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Risk Assessment Capacity Building Program in Zaporizhzhia Ukraine: Emissions Inventory Construction, Ambient Modeling, and Hazard Results

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ABSTRACT

Historically, Ukraine has been a major source of industrial production for the former Soviet Union and the source of pollution associated with an aging industrial infrastructure. The US Environmental Protection Agency (US EPA) and the Ukrainian Ministry of Environment and Natural Resources (MENR) entered into partnership to develop Ukrainian expertise and capacity in risk assessment so that Ukraine could more effectively use its National and Regional Environmental Protection Funds and set priorities for cleanup and regulation. Ukrainian scientists, local officials, and EPA consultants conducted a pilot study in the heavily industrialized Zaporizhzhia Oblast so that the process, analytical tools, and approach for a risk assessment could be developed for and tailored to Ukrainian needs. As a first step, site-specific information was obtained from multiple sources of air pollution and an emissions inventory of air pollution developed. Efforts by local officials were critical for emissions inventory construction. After refinements were made to the inventory, Ukrainian scientists then performed exposure modeling using this information so that ambient concentrations of pollutants could be estimated. 11 industry types (*i.e.*, enterprises) were identified as a major emission source. Results of the modeling effort demonstrated that emissions estimates of particulate matter (as measured by particles of less than 10 micron diameter or "PM_{10}") and a number of carcinogens were consistent with those from other cities with high concentrations of metallurgical industries in former Soviet Union countries, and were above safety standards. Hazard information was gathered from international databases for each of the estimated pollutants. Using such data, prioritization and identification of potential health concerns can be made, but most importantly, the expertise and experience gained from the pilot allowed for continued support of risk assessment capacity building in the Ukraine and support by the World Bank.

Keywords: Air Pollution; Exposure Modeling; Ukraine; Risk Assessment

1. Introduction

Although constituting a small percentage of the overall landmass of the former Soviet Union, Ukraine was responsible for a significant amount of its overall industrial production. After the breakup of the Soviet Union and especially in years not as affected by worldwide recessions, the aging industrial infrastructure of Ukraine continued to emit large volumes of air and water pollution, and wastes. The Ukrainian Ministry of Environment and Natural Resources (MENR) has reported that these emissions contain a number of pollutants [1] also described in a number of international databases to be associated with developmental effects, chronic long-term health effects, and cancer (e.g., US EPA IRIS assessments and IARC

Monographs on carcinogenic risks to humans). Ukraine also has been identified as a major source of transboundary air pollution for the eastern Mediterranean region and a significant source of greenhouse gases emissions [2]. After independence, Ukraine had set up a limited fund to begin to address its environmental problems. However, the system of pollution management in Ukraine was based on the Soviet System in which pollution limits were set to very low levels and generally not complied with [3].

Despite setting standards for numerous individual compounds, no system to prioritize the control of pollution and its sources were in place; nor had expertise been developed to perform those evaluations. The choices of which sources and pollutants to address and control were also made difficult by the magnitude of pollution, number of the pollutants emitted, and number of significant pollution sources. By contrast, the US EPA has been tasked through a number of laws (e.g., 1990 Clean Air Act Amendments) to use risk assessment to rank the relative risk of different industrial emission and sources, and to aid in the development of decision criteria for efficient and effective regulatory actions. The US system and methodologies have been modified and adopted by Russia for similar applications. The US EPA has provided training to develop risk assessment capabilities in Russia for a number of years [3].

To help address some of the problems cited above and strengthen Ukraine's capacity to set environmental priorities, the US EPA set up a partnership with Ukraine's Ministry of Environment and Natural Resources (MENR) to develop expertise in environmental risk assessment and economic analyses. This Capacity Building Project (CBP) was funded through an US EPA Cooperative Agreement (CX4-831993) with the Environmental Defense Fund (EDF); support also came from US EPA's Offices of Research and Development, International Affairs, and the Chief Financial Officer. The CBP was initiated in 2002 and has been described previously [3]. In order to introduce the US system and provide risk assessment, management, and environmental finance information, the project began with a series of workshops and consultations. Ukrainian representatives at the national and oblast level scientists from Ukrainian research institutes, EPA consultants, representatives of the World Bank (Washington DC and Kyiv), specialists from US non-governmental organizations (NGOs) (*i.e.*, Counterpart International and the Environmental Defense Fund), and environmental finance specialists from the State of Pennsylvania water infrastructure management agency were involved.

So that a template for data development and analyses could be implemented at the local level and then be adapted on a broader scale, a model case study was developed with the assistance of municipal officials of the Zaporizhzhia Oblast. An Oblast is most analogous to a county in the US Resting on both sides of the Dnipro River with relatively flat topography, Zaporizhzhia is comprised of five administrative municipal zones on the left bank and two others on the right. The Dnipropetrovsk water reserve is situated on the north from the city, the Kakhovske water reserve on the south. Data from the Statistics Administration in Zaporizhzhia Oblast (2007) indicate a population of ~800,000 for the year 2001 in a city area of 330 km^2 [4]. The choice was ideal as model of significant Ukrainian air pollution sources as the Oblast is the country's largest producer of high quality steel, nonferrous metals, ferrous-alloys, power transformers, various equipment, and automobiles.

