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Source Apportionment of Airborne Dioxins, Furans and Polycyclic Aromatic Hydrocarbons at A U.S. Forward Operating Air Base During the Iraq War

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ABSTRACT

Objectives: The objective was to apportion the sources of the ambient polycyclic aromatic hydrocarbon (PAH), polychlorinated dibenzo-p-dioxin (PCDD) and polychlorinated dibenzofuran concentrations measured at Joint Base Balad in Iraq.

Methods: Positive Matrix Factorization (PMF) was applied to the data to obtain the chemical profiles and contribution time series of the PAHs, PCDDs, and PCDFs. Conditional probability function (CPF) analyses were performed to assess the source directionality relative to the monitoring sites.

Results: Three source types were identified and apportioned. The sources were: the burn pit, diesel vehicles and generators, and aircraft emissions. The CPF plots were consistent with the assigned source types.

Conclusions: The PCDDs and PCDFs originated primarily from the burn pit. Higher molecular weight PAHs were associated with vehicle emissions while the aircraft emissions were enriched in low molecular weight PAHs.

Keywords: burn pit, dioxins, furans, particulate matter, polycyclic aromatic hydrocarbons
During the last decades, atmospheric pollution has received increasingly interest because of its effects upon human health\textsuperscript{1,2} and climate.\textsuperscript{3} Combustion is recognized as a major source having significant impacts on air quality at local, regional, and even global scales.\textsuperscript{4} Among the various combustion processes, unenclosed combustion of various materials, termed “open burning,” typically has higher emission factors (mass pollutant per mass fuel) than other well-controlled combustion sources, e.g., mobile and industrial sources.\textsuperscript{5} The differences in the emissions are due to the high variability of burned materials and to the suboptimal burning conditions that favor smoldering combustion. Thus, there is the release of large amount of soot, unburned byproducts and aerosolized materials into the atmosphere. In addition, open burning may emit higher amounts of many toxic pollutants, such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated dibenzo-dioxins (PCDDs) and -furans (PCDFs).\textsuperscript{6}

During the deployment to war zones, the US Department of Defense (DoD) has estimated that about 3.6—4.5 kg day\textsuperscript{−1} of waste are typically produced by a soldier at forward operating bases.\textsuperscript{7} However, during wartime, conventional waste-disposal options such as incinerators and landfills are generally unavailable at operating bases for a number of logistic, safety, strategic and practical reasons. Thus, large amounts of waste produced on bases need to be disposed of in unconventional ways. During the recent Iraqi and Afghanistan conflicts, the most common practice was the use of open-air, burn-pits (BPs), where the solid waste was set in piles, rows, or holes in the ground and simply ignited with fuels (e.g., jet fuel) as ignition accelerant. Since BPs may generate large quantities of hazardous airborne pollutants and are generally set along the base perimeter, this practice has potential harmful effects on military personnel and people living in the area surrounding the base.
This study aims to identify, quantify, and localize the most probable sources of airborne hazardous pollutants at the Joint Base Balad (JBB), Iraq, during the Iraqi War. The daily levels of total airborne (particulate + gaseous phase) polychlorinated dibenzo-dioxins (PCDDs), -furans (PCDFs) and polycyclic aromatic hydrocarbons (PAHs) were quantified at JBB in 2007. Raw data and some preliminary analyses are presented in a companion paper,\(^8\) along with an analysis of the potential exposure of military personnel and maps of concentrations. Here, several receptor modeling methods were applied to the data. Positive matrix factorization (PMF) was used to identify and apportion the most probable potential sources of the measured toxic air pollutants, while the conditional probability function (CPF) was applied to PMF factors to localize the potential sources with respect the wind directions.

**METHODS**

**Study Area**

During the Iraqi War, JBB (33.95 N; 44.35 E; 50 m. a.s.l.) formerly called Logistics Support Activity (LSA) Anaconda), was the second largest U.S. Base in Iraq (~25 km\(^2\)-wide, ~25,000 military, civilian, contractors and coalition personnel) and hosted the largest operating burn-pit on any U.S. base (up to 200 tons per day in 2007).\(^9\) JBB waste was a heterogeneous mixture of various materials, including food waste, plastic (e.g., bottles, styrofoam trays, meals-ready-to-eat packages, rubber), human waste, shipping and packaging materials, wood (e.g., treated and untreated pallets), chemicals (paints, solvents), oil, grease, petroleum, and metal/aluminum items (e.g., cans, wires), and was ignited with jet fuel JP-8. In addition, electronics, tires, batteries, medical waste and expired pharmaceuticals were also occasionally burned.\(^7\)
Experimental Methods

