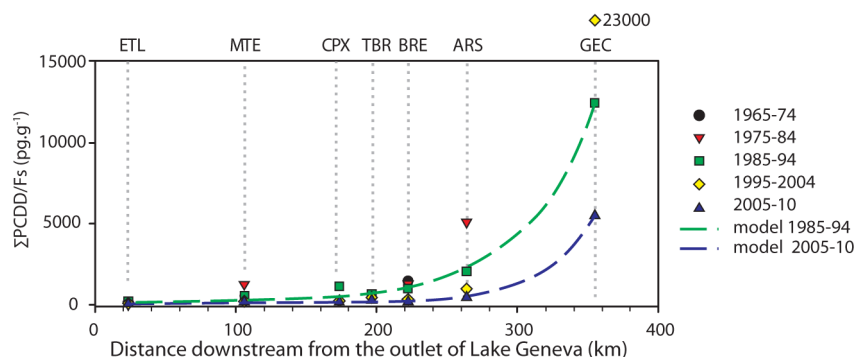


**Figure 2.** Natural logarithm transformed  $\Sigma$ PCDD/Fs concentrations and TEQs for the period following the peak concentration (see Figure 1) for sediment cores collected from seven sites on the Rhone River. Site abbreviations are defined in SI Figure S-1.

orders of magnitude, from  $<1$  to  $67\,200 \text{ pg g}^{-1}$  (dry weight), and concentrations of  $\Sigma$ PCDFs have a similarly large range, from  $<1$  to  $5820 \text{ pg g}^{-1}$  (SI Table S-3). The most upstream site (ETL) has the lowest detection frequency and concentrations and the most downstream site (GEC) has the highest detection frequency and concentrations (Figure 1; SI Table S-4). 1,2,3,7,8,9-HexaCDF is the least frequently detected congener

(overall nondetection frequency of 77%), followed by 2,3,7,8-TetraCDD. The percentile distributions of congener concentrations across all sites are summarized in SI Table S-5. The octa-congener had the highest concentrations for both PCDDs and PCDFs.

The most toxic congener to mammals and the largest contributor to TEQ, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin



**Figure 3.** Relation between distance downstream from the outlet of Lake Geneva and median  $\Sigma\text{PCDD}/\text{Fs}$  concentrations for selected time periods.

**Table 1. Results of Trend Test Using Kendall's Tau and Calculated  $t_{1/2}$  for  $\Sigma\text{PCDDs}$ ,  $\Sigma\text{PCDFs}$ , and  $\Sigma\text{PCDD}/\text{Fs}$  in Cores<sup>a</sup>**

site	period	n	trend (Kendall's tau)			$\Sigma\text{PCDDs}$		$\Sigma\text{PCDFs}$		$\Sigma\text{PCDD}/\text{F}$	
			$\Sigma\text{PCDDs}$	$\Sigma\text{PCDFs}$	$\Sigma\text{PCDD}/\text{Fs}$	Adj. $R^2$	$t_{1/2}$ ( $\pm$ std. error)	Adj. $R^2$	$t_{1/2}$ ( $\pm$ std. error)	Adj. $R^2$	$t_{1/2}$ ( $\pm$ std. error)
ETL	1993–2010	17	−0.87	−0.77	−0.87	0.76	5.8 (1.6)	0.76	6.6 (1.9)	0.77	5.9 (1.6)
MTE	1981–2008	19	−0.85	−0.78	−0.86	0.77	6.4 (1.7)	0.6	8.7 (3.5)	0.76	6.6 (1.8)
CPX	1993–2008	31	−0.71	−0.57	−0.70	0.6	5.7 (1.7)	0.4	10.9 (5.0)	0.59	6.0 (1.8)
TBR	1992–2010	41	−0.44	−0.47	−0.44	0.24	12.4 (7.2)	0.25	14.6 (8.2)	0.25	12.7 (7.2)
BRE	1985–2009	23	−0.73	−0.68	−0.74	0.69	6.9 (2.0)	0.59	8.1 (2.9)	0.69	7.0 (2.0)
ARS	1981–2010	24	−0.86	−0.88	−0.86	0.92	7.0 (0.84)	0.94	8.9 (0.9)	0.93	7.2 (0.8)
GEC	1994–2011	19	−0.68	−0.57	−0.67	0.69	4.2 (1.3)	0.42	5.8 (3.3)	0.68	4.3 (1.6)