This paper describes some of the key results of the Ukrainian pilot project included in the "Final Report on the project "Environmental Capacity Building in the NIS" US EPA grant registration # X4-83199301 (US Environmental Protection Agency (EPA), Environmental Defense Fund (EDF), Marzeev Institute of Hygiene and Medical Ecology AMSU (IHME), Center of Environmental Health and Risk Assessment (CEHRA) [4]. EPA collaborators had access to the final report, which formed the basis of this paper, but not the original data. Specifically, this paper focuses on the development of the emissions inventory and dispersion modeling for derivation of ambient concentrations of pollutants at various population receptor points at the Zaporizhzhia oblast level. More recent hazard data from international sources is also presented for modeled pollutants.

2. Methods

2.1. Exposure Data Collection

Because of Ukraine's system of legally binding monitoring systems and related information used for permitting and fees, local emissions data from stationary sources were generally available for Zaporizhzhia. An emission inventory was assembled that is analogous to those of EPA (*i.e.*, the Toxic Release Inventory and the National Air Toxics Assessment) [5]. The inventory information included: 1) volumes of air emissions from standard State form "2-TP" ("AIR"); 2) emission permits for atmospheric air pollutants; 3) stationary source location information on industrial sites; and 4) source and emission characteristics through Ukrainian inventory reports (*i.e.*, "Instructions on the Content and Order of the Report on the Pollutant Inventories on the Enterprise", approved by the Decree of the Ministry of Environment Protection and Nuclear safety from 10.02.95 No. 7 registered in the Ministry of Legal Affairs of Ukraine

(15.03.95 # 61/597). The "2-TP" ("AIR") form was introduced in the Soviet Union in the 1980s with reporting required by law in Ukraine. Inventory information for particulate matter (PM) was given in the form of total suspended particles (TSP). The list of 30 major industrial Zaporizhzhia enterprises in the 2007 emissions inventory were those used to model emissions. Some of the specific enterprises have since been renamed or are no longer functioning. Unlike the EPA emission inventories, Ukrainian plant emissions data are not public so that further examination or update of emissions in the inventory cannot occur. The 2007 inventory includes a number of industries that include not only steel-associated facilities but also silicon, asphalt, car repair, transformer, and a number of public corporations. The top source types that contributed 63% of emissions are shown in **Table 1**.

2.2. Dispersion Modeling

Pollutant dispersion is dependent on terrain characteristics, land use type, and meteorological data. Dispersion modeling methods officially certified in Ukraine are adopted from the official risk assessment methods of Russia (Human Health Risk Assessment from Environmental Pollutants) [6] that were, in turn, modeled on EPA approaches [3]. Although the official Ukrainian air pollutant dispersion model is the EOL model (*i.e.*, an interface based on the OND-86 methods, see Onischenko *et al*. as an example [7]), the ISC-AERMOD program (a more modern model) was used for the Zaporizhzhia project instead [8]. That model (ISC short term stack model) uses the steady-state Gaussian plume equation for a continuous elevated source. For each source and each hour, the origin of the source's coordinate system is placed at the ground surface at the base of the stack. Model parameters included: digital elevation models (*i.e.*, relief of the territory), meteorology, land-use data (*i.e.*, residential building density, surrounding "greenness", industrial areas, presence of surface waters), stationary source parameters, and emission-specific data.

Table 1. List of the major source types of industrial Zaporizhzhia enterprises in the emissions inventory.

No	Types of industry	Contribution of emissions, %
1	Coke industry	2
2	Steel-rolling industry	1
3	Silicon industry	1
4	Steel production	41
5	Alluminium industry	6
6	Abrasive industry	3
7	Transformer industry	1
8	Graphite industry	2
9	Titano-magnesium industry	1
10	Ferro-alloy industry	4
11	Glass factory	1

The input data for model preprocessing included meteorological data (*i.e.*, 1 hour interval measurements) and specific territorial factors that characterize vertical mixing in ground atmospheric layers. Meteorological data for the entire year of 2005 were provided by the Zaporizhzhia Hydro-Meteorological Service (HydroMet). Dominant wind directions were to the southwest and west. Southwestern wind with speed starting from 3 - 4 m/s dominated during the greatest number of hours (14.9 %) with almost equal number of hours dominating Western and Southeastern directions. Zaporizhzhia belongs to the zone with continental type of climate with hot summer and moderate cold winter. The coldest month of the year is January (*i.e.*, average monthly temperature −4.3˚C, absolute minimum −34˚C) and the warmest month is July (*i.e.*, average monthly temperature +22.3˚C with absolute maximum +41˚C). The yearly precipitation rate is 469 mm and average snow cover is 14 cm with a maximum of 35cm. Land use was not accurately recorded in the stationary source inventory. Therefore, land-use data were provided by remote sensing images of high resolution (*i.e.*, Quick Bird Standard Imagery PAN+MSI, 05/04/ 2005, product for Zaporizhzhia territory, "Grandproject" Co. Zaporizhzhia) and processed by ArcGIS software to pinpoint 5000 emission points using US Geological Survey methods [4].