A sampling campaign was carried out in 2007 at five sampling sites on JBB shown in Figure 1. Sites were selected to be representative of various base areas with differing activities: (i) mortar pit (MP) was selected as a “background” site because it was frequently upwind of the BP emissions; (ii) guard tower (GT) was a location outside the base perimeter and downwind of BP during prevailing wind regimes; (iii) transportation field (TF) was located at a site close to BP but also potentially affected by emissions from diesel-powered heavy trucks. There was also a helipad between the TF and BP where helicopters would land and take-off. The last two sites were placed near “living areas” in JBB: (iv) H-6 housing (H6) and (v) contingency aeromedical staging facility (CASF, CA). Sampling and analytical procedures were summarized elsewhere, and generally followed US-EPA TO-9A and TO-13A methods. Briefly, samples were collected using high volume samplers equipped with quartz fiber pre-filters as media to collect particles with aerodynamic diameter less than 10 µm (PM$_{10}$) and XAD-2 polymeric adsorbent foam plugs to retain the gaseous compounds. Filters and foam cartridges were then extracted together using mixtures of organic solvents and analyzed by GC-MS techniques to quantify the concentrations of total (gaseous + particulate phases) PCDDs, PCDFs and PAHs. Target compounds included 17 PAHs, naphthalene (NAP), acenaphthylene (ACY), acenaphthene (ACE), fluorene (FLU), phenanthrene (PHE), anthracene (ANT), fluoranthene (FLT), pyrene (PYR), benz[a]anthracene (BaA), chrysene (CHR), benzo[b]fluoranthene (BbF), benzo[k]fluoranthene (BkF), benzo[a]pyrene (BaP), benzo[e]pyrene (BeP), indeno[1,2,3-cd]pyrene (IP), dibenz[a,h]anthracene (DBahA), benzo[g,h,i]perylene (BghiP), 7 dioxins, 1,2,3,4,6,7,8-HeptaCDD, 1,2,3,4,7,8-HexaCDD, 1,2,3,6,7,8-HexaCDD, 1,2,3,7,8,9-HexaCDD, 1,2,3,7,8-PentaCDD, 2,3,7,8-TetraCDD, OctaCDD, and 10 furans, 1,2,3,4,6,7,8-HeptaCDF, 1,2,3,4,7,8,9-
HeptaCDF, 1,2,3,4,7,8-HexaCDF, 1,2,3,6,7,8-HexaCDF, 1,2,3,7,8,9-HexaCDF, 1,2,3,7,8-PentaCDF, 2,3,4,6,7,8-HexaCDF, 2,3,4,7,8-PentaCDF, 2,3,7,8-TetraCDF, OctaCDF. Suitable labeled internal standards were used to quantify the compounds and assess the recoveries. Data below the detection limits were set to DL/2.

Some micro-meteorological data were simultaneously recorded. Data recorded at the station are considered as representative of the weather parameter over the whole base, and include air temperature, atmospheric pressure, wind speed and direction.

**Receptor Models**

To identify and apportion the sources of the PAH, PCDD, and PCDF species, positive matrix factorization (PMF) was applied to the ambient data. Details of the PMF model are reported elsewhere, and have been applied extensively. In this study, EPA PMF 5.0.14 was used to identify and apportion the most probable sources of PCDDs, PCDFs and PAHs at JBB. Given the low number of collected samples per site, the data from all five sampling sites were used as a single input matrix to PMF since the sites were relatively close to the source areas like the burn pit and transportation field and thus could be expected to be affected by the same set of sources. EPA PMF V5 has been given the capability of handling multiple site data and has been used in other such studies. Assuming that different sites would be affected by the same set of potential sources and that such sources may differently influence the sites depending on wind speed and direction, it was possible to use spatial variability to provide a source resolution with less rotational ambiguities.

The multiple site data can be used in conditional probability function (CPF) analyses on the resulting resolved source contributions at the different sites to investigate the location of the
sources within the sampled domain. Briefly, the CPF analyzes local source impacts from varying wind directions using the source contribution estimates from PMF coupled with time-resolved wind directions. CPF essentially assesses the probability that a source contribution from a given wind direction exceeds a predetermined threshold criterion (e.g., concentrations >75th percentile, in this case). Sources are likely to be located along the directions that have high conditional probability values and can triangulate on sources when multiple site data are available.