<sup>a</sup>Periods tested are the time of peak concentration to the top of the core (Figure 1) and all regressions are significant at p-value <0.005. Sites are listed in downstream order.

(TCDD), was detected in 69% of samples; at five of the seven coring sites it was detected in more than 85% of samples. TEQ<sub>31</sub> ranged from <1 (24 of 33 samples from ETL) to 284 in a sample deposited about 1994 at GEC (SI Table S-6). The maximum concentration measured ( $\Sigma\text{PCDD}/\text{Fs}$  = 1680 pg g<sup>−1</sup>) and corresponding TEQ ( $\Sigma\text{PCDD}/\text{Fs}$  TEQ = 8.93) in the most recently deposited sediment also were at GEC. Spatial and temporal patterns in concentrations of TCDD and  $\Sigma\text{PCDD}/\text{Fs}$  and of TEQs are similar (Figure 2). Although concentrations and TEQs increase in the downstream direction across all sites, the change between ARS and GEC, the two most downstream sites, is much larger than the changes between other sites (Figures 2 and 3).

**PCDD/F Trends.** Concentrations peak between 1980 and 1985 in the three cores that extend back in time to at least the 1970s (Figure 1; MTE, BRE, ARS). In the other four cores, maximum concentrations occur near the bottom of the core, in the early 1990s (CPX, TBR) or in the 1990s but where deeper samples in the core predate a change in depositional setting (ETL, GEC). It is unclear whether the sediments deposited in ETL and GEC before and after this change are recording contaminant occurrence in the Rhone River comparably, thus, we limited trend testing to the period after the change in setting (Figure 1). Superimposed on long-term decreases in concentrations are short-term variations (secondary peaks and valleys) and, at three sites, modest increases in the uppermost sediment layers: at sites ETL and TBR, both PCDDs and PCDFs, and at site MTE, PCDFs. At sites ETL and TBR, recent increases in concentrations are associated with increases (about 0.5–1.0%) in organic carbon content at the top of the core.

Concentrations of  $\Sigma\text{PCDDs}$  and  $\Sigma\text{PCDF}$  decreased systematically over time at all seven sites after the 1980s or 1990s maxima (Figure 1). The nonparametric Kendall's tau test for monotonic trend was applied to  $\Sigma\text{PCDD}$ ,  $\Sigma\text{PCDF}$ , and