Based on information in air pollution modeling software and "2-TP" ("AIR") form, 76 pollutants were identified in the inventory. As a first step, initial ground level calculations of annual concentrations for 34 pollutants were estimated for 6 population-based receptor points. However, more refined modeling was conducted for the emissions of 51 priority pollutants (that included the initial 34) at the 6 population-based receptor points after: 1) conducting a more detailed emission analyses of 12 major Zaporizhzhia sources; 2) prioritization by potential risk using volume and hazard information; and 3) taking into account difference between "2-TP" and permitted emissions through consideration of operating mode, emission source specification, and physicochemical conditions (wet and dry concretion of the substances). Additional calculations were done for total suspended particles (TSP), using a specialized model of calculation TSP in the ISC-Aermod program. The accurate locations of 5000 stationary sources of emissions from the 30 enterprises in the Zaporizhzhia industrial sites were identified for the 52 priority pollutants (*i.e.*, 51 priority pollutants plus TSP) with a spatial accuracy of several meters. Input information for each of these emission points within the enterprises were used in the modeling calculations. Emission point source parameters, wind speed profile adjustments, and pollutant removal by physical or chemical processes methods were given in the report [4] and are not shown here.

The gender and age structure of the population in Zaporizhzhia, the number of residents in each neighborhood, and density of residents was collected from the Zaporizhzhia Regional Statistical Administration. Population data were geocoded and linked to the residential living places in the "ArcGIS environment". Population-based receptor points were linked to population density so that all of the population in each receptor point was similar with respect to the impact of ambient air pollution impacts. Dispersion model outputs were hourly concentrations produced at each receptor by combined source emissions: they were summed to obtain total 1-hour, 24-hour, month, and annual concentrations. The land use classifications and population receptor points are shown in **Figure 1** and the wind speeds are demonstrated by a wind rose in **Figure 2**.

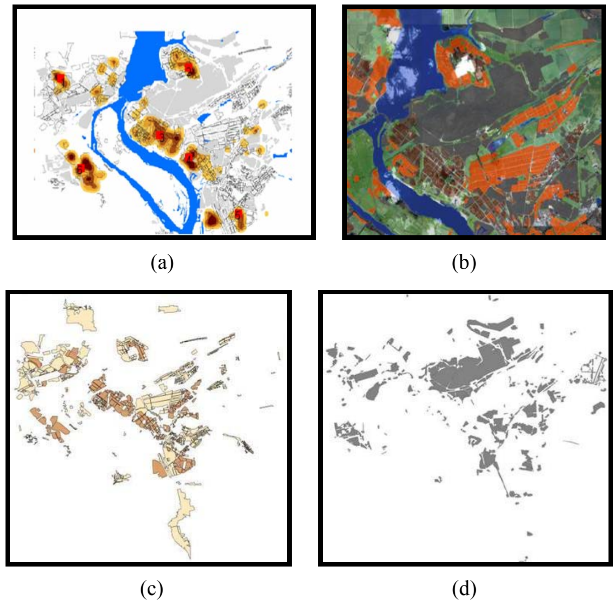

Figure 1. Zaporizhzhia Population Receptor Points (a); Composite for Receptor Modeling (b); Housing Zone (c); and Industrial Zone (d). The map of Zaporizhzhia shows 6 receptor points in areas of significant population for estimation of exposure to priority air pollution emissions with 1010, 3292, 6197, and 17,744 people/km^2 grids from no color to dark brown (a). The composite overview of land use along the Dnipro River basin and Zaporizhzhia includes: Grey as an industrial zone, Brown as low-rise housing zone, Orange as high-rise housing zone, Blue as the Dnipro River, and Green as flora. For the housing zone (c); light brown indicates high-rise housing and darker brown low-rise housing. The industrial zone is indicated as grey (d). Each part of the figure is drawn to the same scale.

2.3. Hazard Characterization

Of the 52 priority pollutants modeled for ambient air concentration estimates, a number of pollutants were identified as at least possible human carcinogens. The weight of evidence for human carcinogenicity was determined by either the US EPA [9] or the International Agency for Research on Cancer (IARC) [10]. Others have been regulated primarily on noncancer effects (e.g., particulate matter and other "criteria" pollutants that are subject to National Ambient Air Quality Standards by US EPA). **Table 2** shows the hazard information and the initial emission inventory information derived from the "EOL" air pollution software and the "2-TP AIR" data for the 52 priority pollutants identified by CAS number. In some cases the specific identities of the pollutants in the inventory is not clear and more than one CAS number is given.

3. Results

The 52 priority pollutants cited in the refined Zaporizhzhia emissions inventory are presented in **Table 2**. Those pollutants identified by either US EPA or IARC as at least possible carcinogens and the estimates of their ambient concentrations at the 6 receptor points are shown in **Table 3**. A number of the priority pollutants also belong to chemical groups with potential toxicity variations between members within those groupings. The specificity of the inventory information for such pollutants is dependent on information provided in the 2-TP (AIR) forms. As shown for chromium, valence state has a significant impact on toxicity. The lack of specificity in the inventory makes assignment of appropriate hazard information for these modeled emissions difficult.

