

## CONCENTRATIONS OF PERSISTANT ORGANIC POLLUTANTS IN AMBIENT AIR IN DURBAN, SOUTH AFRICA

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### Introduction

Concentrations of persistent organic pollutants (POPs) have been rarely measured in urban Africa communities. Combustion processes can generate many POPs, e.g., polychlorinated dibenzodioxins (PCDDs), polychlorinated dibenzofurans (PCDFs) and polychlorinated biphenyls (PCBs), and atmospheric transport is often the primary route of transporting these contaminants into the environment. For airborne PCDDs, recent inventories show that the largest single category contributor of emissions is uncontrolled combustion processes, e.g., biomass burning (forest, grassland, crop residue), waste burning, and accidental domestic/industrial fires.<sup>1</sup> Given that uncontrolled burning is prevalent throughout much of Africa, the lack of measurements is significant, and it is likely that measurements conducted elsewhere have limited applicability.

This paper reports on an extensive ambient air quality monitoring program in Durban (eThekweni Municipality), South Africa, on Africa's southeast coast. Following a multistakeholder process coordinated by the Municipality Metropolitan Health authority, a program was undertaken that included measurements of both conventional and toxic pollutants at multiple sites to support health risk assessment and epidemiological studies. Durban is the largest urban and industrial area in KwaZulu Natal Province, which has a population of approximately 4 million. The monitoring program focused on the Durban South Industrial Basin (SDIB), an area with one of the highest concentrations of industrial activity in Africa containing, for example, two large petroleum refineries, a paper mill, an international airport, large chemical tank farm, landfill sites, incinerators, processing and manufacturing industries, major trucking, harbor and rail facilities, and other industry. Residential and recreational areas are intermingled with industry, with approximately 200,000 people living in 25 designated "suburbs", most of which remain racially segregated. Monitoring sites outside the DSIB were also included. Here we present ambient concentrations and spatial gradients of PCDD, PCDF and PCBs, compare concentrations and toxicities in Durban with levels measured elsewhere, and examine the influence of potential source areas using trajectory analyses.

### Materials and Methods

Monitoring was conducted for POPs in both gaseous and particulate phases at three sites: Nizam in the southern part of the SDIB; Wentworth in the central portion of the SDIB; and Ferndale in an urban community located ~20 km north. Durban's central business district lies between these areas. We report on 15 to 20 sampling events at each of the three sites conducted over the period from August 2004 to September 2005. At each site, a high volume air sampler (TE-1000, Tisch Environmental) captured particulate matter on quartz microfiber filters (102 mm dia, Whatman International Ltd, QMA-4 filters) and vapor phase pollutants on polyurethane foam plugs (75 mm dia, SKC). Sampling periods were generally 24 hr, although a few longer samples were taken, and the average sample volume was ~300 m<sup>3</sup>. All sampling and shipping materials were certified clean prior to deployment. In the field, filters and PUF plugs were spiked with surrogates to determine any matrix effects and recoveries. After sampling, samples were shipped to our Michigan laboratory, refrigerated, and analyzed for a subset of compounds, including those considered to be toxic. Filters and PUF plugs were Soxhlet extracted for 36 h; cleaned and fractionated. Each sample was analyzed by GC/MS using a fused silica capillary column (30-mDB-5), selected ion monitoring (SIM), and negative chemical ionization.<sup>2,3,4</sup> All solvents and other materials contacting samples were clean, as confirmed using blank checks. Separate sample preparations and GC/MS runs were performed for PCDD/PCDF,

PCBs, PAHs, persistent and currently used pesticides, and brominated flame retardants, and for particulate and vapor phases. Results presented here combine particulate and vapor phase concentrations for PCDDs, PCDFs and PCBs, and are expressed as concentrations in air and as toxic equivalents (TEQs) of 2,3,7,8-TCDD. Quality assurance activities included interlaboratory comparison of split samples and standards, blanks, spike recovery, surrogate recovery, and collocation studies. Several blanks showed a few PCB congeners at concentrations close to MDLs, but only congeners that were neither toxic nor used in TEQ calculations (i.e., PCBs 74, 84, 149, 118). Spike recovery tests were acceptable (recovery from 80 to 101%). Surrogate recovery tests performed on each sample were acceptable (75 to 110%).