$\Sigma\text{PCDD}/\text{F}$  concentrations beginning at the date of peak concentration for the seven cores; all of the trends were downward and significant with all p-values less than 0.005 (Table 1). Normalization to organic carbon ( $\Sigma\text{PCDD}/\text{F}$  divided by percent organic carbon) yielded similar results, with significant Kendall's tau in all cases and stronger correlations in all but one case (GEC). To evaluate the rate of change in concentrations, log-transformed  $\Sigma\text{PCDD}$ ,  $\Sigma\text{PCDF}$ , and  $\Sigma\text{PCDD}/\text{F}$  concentrations were regressed against date in each core (Figure 2). The slope of each regression line was used to estimate  $t_{1/2}$  for the  $\Sigma\text{PCDD}$ ,  $\Sigma\text{PCDF}$ , and  $\Sigma\text{PCDD}/\text{F}$  concentrations in each core and all of the relations were significant (Table 1). The  $t_{1/2}$  are similar for most of the cores, with an overall mean of 8.0 y. The  $t_{1/2}$  for  $\Sigma\text{PCDDs}$  range from 4.2 to 12.4 years (mean  $6.9 \pm 2.6$  years) and for  $\Sigma\text{PCDFs}$  range from 5.8 to 14.6 years (mean  $9.1 \pm 2.9$  years). The regression equations were used to estimate the percent decreases in concentrations for a common time period for the coring sites; 1992–2010 was chosen because it coincides approximately with the period of monotonic decrease recorded in all of the cores (Figure 1) and with the adoption of the fifth European Community Program of policy and action on the environment in 1993.<sup>9</sup> The regression equations smooth out short-term variations in the concentration profiles. The mean percent decreases over the 18-year period in  $\Sigma\text{PCDDs}$ ,  $\Sigma\text{PCDFs}$ , and  $\Sigma\text{PCDD}/\text{Fs}$  were  $84 \pm 9.9\%$ ,  $76 \pm 10\%$ , and  $83 \pm 10\%$ , respectively (SI Table S-6). The largest percent decrease was at GEC, where  $\Sigma\text{PCDD}/\text{Fs}$  decreased by 94%.

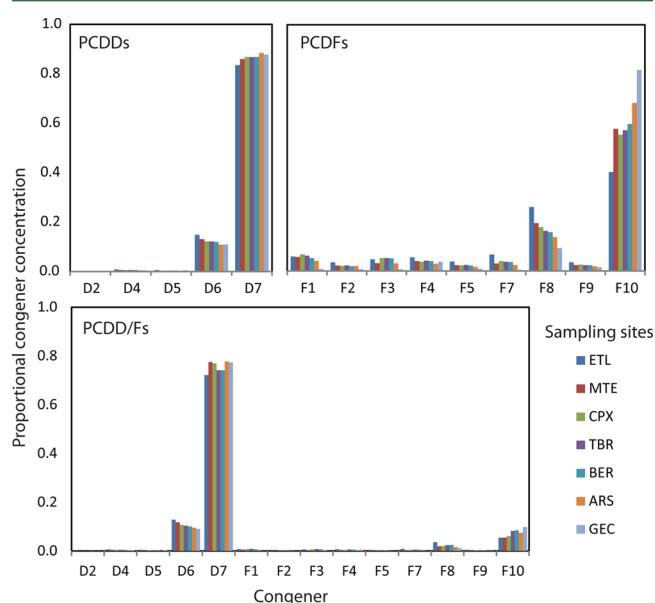
Median concentrations of  $\Sigma\text{PCDDs}$  and  $\Sigma\text{PCDFs}$  for each of five periods (1965–1974, 1975–1984, 1985–1994; 1995–2004; and 2005 to top of core) increase systematically in the downstream direction. Exponential models fit to median values of  $\Sigma\text{PCDDs}$  and  $\Sigma\text{PCDFs}$  for two of these multiyear periods and distance downstream from Lake Geneva indicate two

superimposed gradients (Figure 3): an upstream-downstream increase in concentrations during each decadal time period and a decrease in concentrations over time across the river basin. Models are of the form:

$$y = a \times e^{bx} \quad (1)$$

where  $x$  is the distance from Lake Geneva outlet and  $y$  is the median  $\Sigma$ PCDD/Fs for the period. For the period 1985–1994, adj.  $R^2 = 0.992$  ( $p$ -value  $< 0.0001$ ;  $a = 13.1 \pm 6.58$ ;  $b = 0.019 \pm 0.001$ ). For the post 2004 period, adj.  $R^2 = 0.996$  ( $p$ -value  $< 0.0001$ ;  $a = 0.38 \pm 0.33$ ;  $b = 0.027 \pm 0.002$ ). A model was not fit to the 1995–2004 period because site GEC had anomalously high concentrations during this period. Data for the 1967–1975 and 1976–1985 time windows were not modeled as data were not available for several of the sites.