One of the pollutants whose ambient concentrations were estimated in the Zaporizhzhia case study was TSP/PM_{10} (see **Table 4**). American regulatory standards apply to PM_{10} and to $PM_{2.5}$ (a more respirable and potentially toxic particle size) [11,12]. Over the last 15 years those standards have been modified with an increasing emphasis on the health effects of $PM_{2.5}$. In 1997 the US EPA National Ambient Air Quality Standards for $PM_{2.5}$ were 65 μg/m^3 (24-hour) and 15 μg/m^3 (Annual) and for PM_{10} were 150 μg/m^3 (24 hour) and 50 μg/m^3 (Annual) [13]. In the 2006 the 24-hour $PM_{2.5}$ standard was lowered to 35 μg/m^3 and the annual PM_{10} standard dropped. In December 2012 the annual $PM_{2.5}$ standard was lowered to 12 μg/m^3 [13]. The three primary sources of PM_{10} were aluminum production, abrasive materials industry and steel production; they were also major sources of other pollutants. Emission inventory-based estimates of

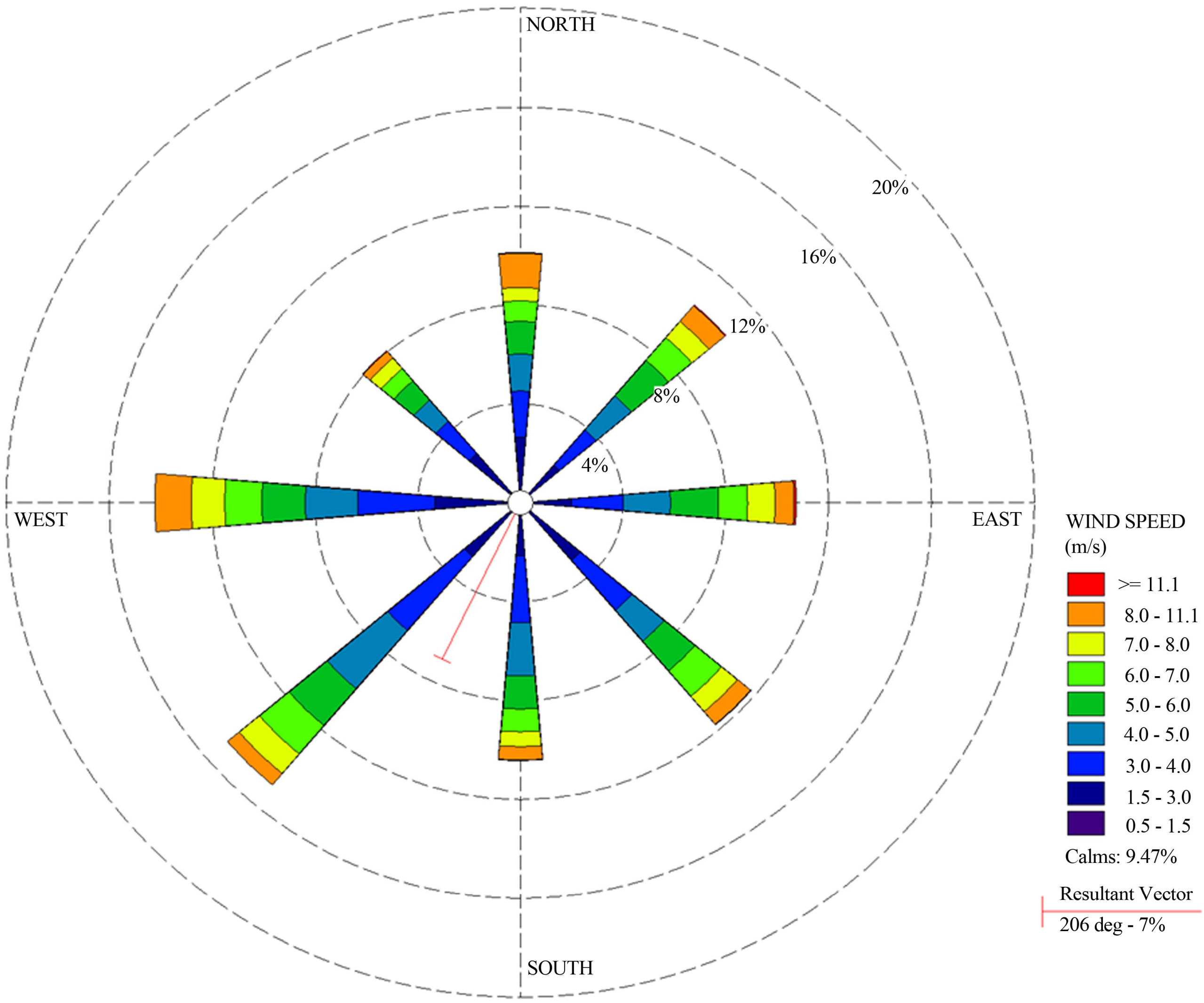

Figure 2. Annual wind rose in year 2005 for Zaporizhzhia. The annual wind rose for Zaporizhia is shown for the year 2005. The dominant wind directions were Southwestern and Western.

annual ambient TSP concentrations were subsequently converted to estimates of PM_{10} and corresponding population estimates are shown in **Table 4** for the 6 receptor points. These annual estimates exceed the older annual and more recent 24-hour US EPA national standards for particulate matter.

After TSP inventories were modeled, the results were extrapolated to estimates of PM_{10} and $PM_{2.5}$ for comparative purposes to US health standards and other ambient estimates. Avaliani and Revich [14] proposed a 0.55 conversion coefficient to convert TSP into PM_{10} for Russia. This value is slightly below the 0.6 conversion coefficient suggested in Larson *et al*. [15] for Russia and Strukova *et al*. [16] proposed for Ukraine. Because many former Soviet regions have more combustion-related activities than average, a higher conversion coefficient was used than that for the world average 0.5 [17]. The conversion ratio used in the final report [4] was 0.55. Further conversions of PM_{10} estimates to $PM_{2.5}$ include greater uncertainty in relation to the original data in the emissions inventory (*i.e.*, TSP). In Russia, the $PM_{2.5}$/PM_{10} ratio has been estimated to range from 0.55 to 0.75 [15,17]. For this article we have chosen a conversion ratio of 0.65 (*i.e.*, a ratio in the middle of that range) for estimates of PM_{10} to $PM_{2.5}$ with the resulting modeled estimates for TSP and all conversions to smaller particle sizes shown in **Table 4**.

