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Global deposition of airborne dioxin

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ABSTRACT

We present a global dioxin model that simulates one year of atmospheric emissions, transport processes, and depositions to the earth's terrestrial and marine habitats. We map starting emission levels for each land area, and we also map the resulting deposits to terrestrial and marine environments. This model confirms that 'hot spots' of deposition are likely to be in northern Europe, eastern North America, and in parts of Asia with the highest marine dioxin depositions being the northeast and northwest Atlantic, western Pacific, northern Indian Ocean and the Mediterranean. It also reveals that approximately 40% of airborne dioxin emissions are deposited to marine environments and that many countries in Africa receive more dioxin than they produce, which results in these countries being disproportionately impacted. Since human exposure to dioxin is largely through diet, this work highlights food producing areas that receive higher atmospheric deposits of dioxin than others.

1. Introduction

Dioxins and furans consist of 210 structurally similar chemicals that are unintentional byproducts of combustion processes. Of these 210 chemicals, 17 have toxicological properties of concern to human and ecosystem health. The most potent form, 2,3,7,8-tetrachlorodibenzo-*p*-dioxin, is a known human carcinogen (International Agency for Research on Cancer, 1997) and the main exposure route to humans and other organisms is through diet (World Health Organization, 2007). Dioxins are one of the chemicals listed in the Stockholm Convention on Persistent Organic Pollutants. They are listed under Annex C, and, as such, parties must take measures to reduce the unintentional releases with the goal of continuing minimization and, where feasible, ultimate elimination (Olsen, 2003).

When dioxins are emitted to the atmosphere or land, they can subsequently undergo long range atmospheric transport until they are deposited to regions distant from the source (AMAP, 2004). This is due to the 'grasshopper effect' (Gouin et al., 2004) whereby dioxin previously deposited to land surfaces can undergo further transport through successive evaporation cycles. Dioxin has endocrine-disrupting effects and interacts with the components of ecosystems – it is lipophilic and concentrates in lipid tissues of living organisms causing health concerns for ecosystem components and people.

For toxicological purposes, dioxins can be expressed as toxic equivalents (TEQs) as the 17 forms of dioxins and furans of concern have different toxicological properties. TEQs express the toxicity of dioxins relative to the most toxic form – 2,3,7,8-tetrachlorodibenzo-*p*-dioxin. For human health purposes, dioxins have a tolerable daily intake (TDI) of 1–4 picograms-TEQ per kilogram body weight and day, but the United Nations has recommended that the intake of dioxin should be reduced to the lowest possible level because subtle effects can occur at levels of 2–6 picograms-TEQ per kilogram body weight and day (van Leeuwen et al., 2000).

Despite its known toxicity and adverse human health effects, there is little data concerning the global impacts of dioxin. Global emission inventories of dioxin production are incomplete and most inventories are available only for the year 1999 (United Nations, 1999). The importance of this study is that it (1) identifies on a global basis where the most heavily impacted terrestrial and marine ecosystems are likely to be, (2) helps to identify key regions where data are missing that could be of concern, and (3) highlights food production areas that receive higher inputs of dioxin than others. The purpose is to lay the foundation for further research into the effects of dioxin in marine waters and the food webs in marine ecosystems.

2. Methods

The cycling of dioxin in our global model involves the production of dioxin over land, the dispersion of dioxin through

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the atmosphere, the deposition of dioxin onto land and water, and the transportation of dioxin from land in water basins to coastal waters. For methodological details, see the Supplementary material. We use weekly averaged data for dioxin production and atmospheric dispersion. We simulate one year of production, dispersion, deposition and transport of dioxin (Fig. 1) and display the results for land and marine areas separately on a global map with a resolution of 259,200 ½° by ½° cells (79,296 terrestrial, and 179,904 marine). Since some countries are more heavily impacted by dioxin than others, we compare between countries by using a deposition to emission ratio. For each country, the amount of dioxin deposited to land and ocean cells over the one year simulation was compared to the annual amount of emissions.