**Congener Profiles.** Profile analyses were done on the basis of proportional concentrations in the 207 samples in which nine PCDFs and five PCDDs were detected in all samples. PCDD and PCDF congener distributions are dominated, in order of magnitude, by octaCDD, 1234678-HeptaCDD, octaCDF, and 1234678-HeptaCDF (Figure 4). These four



**Figure 4.** Proportional concentrations of congeners relative to the sum of PCDDs, PCDFs, and PCDD/Fs. Site abbreviations are defined in SI Figure S-1. Congener abbreviations are defined in SI Table S-2.

compounds account for  $96 \pm 2.7\%$  of  $\Sigma$ PCDD/F mass considering these 14 frequently detected congeners. The mean ratio of  $\Sigma$ PCDDs to  $\Sigma$ PCDFs is  $8.2 \pm 3.6$ . The distribution of PCDF congeners among sites indicates a small but systematic shift in assemblage in the downstream direction, with increasing dominance of octaCDF (Figure 4). At the most upstream site (ETL) octaCDF is 40% of  $\Sigma$ PCDFs, increasing to 55–60% in the next four sites downstream (MTE, CPX, TBR, and BER), 68% at ARS, and 82% at GEC. A similar but less pronounced shift is indicated for PCDD congeners.

## DISCUSSION

Downward trends in  $\Sigma$ PCDD/Fs and TEQs in the Rhone River from downstream from Lake Geneva almost to the Mediterranean Sea provide evidence of the success of emissions reductions targeting these compounds. Concentrations of

PCDDs and PCDFs decreased systematically beginning in the 1980s and 1990s at the seven sampling locations, which represent most of the French part of the Rhone River basin. Peak dioxin concentrations in the Rhone River occur in the early 1980s in the three cores that extend far enough back in time to be confident of having recorded the peak. The peaks occur later than those of some other European and North American water bodies, generally reported as being in the 1960s–1970s.<sup>18,19,21</sup> Peaks in the Rhone River cores in the 1980s are in reasonable agreement, however, with dates reported for Baltic Sea cores, where the peak in offshore cores was dated  $1991 \pm 7$  years.<sup>23</sup> The 16-year time lag observed for peak dates between offshore and near-shore cores from the Baltic Sea was attributed to lateral diffusion of particles from the coast to offshore areas.

**PCDD/F Sources.** The pronounced increase in concentrations in the downstream direction indicates local emissions and releases within the basin. The much larger concentrations and TEQs at GEC than at upstream sites indicate inputs from industrial and urban areas along the Rhone River and its tributaries downstream from site ARS, the next site upstream (Figure 3 and SI Figure S-1). Potential local sources of PCDD/Fs were identified by matching typical source lists<sup>1,18</sup> and the French contaminated sites inventory,<sup>33</sup> which tracks the industrial history of the country. Electric arc furnace steel manufacturing, a well-documented source of dioxins and furans,<sup>34</sup> was strongly developed in the watershed of the Isere River, which flows into the Rhone River upstream of site GEC and downstream of site ARS. Numerous other industrial activities (e.g., metallurgy, chemical production) identified as historical sources of dioxins<sup>7,35</sup> were present in the Isere watershed in the past, including a plant that produced the herbicide 2,4-D (also known as Agent Orange) at an industrial center at Pont-de-Claix near Grenoble,<sup>33</sup> 2,4-D is a well-known source of TCDD.<sup>2</sup>

Comparison of congener profiles in the cores with congener profiles reported in the literature indicates that the Rhone sediments are similar to bulk atmospheric deposition,<sup>36–38</sup> sediments from a wide variety of settings,<sup>6,19,21</sup> and pentachlorophenol (PCP) related sources<sup>39</sup> (SI Figures S-2 and S-3). Sundqvist et al. (2010) concluded that the atmospheric-deposition profile is indicative of global background air and not recent regional emissions. The dominance of hepta- and octa-CDD/Fs in atmospheric profiles has been attributed to “weathering” effects caused by the loss of the lower molecular weight congeners (tetra-, penta-, and hexa-CDD/Fs) from particle phases by volatilization followed by photochemical reaction.<sup>38</sup> The vapor pressure for tetra-CDD/Fs is 5–6 orders for magnitude higher than those for OCDD and OCDF.<sup>40</sup> The Rhone River core profiles do not indicate recent emissions from thermal industrial processes, which have more complex profiles dominated by tetra-, penta-, and hexa-CDD/Fs.<sup>41</sup>