**Results and Discussion**

Fig. 1 contrasts total (sum of vapor and particulate fractions) PCDD concentrations in TEQs at the three sites. Average levels of PCDFs at the sites were fairly uniform, within about 50%, and the Wentworth site tended to have the highest concentrations of most congeners. PCDDs showed somewhat greater site-to-site variation, and Nizam had the highest levels of most congeners. PCDFs Hx234678 and Pe23478 contributed the most toxicity in the collected samples. All of the PCDDs and PCDFs were found predominantly in the particulate phase. In contrast, PCBs were found predominantly in the vapor phase, and the highest levels were found at the central Wentworth site.

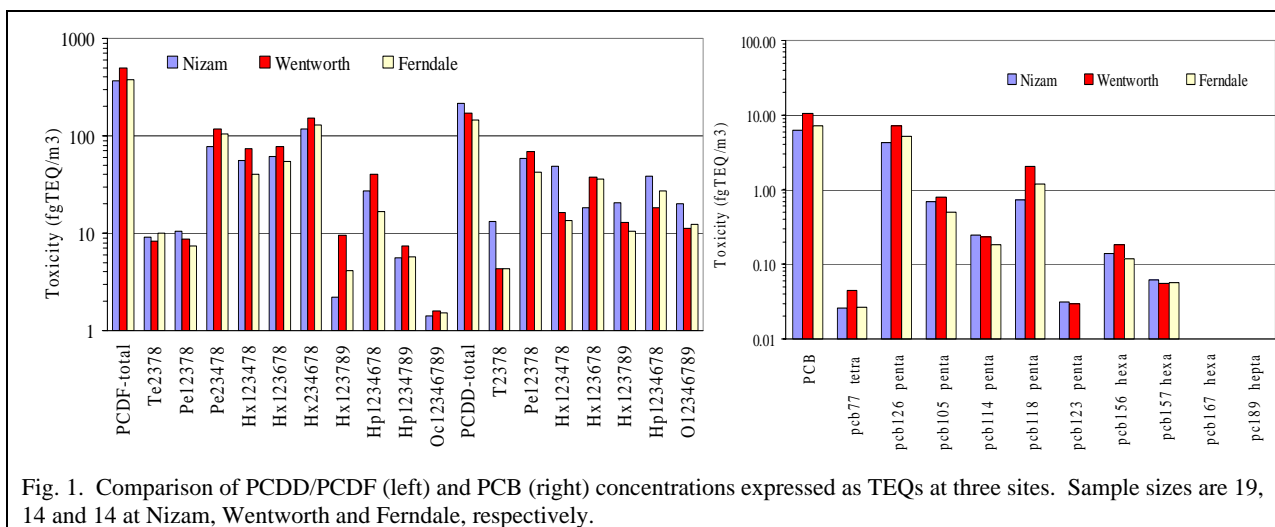


Fig. 1. Comparison of PCDD/PCDF (left) and PCB (right) concentrations expressed as TEQs at three sites. Sample sizes are 19, 14 and 14 at Nizam, Wentworth and Ferndale, respectively.

Fig. 2 compares PCDD/PCDF toxicity (sum of TEQs for all toxic congeners) in Durban to levels in fairly recent studies in New Zealand,<sup>5</sup> US National Parks (US National Dioxin Air Monitoring Network, US NDAMN),<sup>6</sup> Slovakia,<sup>7</sup> Spain,<sup>8</sup> and Japan.<sup>9</sup> PCDD/PCDF TEQ levels in Durban, which averaged 605 (range from 213 – 1465) TEQ fg m<sup>-3</sup>, exceeded levels reported elsewhere with the exception of a 1995 study in Krakow, Poland where PCDD/PCDF concentrations ranged from 950 to 12,000 TEQ fg m<sup>-3</sup> (no average available).<sup>10</sup> PCDD/PCDF levels can be highly elevated – by roughly 5 to 30 times or more – in urban/industrial area as compared to rural areas. PCDD/PCDF toxicity in Durban averaged 41 times higher than in the rural US, using one of the larger studies available, the year 2000 NDAMN data, which represents 13 measurements in 18 rural areas.<sup>6</sup> Fewer studies are available for PCBs. Again using the year 2000 US NDAMN (13 measurements in 18 rural areas), a mean of 1.1 (range from 0.2 to 9.9) TEQ fg m<sup>-3</sup> is reported for the toxic PCBs. In comparison, Durban levels averaged 8.7 (range from 2.1 to 28.9) TEQ fg m<sup>-3</sup>, or 8 times higher. Thus, PCB concentrations in Durban appear relatively less elevated than the dioxin/furan levels. The lower concentrations, vapor phase composition, and small degree of spatial variation across the three monitoring sites suggest the importance of long range transport for PCBs.