A previous global model of dioxin noted that depositions were greater than emissions likely due to the photochemical transformation of pentachlorophenol, a common wood preservative, to dioxin (Baker and Hites, 2000). Thus, global emissions were approximately 12.5 times lower than the estimated total deposits of 13,100 kg, and only 5% of emissions were assumed to be deposited to oceans (Brzuzy and Hites, 1996). However, in a preliminary run of our model (that used monthly averaged wind fields), ocean depositions were shown to be significantly larger than previously thought with estimated dioxin deposits to oceans being approximately 38% of the total annual emissions. Therefore, we increased the global total of dioxin production to 17,226 kg. We refined the initial monthly model by using weekly averaged wind fields, and we assumed 1/52 of the annual global dioxin production was emitted each week from land to the atmosphere and used a factor of 60 to convert the production of dioxin to toxic equivalents (TEQs) of the most toxic congener 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (Thomas and Spiro, 1995).

The production of dioxin over land used a global spatialized data set of gross domestic product (GDP; Dilley et al., 2005) as the estimate for countries' dioxin production based on an environmental Kuznets curve (Fig. 2). Within each country, the production of dioxin was made proportional to the GDP of each country's land cells. The atmospheric dispersal of dioxin was modeled using a Geographic Information Systems (GIS)-based model incorporating diffusion of $4.86 \times 10^{-6}\ m^2\ s^{-1}$ (Chiao et al., 1994), wind speed and direction. Wind speed and direction were computed as weekly means from ten years of data (1991–2000) from the European Centre for Medium-Range Weather Forecasts (Anon., 2006) and were interpolated to ½° by ½° resolution from the original 2.5° by 2.5° format. Deposition of dioxin was simulated using a temperature-dependent characteristic travel distance (CTD) approach for 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (Bennett et al., 1998; Klasmeier et al., 2004) that incorporates the grasshopper effect (Gouin et al., 2004).

Once atmospheric dioxin was deposited to land, the movement of dioxin through water basins to marine coastal areas was also incorporated. All land areas were made part of a global network of water basins (n = 6,031) and dioxin was transported from land within water basins to coastal marine waters unless basins were identified as being landlocked and had no ultimate drainage to oceans (n = 166). Spatial data concerning water basins were made available by Prof. C.J. Vörösmarty of the Water Systems Analysis Group (<www.wsag.unh.edu>) at the University of New Hampshire. We based the amount of dioxin transported through water basins on a relationship between water run-off and the fraction of dioxin transported from soil in water basins (Kanematsu et al., 2009; Vasquez et al., 2004).

3. Results

The approach used for the initial distribution of dioxin emissions suggested several areas of likely high local production of dioxin due to higher levels of economic activity (Fig. 3). These were dominated by eastern North America, Europe, South Asia (particularly the Indian subcontinent), and East Asia (China, Japan and South Korea). Countries belonging to the G20 account for over 80% of the estimated annual emissions with Japan, the U.S., and China accounting for 30% of the annual global emissions. However, it is smaller states such as Singapore and Malta that have the highest emissions on a *per* area basis.

The annual global dioxin production of 17,226 kg is equivalent to approximately 287 kg-TEQ. After we ran the model to simulate one year's production, dispersion, deposition and transport of dioxin, approximately 9 kg-TEQ (3%) of the annual dioxin production remained in the atmosphere. The model predicted that most of the annual production of dioxin, 163 kg-TEQ (57%), was deposited to land areas, while ocean waters received approximately 115 kg-TEQ (40%). Large parts of North America, most of central, northern and Eastern Europe, as well as much of the Indian sub-continent