The PCDD/F congener profiles in the Rhone cores (Figure 4) are generally similar to congener profiles reported for many lake and stream sediments, including, for example, from western Ireland<sup>42</sup> (SI Figure S-2), Switzerland,<sup>21</sup> China,<sup>43</sup> the United States,<sup>44</sup> and the Yser and Upper-Scheldt Rivers in northern France and Belgium.<sup>45</sup> The OCDD congener represented 73 to 85% of the total PCDD/F concentration in four representative samples each from the Yser and Upper-Scheldt Rivers,<sup>45</sup> whereas in the Rhone cores, the means for the seven sites ranged from 72 to 78%. The PCDD/F congener

profiles in the Rhone cores also are very similar to congener profiles for several technical-grade PCP products (SI Figure S-3) and there is at least some evidence of historical PCP production in the Rhone basin near Lyon.<sup>46</sup> We therefore conclude that the PCDD/Fs in Rhone sediments are from diffuse regional sources and historical industrial and wastewater sources in the watershed. We further conclude that the large increase in concentrations and TEQs at GEC relative to the upstream sites indicates substantial historical inputs of PCDD/Fs to the Rhone downstream from site ARS (SI Figure S-1).

**Rates of Decrease.** The rates of decrease in concentrations of  $\Sigma$ PCDDs,  $\Sigma$ PCDFs, and  $\Sigma$ PCDD/Fs (Table 1) are rapid relative to those reported for more remote areas of Europe, yet comparable to some reported for urban settings. A typical  $t_{1/2}$  of 30 years for  $\Sigma$ PCDD/Fs in remote areas was cited by ref 23, and a  $t_{1/2}$  of 9 years was reported for an urban lake sediment core near Zürich, Switzerland.<sup>21</sup> This difference was explained by ref 23 by slower diffusion processes in remote areas, which involve long-range atmospheric deposition and redistribution processes. Concentrations in air and deposition fluxes of PCDD/Fs in ambient air in northwestern Germany decreased by a factor of 5 or more from 1988 to about 2005 but have leveled out since then; half-lives were estimated to be on the order of 5–15 years.<sup>47</sup> The relatively rapid decreases in the Rhone River cores (mean  $t_{1/2}$  for  $\Sigma$ PCDD/Fs of 7.1 y) suggest that the system is responding on the time scale of sites with local urban and industrial influences.

The  $t_{1/2}$  in the Rhone River cores are similar to or smaller than those for particle-associated contaminants (Cs, PCBs, DDT) reported for sediment cores from 11 reservoirs from the central and eastern U.S., which had a median  $t_{1/2}$  value of 9.8 years and an interquartile range of 5.0 years, generally during the 1970s–1990s.<sup>48</sup> Similarity of  $t_{1/2}$  values among contaminants was explained by a combination of factors, including similar distribution in the environment, similar fate (adsorption to particles and resistance to degradation), and similar use histories (concomitant release and ban). Land-use factors, such as differences in soil erosion rates, might explain some of the spatial variability in  $t_{1/2}$  for persistent organic contaminants.<sup>49</sup>