4. Discussion

Often, former Soviet countries (including Ukraine) have used a retrospective rather than prospective approach for assessment of health effects from pollution. Epidemiological methods have been used to try to identify risk after

Table 2. List of priority pollutants from Zaporizhzhia emissions inventory used for more refined dispersion modeling.

CAS#	Pollutant	IARC WOE for Cancer**	EPA WOE for Cancer**	Emissions Inventory*** (Tons/year)
106-99-0	1,3-Butadiene	Carcinogenic to humans	Carcinogenic to humans	**0.039**
10102-44-0	Nitrogen dioxide	Not assessed	Not assessed	**8937.296**
10102-43-9	Nitrous oxide	Not assessed	Not assessed	**3.276**
107-13-1	Acrylonitrile	Possibly carcinogenic to humans	Probable human carcinogen (UR)	**0.422**
107-02-8	Acrolein	Not classifiable as to human carcinogenicity	Cannot be determined	**7.882**
1344-28-1	Aluminium oxide	Not assessed	Not assessed	**3359.415**
7664-41-7	Ammonia	Not assessed	Cannot be determined	**134.209**
75-07-0	Acetaldehyde	Possibly carcinogenic to humans	Probable human carcinogen (UR)	**0.173**
67-64-1	Acetone	Not assessed	Cannot be determined	**35.51**
50-32-8	Benzo[a]pyrene	Carcinogenic to humans	Probable human carcinogen (UR)	**0.422**
100-44-7	Benzyl chloride	Not assessed	Probable human carcinogen	****
8006-61-9	Automotive gasoline	Not assessed	Not assessed	****
71-43-2	Benzene	Carcinogenic to humans	Human carcinogen	**52.058**
123-86-4	Butyl acetate	Not assessed	Not assessed	**151.458**
7440-62-2	Vanadium as dust and fumes	Vanadium dust and fumes—Not assessed Vanadium pentoxide (CAS 1314-61-1)-Possibly carcinogenic to humans	Vanadium dust and fumes—Not assessed Vanadium pentoxide (CAS 1314-61-1)—Not assessed	**3.885**
75-01-4	Vinyl chloride	Carcinogenic to humans	Human carcinogen	**0.796**
7647-01-0	Hydrogen chloride	Not classifiable as to human carcinogenicity	Cannot be determined	**131.408**
630-08-0	Carbon monoxide	Not assessed	Not assessed	**103662.5**
106-89-8	Epichlorohydrin	Possibly carcinogenic to humans	Probable human carcinogen	****
141-78-6	Ethyl acetate	Not assessed	Cannot be determined	**16.675**
100-41-4	Ethylbenzene	Possibly carcinogenic to humans	Cannot be determined (UR)	**3.622**
1332-37-2	Iron oxide	Not assessed	Not assessed	**1897.246 Ferum and its compounds**
7720-78-7	Ferous sulfate	Not assessed	Not assessed	
7440-43-9 13477-23-1	Cadmium metal Cadmium sulfite	Carcinogenic to humans Not assessed	Probable human carcinogen (UR) Not assessed	**0.19 Cadmium and its compounds**
1330-20-7	Xylene	Not classifiable as to human carcinogenicity	Cannot be determined	**15.944**
7439-96-5	Manganese and its compounds	Not assessed	Cannot be determined	**477.276**
74-82-8	Methane (gas)	Not assessed	Not assessed	**736.649**
78-93-3	Methyl ethyl ketone	Not assessed	Cannot be determined	**61.548**
7440-50-8 7758-98-7	Copper metal Copper sulfate	Not assessed Not assessed	Cannot be determined (UR) Not assessed	**3.405 Copper and its compounds**
13814-81-8	Copper (1+) disulfide dihydrate	Not assessed	Not assessed	
1317-39-1	Cuprous oxide	Not assessed	Not assessed	