**Toxic equivalents**

The toxic effects of the PAHs and dioxins/furans can be estimated using additive models (although affected by large variations). Such models use the relative toxic equivalency factors (TEFs) assigned to individual congeners to produce total toxic equivalents (TEQs) relative to a reference compound. Operationally, TEQs are computed by the sum of the products of the concentration of each compound multiplied by its TEF value. In this study, TEFs reviewed in 2005 by WHO are used to calculate the TEQs for the PCDDs and PCDFs relative to 2,3,7,8-TCDD (TCDD-TEQ). The modified TEF lists provided by Nisbet and LaGoy, Malcolm and Dobson, and Larsen and Larsen were used for PAHs relative to BaP (BaP-TEQ). From the results of the source apportionment, the TEQ for the emissions from each of the resolved sources can be calculated using these methods and the relative potential toxicity of the different emissions can be estimated.

**RESULTS AND DISCUSSION**

The monitoring data were presented in a companion paper. Briefly, the highest concentrations of PCDD/Fs were recorded at GT, whereas the highest PAH concentrations were
measured at TF. Generally, preliminary analyses including scatter plots and the maps presented in Masiol et al.\textsuperscript{8} indicated at least two sources of airborne pollutants at JBB. The ratios among PAH congeners and PAH to PCDD ratios were in good agreements with data reported in the literature for the open burning of simulated military waste and emissions from diesel engines.\textsuperscript{25} Moreover, spatial analysis coupled with wind directions indicated that PCDD/Fs over the base were often highly related to the dispersion of BP plumes, while PAHs can be attributed to the presence of multiple sources.

Before running PMF, preliminary data checks, handling and clean-up were conducted to ensure robust and reliable results:

- Data and uncertainties were handled according to Polissar et al.\textsuperscript{26} (i) data below DLs were set as DL/2, with an uncertainty of 5/6 of the corresponding DL; (ii) data >DLs were matched with uncertainties determined by the analytical methods with the addition of 1/3 of the DLs. Finally, average percent uncertainties to concentration for data >DLs were approx. 30-35% for PCDDs and PCDFs and about 20-25% for PAHs;
- Since there is no total variable available such particulate matter mass concentrations, PMF apportions the sources over a range of variables ($\Sigma$PCDDs, $\Sigma$PCDFs, $\Sigma$TCDD-TEQ, $\Sigma$PAHs and $\Sigma$BaP-TEQ), which are thus inputted into the model with very high associated uncertainties (400%) and also marked as “weak” to avoid driving the model;\textsuperscript{19}
- Using the signal-to-noise ratio criterion,\textsuperscript{27} 1,2,3,7,8,9-HexaCDF was included as “weak” by tripling it uncertainty values;
- The final PMF dataset included 33 “strong” variables. The PMF solutions were examined from 2 to maximum 4 sources. Despite the limited number of available samples and the relatively high analytical uncertainty of analyzed classes of compounds,
a limited number of interpretable sources can be extracted. The best solution was identified on the basis of (i) the knowledge of sources impacting the study area, (ii) by considering the minimization of the function $Q$, (iii) by analyzing the stability of sources and the absolute scaled residuals within ±3, and (iv) by keeping the result uncertainties within an acceptable range with bootstrap (BS) and displacement (DISP) methods;\textsuperscript{28}

- An additional 3% uncertainty was added to the model to encompass errors not considered in the uncertainty assessment: this value was selected after various runs using different values;

- The potential for rotational ambiguity were checked by analyzing the G-space plots and running the model solutions over multiple FPEAK values.\textsuperscript{17,18}

The most stable, robust and interpretable results were found for a 3-factor solution and FPEAK=-0.2. The extracted solution was stable and reliable: all runs converged; all species had stable results; modeled concentrations were successfully predicted ($R^2$ ranging from 0.76 to 0.99 for all the species and slopes≈1); scaled residuals were normally distributed; no factor swaps occurred for DISP analysis indicating that there were no significant rotational ambiguities and the solution was sufficiently robust to be used; all factors had >95% in mapping from the BS run, suggesting that the BS uncertainties can be interpreted and the selected number of factors is appropriate.

Figure 2 presents the resolved factor profiles, while the apportioned mass contributions to the various chemical species are given in mass concentrations and total percentages in Figure 3. Figure 4 provides the contributions of the resolved sources at each of the sites. The CPF plots (Figures 5 to 7) were calculated for each of the three factors at each of the sites, i.e., MP, GT, TF and H6+CA.
Factor 1 consists of 67 to 84% of all of the PCDD and PCDF homologues and 11 to 23% of the PAHs. On average, it contributes approximately 75% of ΣPCDDs, ΣPCDFs and ΣTCDD-TEQ, but only 13% of ΣPAHs and 12% of ΣBaP-TEQ. Thus, factor 1 is interpreted as burn-pit emissions. Figure 4 shows that the sites with the highest impacts from the BP are GT, TF, and CASF although the CASF value is about 50% of those at the other 2 sites. The CPF plots (Figure 5) show that data >75th percentile generally point toward the BP. The TF plot also shows a small lobe pointing toward the WSW. Because the CASF and H-6 data were combined, the CPF direction does not point toward the BP. However, given its position relative to the prevailing NW wind direction, it is expected that CASF would be more highly affected by the BP.