**Deposition Patterns.** Temporal profiles suggest that PCDD/Fs in Rhone River sediments at most of the sites sampled here are affected by sediment deposition patterns associated with flooding and river-management operations. Concentrations in sediments deposited before 1990 at ETL and before 1984 at BRE were not tested for trends because they predate cessation of quarrying activity at ETL and removal of debris that established a connection to the Rhône at the upper end of the secondary channel at BRE.<sup>28</sup> Deeper samples in both cores were assumed not to represent the same depositional conditions as more recent samples. Some short-term variations in PCDD/F profiles observed at CPX and TBR sites correspond to the timing of major flood events that occurred in the early 1990s and 2000s, indicated in part by increased sand content in some layers in the cores.<sup>29</sup> The shortest  $t_{1/2}$  are observed at sites ETL and GEC (5.9 and 4.5 years, respectively, for  $\Sigma$ PCDD/Fs). Both sites are influenced by intentional sediment flushes, from the dam system on the Arve and Rhone Rivers for ETL,<sup>50</sup> and from hydropower dams<sup>51</sup> on the Isere River for GEC.<sup>52</sup> Sediment flushes from the Isere River affect sediment deposition at GEC and might explain the large variations in PCDD/F concentrations at this site through time and rapid decrease in concentrations compared to other sites. At site BRE, which is subject to periodic flooding from the

Rhone River, the variations in the dioxin and grain-size profiles are quite similar (SI Table S-3). Conversely, the smooth profiles at site ARS for dioxins (Figure 1) and small variation in grain-size distribution<sup>29</sup> are a consequence of steady input of river water, resulting from the connection of the sampling site to the Rhone River at its downstream end only.

Are rapid decreases in dioxins a consequence of emission reduction policies? The systematic decrease in dioxin concentrations in the Rhone cores is temporally consistent with the implementation of emissions controls in France and across Europe. Atmospheric emissions of dioxins in France began to decline around 1992–1993,<sup>53</sup> concomitant with the regulation of domestic waste incinerators handling more than 6 tons per year.<sup>54</sup> For iron ore sintering and municipal solid waste incineration, which are the most important sources of emissions to the atmosphere, the European Dioxin Air Emission Inventory<sup>35</sup> estimated that a decrease of about 90% from the 1987 estimated level was achieved in 2000–2005. Other industrial and nonindustrial sources showed variable rates of decrease, somewhat below the targeted 90% threshold. A recent study of trends in atmospheric contamination by PCDD/Fs using lichens in Portugal reported a 70% decrease in PCDD/F concentrations from 2000 to 2009–2011.<sup>55</sup> Reductions in the cores from 1992 to 2010 for  $\Sigma$ PCDD/Fs average 83%, similar to the European target and to the reductions achieved.

The rapid and substantial decreases in dioxin concentrations and TEQs suggest that risks contributed by dioxins in fish have been greatly reduced during the past two decades in the Rhone River basin. Dioxins are known to exert adverse effects on top predators through biomagnification in food-webs,<sup>4,56</sup> however, PCDD/Fs represent less than 10% of the overall dioxin TEQ in Rhone River fish,<sup>57,30,31</sup> with most of the TEQ caused by dioxin-like PCBs.<sup>58</sup> PCB concentrations also are decreasing in the Rhone River basin, but trends in PCBs tend to be much more variable than trends in dioxins at these seven coring locations.<sup>28,29</sup> Dioxins were recently added to the WFD priority substances list.<sup>59</sup> Member States will thus have to determine the status of water bodies by comparing monitoring data to environmental quality standards for dioxins, and to evaluate temporal trends. The rapid decreases in concentrations of dioxins and associated diminishing risks across a large basin like the Rhone River might mean that continued trend monitoring at a few sites in the watershed will be a sufficient management response.

## ■ ASSOCIATED CONTENT

### ● Supporting Information

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

## Notes

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## ABBREVIATIONS

PCDD	polychlorodibenzodioxin
PCDF	polychlorodibenzofuran
EQS	Environmental Quality Standard
WFD	Water Framework Directive
ND	nondetect
AHC	agglomerative hierarchical clustering
$t_{1/2}$	time for a 50% reduction of the measured concentration sense

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