Continued

91-20-3	Naphthalene	Possibly carcinogenic to humans	Possible human carcinogen (UR)	**16.859**
7440-02-0	Nickel refinery dust	Possibly carcinogenic to humans	Human carcinogen Nickel Carbonyl (CAS 13463-39-3)—Probable human carcinogen	**9.814 Nickel and its compounds**
	TSP (PM_{10})	Not assessed	Not assessed	**17009.138 (Substances featured as suspended solid particles)**
10045-94-0	Mercury nitrate hydrate	Not assessed	Not assessed Mercuric chloride (CAS 7487-94-7)—Possible human carcinogen	**0.029 Mercury and its compounds**
7439-97-6	Mercury (elemental) and inorganic mercury	Not classifiable as to human carcinogenicity	Cannot be determined	
8007-45-2	Soot* (coke oven emissions) IARC lists as coal tars (distillation)	Carcinogenic to humans	Human carcinogen	**207.579**
7439-92-1	Lead and its compounds	Possibly carcinogenic to humans	Probable human carcinogen	**8.91**
7446-095	Sulfur dioxide	Not classifiable as to human carcinogenicity	Not assessed	**10647.656**
7783-064	Hydrogen sulfide	Not assessed	Cannot be determined	**72.964**
75-15-0	Carbon disulfide	Not assessed	Cannot be determined	****
100-42-5	Styrene	Possibly carcinogenic to humans	Assessment not available (UR)	**4.564**
7664-93-9	Sulphuric acid Listed by IARC as strong inorganic acid mists containing sulfuric acid	Carcinogenic to humans	Not assessed	**49.747**
108-88-3	Toluene	Not classifiable as to human carcinogenicity	Cannot be determined	**27.755**
8030-30-6	Petroleum ether or naphtha	Not assessed	Not assessed	****
108-95-2	Phenol	Not classifiable as to human carcinogenicity	Cannot be determined	**13.379**
50-00-0	Formaldehyde	Carcinogenic to humans	Probable human carcinogen (UR)	**1.971**
7664-39-3	Hydrogen Fluoride	Not assessed	Not assessed	**5.529**
7782-50-5	Chlorine and its compounds	Not assessed	Not assessed	**193.873**
16065-83-1 18540-29-9	Chromium compounds	Chromium (III) (CAS 16065-83-1)—Not classifiable as to human carcinogenicity Chromium (VI) (CAS 18540-29-9)—Carcinogenic to humans	Chromium (III) (CAS 16065-83-1—Cannot be determined Chromium (VI) (CAS 18540-29-9)—Human carcinogen	**55.056**
108-93-0 108-94-1	Cyclohexanol Cyclohexanone	Not assessed Not classifiable as to human carcinogenicity	Not assessed	**1.059 CAS# in inventory is for cyclohexanol but listed as cyclohexanone**
1314-13-2 7440-66-6	Zinc oxide Zinc and its compounds	Not assessed Not assessed	Not assessed	**14.988 Zinc and its compounds**

*Soot is identified in the emissions inventory with the EPA equivalent of coke oven emissions. **For IARC and EPA chemicals that are "not assessed" have not been examined for carcinogenicity in the IARC or IRIS databases. For EPA and IARC "Cannot be determined" and "Not classifiable as to human carcinogenicity" mean that the chemicals have been assessed but a determination has been made that the available data do not support a classification. This is not the same as the determination that the chemicals are probably not carcinogenic. For EPA UR designates under review. ***The emissions in tons/year are derived from the initial data from "EOL" (air pollution modeling software) data and the available report "2-TP" ("AIR"). ****Added after additional consideration, not present on initial reporting forms.

exposure has occurred [4]. However, such approaches have little ability to ascertain the environmental sources of pollution that may affect health. For an endpoint such as cancer, the 15 - 20 year lag time from exposure to manifestation of disease makes epidemiological approaches for prevention of this health effect using current

Table 3. Annual estimated concentrations for priority pollutants with a WOE of at least possibly carcinogenic to humans at 6 receptor points in Zaporizhzhia.

CAS	Pollutants	Estimated Average Annual Concentration at 6 Population Receptors (Concentration in μg/m^3)						
		1	2	3	4	5	6	Mean
106-99-0	1,3-Butadiene	0.002	0.016	0.043	0.091	0.178	0.402	0.122
75-07-0	Acetaldehyde	0.0001	0.0026	0.0091	0.023	0.0459	0.0789	0.0266
107-13-1	Acrylonitrile	1.5E−5	0.025	0.06	0.125	0.235	0.425	0.1452
50-32-8	Benzo[a]pyrene	7E−07	0.0015	0.0029	0.0052	0.0089	0.0197	0.0064
71-43-2	Benzene	0.634	2.311	5.875	13.003	25.582	54.094	16.917
8006-61-9	Automobile gasoline (Benzine)	0.115	0.706	1.711	3.426	6.973	15.19	4.6868
100-44-7	Benzyl chloride	0.0064	0.0492	0.1584	0.3579	0.6096	1.2176	0.3998
141-78-6	Epichlorohydrin	0.0011	0.0087	0.0239	0.0529	0.0979	0.195	0.0633
1332-37-2	Ethylbenzene	2.989	20.261	53.08	113.54	210.26	443.45	140.6
50-00-0	Formaldehyde	0.137	1.052	2.982	7.045	12.632	26.042	8.315
7439-92-1	Lead and its compounds	0.0009	0.0065	0.02	0.044	0.0789	0.145	0.0497
630-08-0	Nickel and its compounds*	0.02	0.07	0.192	0.471	0.895	1.949	0.5828
1330-2-7	Cadmium Sulfite	1.6E−8	1.1E−5	2.3E−5	4.5E−8	8.2E−5	0.0002	5.8E−5
See **Table 1**	Chromium and its compounds	0.028	0.18	0.55	1.18	2.17	4.51	1.4363
See **Table 1**	Soot*	5.962	15.067	26.244	45.311	76.871	173.52	57.146
100-42-5	Styrene*	0.029	0.093	0.181	0.338	0.573	1.279	0.4255
75-01-4	Vinyl Chloride	0.002	0.0167	0.052	0.121	0.214	0.419	0.1375

*Two tables appear in the original report with slight difference in estimates for one receptor point. Values from the table used to identify cancer risk were shown as the default value.

exposures problematic. One of the strengths of the approach used in the Zaporizhzhia case-study is that it allows for identification of risk and the opportunity to change risk before detection of disease through retrospective epidemiological approaches. Ambient monitoring also cannot identify specific sources for control but the approach used in the EPA Cumulative Exposure Project (CEP) [18-23], National Air Toxics Assessment [24], adaptations of the CEP applied for a more localized level in the State of California [25], and taken here (*i.e.*, that uses modeling of emission inventories to predict ambient concentrations) can. This approach also does not wait for harm to occur such as an epidemiology retrospective study would.