Fig. 3 contrasts average levels of the POPs in Durban to levels in the rural US (NDAMN data). Within each class, similar distributions are seen, e.g., the most prevalent dioxin congeners are penta-12378 hexa-123678, and hepta-1234678. However, PCDF levels in Durban are ~126 times higher than those in the rural US, PCDDs are ~33 times higher, and PCBs are ~18 times higher. (Unlike the previous analysis that used TEQs, here we use concentrations directly, and ratios are based on the regression line.) The elevated PCDF levels suggest local sources.

Meteorology in Durban involves the semi-permanent south Atlantic and south Indian high pressure cells that dominate circulation and cause lows with unstable conditions in the summer and persistent highs in the winter, often with light winds and inversions that are unfavorable to pollutant dispersion. During these periods, however, the temperate control system produces frequent traveling low pressure systems associated with fronts, moderate winds and precipitation. Local influences include katabatic, valley and slope wind systems that develop inland (~150 km distant) near the Drakensberg Mountains, and local coastal ridges and valley systems that affect air flows, including diurnal shore/breezes. Air quality can change dramatically when either clean or polluted air is brought into the basin.

To examine possible source regions, the NOAA Hysplit model was used to simulate 3-day back trajectories every 4 h during each of the 24-h sampling periods, i.e., a 6 back trajectories were computed for sampling event. These trajectories used the central Wentworth monitoring station (trajectories at other sites were largely indistinguishable) and receptor heights of 10 and 1000 m. The percentage of time that each trajectory was inland or over the ocean was determined and used to weight concentrations to help separate local and regional sources. Simulations for two days representing two “classes” of trajectories are depicted in Fig. 4. On September 4, 2004, winds arrived from the mid-Indian Ocean, though some air is first swept over Durban and then returned back. Generally, such mid-ocean trajectories represent air masses that are expected to reflect less influence from local sources and more influence from regional and/or distant sources, e.g., India and Asia. Of course, many trajectories can terminate at the monitor over the 24-hr sampling period, including those that may reflect local emissions; moreover, the monitoring sites are several km inland, thus even a “pure” ocean trajectory will reflect local sources. Nonetheless, trajectories with mid-ocean origins (like Sept. 4, 2004) lowered concentrations of PCDDs and PCDFs by 24% and 14%, respectively, from average levels; reductions of PCBs were larger, 30%. Trajectories from the

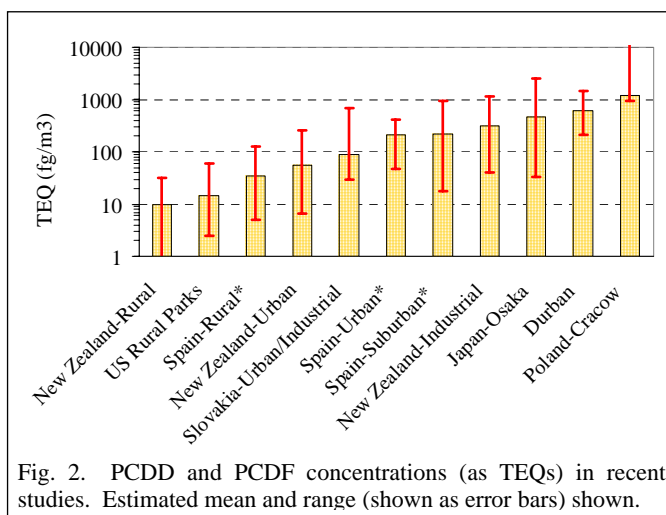


Fig. 2. PCDD and PCDF concentrations (as TEQs) in recent studies. Estimated mean and range (shown as error bars) shown.