Factor 2 includes a very high fraction of the lower molecular weight PAH compounds (ranging from 47 to 65% for 2- and 3-ring, i.e. NAP, ACY, ACE, FLU, PHE, ANT), moderate contributions of >3-ring PAHs (18 to 38%) and low values for PCDDs + PCDFs (3-16%). Its average contribution to ΣPAHs is significant (55.6%), but it account for only 20% of the ΣBaP-TEQ because it is mainly composed of light PAHs with generally low TEQs. The share for PCDDs/PCDFs TEQs are around 10 to 11%. Prior studies near airports have reported high concentrations of low molecular weight PAHs, particularly naphthalene. Figure 4 shows that the highest contribution from this factor is at CASF followed by H-6. The CPF plots (Figure 6) at MP, TF, and GT point weakly toward the location of the helipad while the CA/H6 plot points east and west that are not clearly associated with any source. There is also a weak lobe at MP that points toward the end of the runway that would have been a source on those few days when the wind was from the S or SE.
Factor 3 is primarily composed of the highest molecular weight PAHs (>50% for 4- to 6-ring congeners), and accounts for 34% of the lighter PAHs and 11 to 18% of the PCDDs + PCDFs. The TCDD-TEQ is low (13%). However, this factor is associated with most of the BaP-TEQ (70%). Factor 3 is assigned to diesel engine emissions from vehicles, electricity generators, and possibly space heating. This assignment is based on multiple evidence. Higher molecular weight PAHs are typical molecular markers of vehicular emissions and are often associated with mobile sources. Similar emissions would be anticipated from diesel powered electricity generators. The highest concentrations were observed at the CASF and TF sites that would be expected to be affected by the idling vehicles at the inspection area. The CPF plots (Figure 7) show that highest levels of this factor are found when winds blow from multiple sectors with respect to BP and are generally orientated toward the area where the vehicles are being inspected and toward the helipad. The CPF plots also reveal a strong directionality at TF when winds blow from South, which is compatible with an area heavily affected by truck emissions.

CONCLUSIONS

This study has investigated the main sources of PCDDs, PCDFs and PAHs at JBB during 2007. The application of PMF has extracted three factors, which were subsequently interpreted as potential sources based on their chemical profiles, source directionality, and differences among the sites. Results revealed that BP-related emissions were the most important source of dioxins and furans (76-78%), while aircraft emissions and the emissions from diesel vehicles were the overwhelming sources of lighter and heaviest PAHs, respectively. As a consequence, approximately 75% of the overall potential toxicity of air pollution related to
PCDD/Fs can be attributed to the BP, while the higher potential toxicity related to PAHs is likely due to the mobile emissions from vehicles operating at JBB.

REFERENCES


FIGURE CAPTIONS

Figure 1. Map of the study area and wind roses computed seasonally on 2007 data. JBB sites: burn-pit (BP); guard tower (GT); transportation field (TF); H6-Housing (H6); contingency aeromedical staging facility (CASF, CA).

Figure 2. PMF factor profiles. Bars are concentration of species in pg m\(^{-3}\), crosses are on percentage on species sum. Note that the exes for concentration of species are shown in logarithmic bases.

Figure 3. PMF factor apportionment of \(\Sigma\)PCDDs, \(\Sigma\)PCDFs, \(\Sigma\)TCDD-TEQ, \(\Sigma\)PAHs and \(\Sigma\)BaP-TEQ expressed as concentration (top) and percentage (bottom).

Figure 4. PMF factor contributions to each of the individual monitoring sites at JBB. (Top) Contributions at each site; (Bottom) Fractional contributions at each site.

Figure 5. CPF results for factor 1: threshold was set to 75th percentile; only records with wind speed > 1 m s\(^{-1}\) are included.

Figure 6. CPF results for factor 2: threshold was set to 75th percentile; only records with wind speed > 1 m s\(^{-1}\) are included.

Figure 7. CPF results for factor 3: threshold was set to 75th percentile; only records with wind speed > 1 m s\(^{-1}\) are included.
Figure 1
Figure 3.
Figure 4
Figure 5. CPF results for factor 2: threshold was set to 75th percentile; only records with wind speed $> 1 \text{ m s}^{-1}$ are included.
Figure 6. CPF results for factor 3: threshold was set to 75th percentile; only records with wind speed > 1 m s\(^{-1}\) are included.