A number of studies in the region conducted between 1996 and 2008 have estimated health risks from air pollution in Russia and Ukraine [3,4,6,7,16,26] or Kazakhstan [27] and have generally concluded that there are significant health risks from inhalation of pollutants, particularly particulate matter. Ambient air pollution standards in the former Soviet Union required short-term pollutant estimates for all major pollution sources. Risk assessment methodologies have evolved to fit advances in the science that supports them. More recently, former Soviet Union countries have started to use more specific meteorological data in dispersion modeling, similar to the approach used in this Zaporizhzhia case-study. For example, Larson *et al*. [15] recalculated dispersion model outputs to obtain annual average pollutant concentrations in Volgograd Russia. In comparison to the EOL model, the ISC-Aermod has the advantage of a more state of the art design and is capable of greater utilization of the Zaporizhzhia HydroMet data. This modeling tool estimates atmospheric stability classes rather than the "worst weather conditions" used by the EOL. In addition, annual average pollutant concentrations are estimated rather than maximum 20-minute concentrations. Consequently, because of dependence on short term higher estimates,

Table 4. Estimation of the annual average TSP and PM_{10} concentrations and population at receptors (*i.e.*, receptor points, RP) in Zaporizhzhia.

RP	TSP (modeled) ($\mu g/m^3$)	PM_{10} (ext.) ($\mu g/m^3$)	$PM_{2.5}$ (ext.) ($\mu g/m^3$)	Population
1	330	180	120	52,958
2	420	230	150	62,146
3	510	280	180	323,963
4	580	320	210	144,292
5	640	350	230	61,695
6	690	380	250	78,978

*Total population at all listed receptors (9) was 83,480; ext. = extrapolated.

EOL estimates tend to be much higher. Thus, the Zaphorizhzhia study uses a more accurate state-of-the art air dispersion methodology than previously practiced in Ukraine. Through the successful development of the Zaporizhzhia pilot, not only has Ukrainian risk assessment expertise been further developed, but centers of risk assessment expertise have also been established for continuing applications across Ukraine.

The 2007 emissions inventory and the subsequent dispersion modeling developed for the Zaporizhzhia pilot study show a range of pollutants to which significant segments of the population are exposed; these exposures include particulate matter and a number of carcinogens. The results of the pilot study identified major sources of pollution, what types of pollutants were expected to be emitted, and areas in the Zaporizhzhia with the greatest exposure. Such information is critical for the placement of monitors to both confirm the distribution of the pollution geographically and identify pollutants in the plume that should be monitored. Although monitoring data of the Sanitary and Epidemiologic stations of Zaporizhzhia were briefly mentioned in the final Ukrainian report, no monitoring data for any pollutants were provided or compared to the modeled ambient concentration estimates. The report also noted that the content of respirable fine particles (PM_{10} and $PM_{2.5}$) was not monitored and accounted for (*i.e.*, they were not monitored). The UN Economic Commission for Europe [28] stated that in specific areas, such as Zaporizhzhia Oblast (in the highly polluted Donetsk-Dnieper area), a regional monitoring system and observation network was created to bring together all active monitoring entities. The most recent UN report for Ukraine [29] was published in 2007 and notes that:

Self-monitoring by enterprises is not properly carried out and related data are not closely analyzed. Last but not least, findings from inspections end up in statistical databases and are not followed up with in-depth analysis and appropriate actions. Even though a monitoring programme was adopted in 2004, the related budget strengthened and the monitoring network developed, there are still significant gaps in the monitoring coverage; priorities are often absent or contradictory; the treatment of data is inappropriate; and the data are practically unavailable. Moreover, there is no process for reconciling the data collected by different ministries, which results in different sets of values being issued for the same indicator. Some oblast environmental authorities have recently established online databases linking all monitoring institutions and polluting enterprises in their regions, an effort that needs to be replicated in other oblasts and at the national level.

Descriptions of chemical classes such as nickel and chromium compounds in the existing emission inventories lack speciation of the emissions; the appropriate apportionment of emissions cannot be done between members of the group that have differing carcinogenic potencies. For example in the case of Chromium compounds, assignment of the highest carcinogenic potency estimate for all chromium emissions can lead to an overestimation of risk.