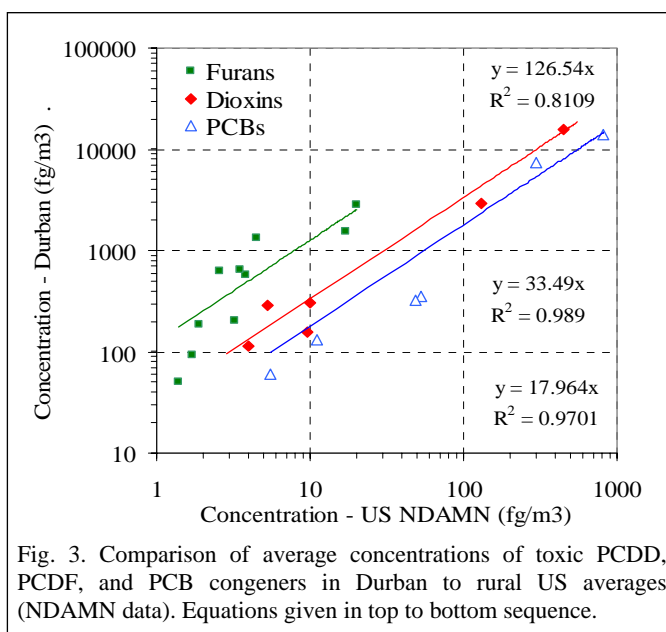


Fig. 3. Comparison of average concentrations of toxic PCDD, PCDF, and PCB congeners in Durban to rural US averages (NDAMN data). Equations given in top to bottom sequence.

## Environmental transport and deposition

southern Indian Ocean were associated with a 30% drop in  $PM_{10}$  levels. Interestingly, trajectories from the north Indian Ocean did not alter  $PM_{10}$  levels, showing limits of this analysis. Trajectories with ocean origins also increased levels of many persistent pesticides, suggesting different sources.

The lower panel in Fig. 4 shows a contrasting trajectory pattern for July 14, 2005. Such wintertime periods are often associated with poor air quality. The terrestrial origin and recirculation shown in the trajectory, coupled with extensive burning of fields to both the west and north of Durban, and frequent inversions occurring in the winter, would be expected to increase pollutant levels. Such continental trajectories were associated with PCDD and PCDF concentrations that increased by 26 and 15%, respectively. As before, a larger change was seen for PCBs, which increased by 39% during such periods.  $PM_{10}$  levels increased by 15% with such trajectories, and by 46% for trajectories from the west and north, suggesting the influence of agricultural burning.

While diet (especially meat, dairy products and fish) is the main source of human exposure to PCDDs, PCDFs and PCBs for most individuals, the elevated concentrations measured in Durban are indicative of strong sources that require identification and characterization.

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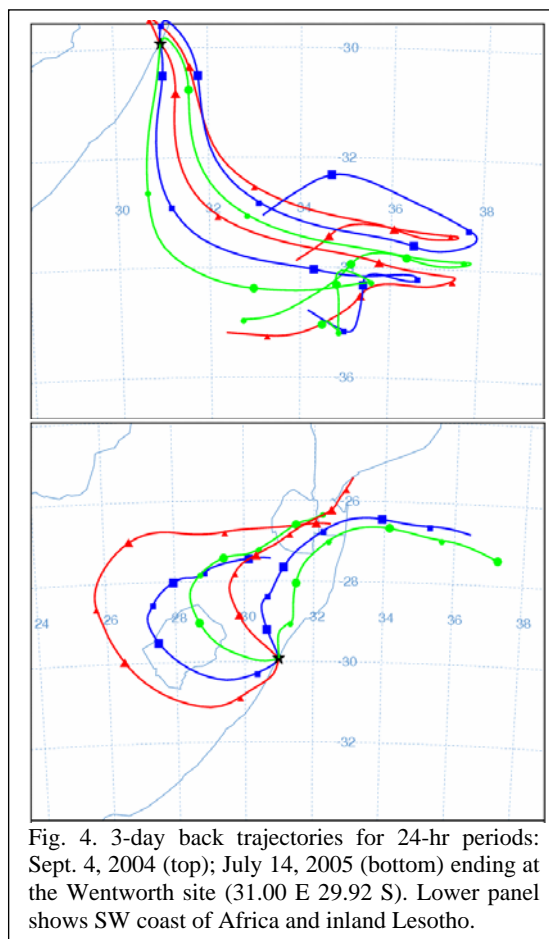


Fig. 4. 3-day back trajectories for 24-hr periods: Sept. 4, 2004 (top); July 14, 2005 (bottom) ending at the Wentworth site (31.00 E 29.92 S). Lower panel shows SW coast of Africa and inland Lesotho.

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