The ratios of $PM_{2.5}/PM_{10}$ vary for emission sources with different types of technologies, industrial sectors, fuels, and by distance from emission sources to monitoring locations, etc. Cities that are not located in arid/ semi-arid or agricultural zones, but have high traffic emissions and relatively low fugitive road dust, will tend to have very high $PM_{2.5}/PM_{10}$ ratios [27]. Because the conditions in Zaporizhzhia closely resemble the general case in Russia and Ukraine where coal-fired power contributes a significant portion of air pollution, the estimates of $PM_{2.5}$ have less variation due to sandstorms and confounding by agricultural dust generation. The Zaporizhzia emission inventory is for major stationary sources of PM and not mobile sources. Therefore even with only capturing a portion of the total particulate load through modeling large stationary sources, the modeled estimates may be underestimates of fine particle loads. The emission inventory for particulate matter would also be improved by the inclusion of speciation between larger and smaller particles (*i.e.*, PM_{10} vs. $PM_{2.5}$) that would allow for a more accurate prediction of risk from mortality. Clearly, the accuracy of a risk assessment of the Zaporizhzhia air pollution is limited by uncertainty in the emissions inventory. Improvement of emissions accuracy would in turn provide the basis of a more accurate assessment of hazard and health risk.

Given the limitations the emissions inventory to discern PM_{10} and $PM_{2.5}$, ambient monitoring would help to verify the modeling results. Ground-level measurements of air pollution, especially those of $PM_{2.5}$ are not available for much of the world [30]. Ambient monitoring in Ukraine is even more limited and the work by Brauer *et al*. using satellite estimates based on population density and assumptions for $PM_{2.5}$ generation without consideration of the local and high industrial PM sources does not give an accurate assessment for comparative purposes. Their study notes that there is no Eastern European (*i.e.*, Russia and Ukraine) monitoring to validate their results. Ambient monitoring estimates for the same period were taken from Brauer *et al*. [30]. Their estimates were derived from global estimates of $PM_{2.5}$ using satellite observations, a global atmospheric model, an econometrics model, and airport observations of visual range. Briefly, satellite-derived and TM5 global atmospheric model estimates were averaged at a $0.1^\circ \times 0.1^\circ$ grid cell resolution (equivalent to approximately 11 km × 11 km at the equator). In this process, population density is used as a proxy to identify high emission ("urban") areas within each $1^\circ \times 1^\circ$ grid cell. The outputs of the Brauer *et al*. [30] model are population-weighted averages and not ambient concentrations and the model assumed that urban primary $PM_{2.5}$ should not exceed the rural concentration by a factor 5. All secondary components (SO_4, NO_3) and primary natural PM (mineral dust, sea salt) are assumed to be distributed uniformly over the native grid cell and hence are not incremented.

Without monitoring data, how realistic are the reported values? The World Health Organization (WHO) Regional publications noted Monitoring in Prague was reported to show average PM_{10} in the city center to be 94 $\mu g/m^3$ with daily concentrations as high as 225 $\mu g/m^3$ during a 3 month period (January-March) in 1997 [31]. For Ukraine, National as well as WHO standards for specific pollutants were reported to be exceeded in almost all major Ukrainian cities with the values for nitrogen dioxide and particulate matter exceeded at almost all of the country's national measurement stations (*i.e.*, National Ukrainian standard of 150 $\mu g/m^3$ of particulate matter and WHO standard *i.e.*, 40 $\mu g/m^3$ for PM_{10}) [29].

A question arises as to whether the conditions described in the pilot still exist. When economic conditions force the shutdown of these industries and thereby limit emissions from these sources, emission estimates from this case-study can result in an overestimation of risk. According to World Bank estimates of GDP [32], 2005 was $86B (current USD), up from about $65B in 2003, the first year in this study. GDP peaked in 2008 at $117B and is still recovering from the recession of 2008. The WHO 2007 [28] report states that the steel industry still dominated the Ukrainian economy and that in 2004, the capacity utilization of Ukraine's steel industry was at a high of 89%, with Ukraine being the seventh biggest metal producer in the world. Donetsk oblast alone accounted for about 40 per cent of total air emissions in Ukraine, followed by Dnipropetrovsk (21%) and Zaporizhzhia (6%) oblasts [28]. Ukraine remains one of the top producers of steel in the world with 2.3% of the world production as of 2011; 2011 levels are similar to the average production from 2001-2005 [33,34]. Therefore, the emissions inventory estimates in this study have not been reduced by the shutdown of these industries.

As described above, this emission inventory contains uncertainty and the estimation of individual risk to the population living in Zaporizhzhia based upon it is beyond the scope of this paper. Nonetheless, the development of the emissions inventory and subsequent application of more current dispersion modeling should be viewed as a success and did fulfill the goals of the CPB. An important aspect of the project was that not only did local officials and health experts help in providing exposure information, but outside experts in various aspects of risk assessment (e.g., exposure and toxicology) participated from several countries. The results from the case-study provided a useful tool for risk management and environmental policy. They have helped aid further development of risk assessment expertise and capacity. Under the auspices of the CBP, outside experts have also been able to contribute to risk management and policy development. However, the integrity of the process has been maintained as one developed by Ukraine for its specific needs and situation. It is important to note that the types of exposure information needed for the case-study have not been easy to access as the Ukrainian system did not have a tradition of public emissions databases. A great deal of credit is due to the local officials and industrial facilities for providing this information. Hazard information for the pollutant emissions can be obtained from a number of international sources, however exposure information cannot. In addition and as a result of this effort, a center has been established that still is in operation in Kyiv (*i.e.*, Center of Environmental Health and Risk Assessment) within the O. M. Marzeiev Institute of Hygiene and Medical Ecology.

5. Disclaimer

This manuscript has been reviewed by the US Environmental Protection Agency and approved for publication. The views expressed in this manuscript are those of the authors and do not necessarily reflect the views or policies of the US Environmental Protection Agency.

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