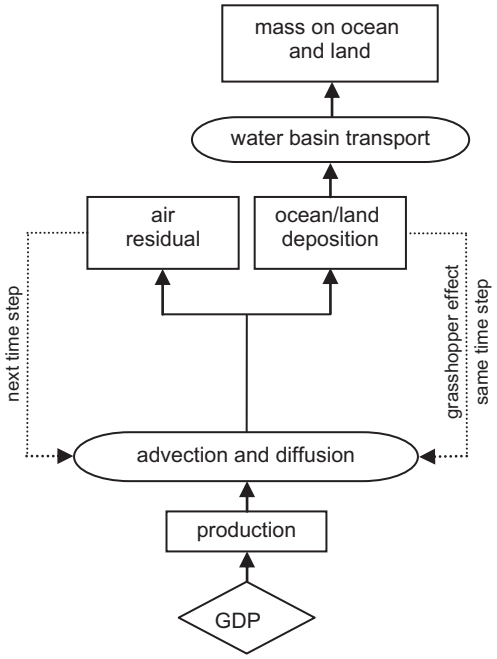

Fig. 1. Flow diagram representing the model simulation of production, atmospheric dispersion, water basin transport and deposition of airborne dioxin to the earth's surface.

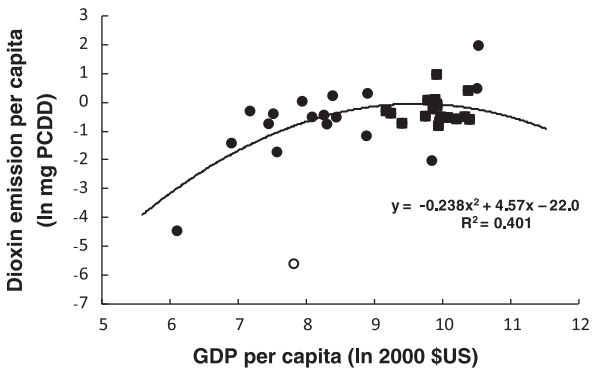

Fig. 2. The environmental Kuznets curve used to estimate countries' per capita dioxin emissions based on GDP per capita. Original data used in Baker and Hites (2000) are shown in square symbols (■), new data are shown in circles (●) with China's data (○) omitted from analysis.

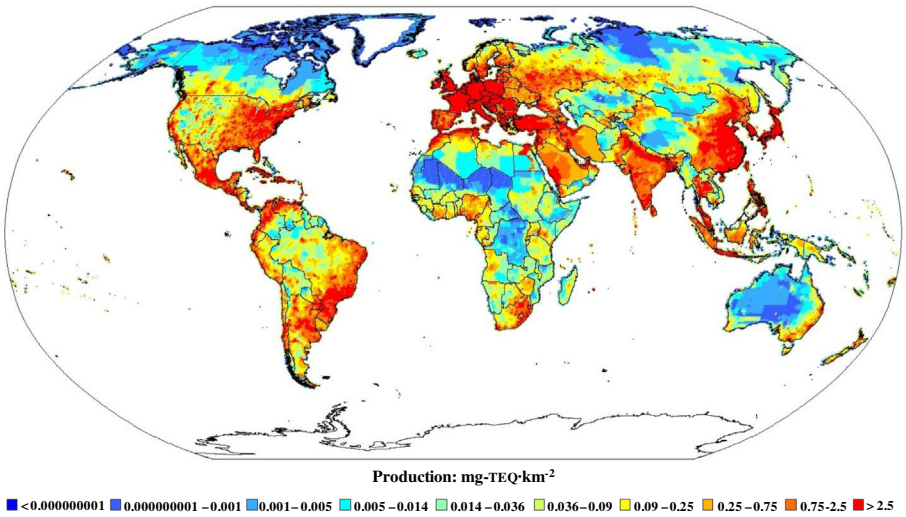

Fig. 3. Global production of dioxin as toxic equivalents of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin spatialized over the earth's surface with emissions based on an environmental Kuznets curve.

and East Asia have high terrestrial depositions of dioxins (Fig. 4a). Dioxin depositions to land range from 1×10^{-8} mg-TEQ km^{-2} to 146 mg-TEQ km^{-2} with the lower values in the Antarctic, and the highest values found in Europe and South Korea.

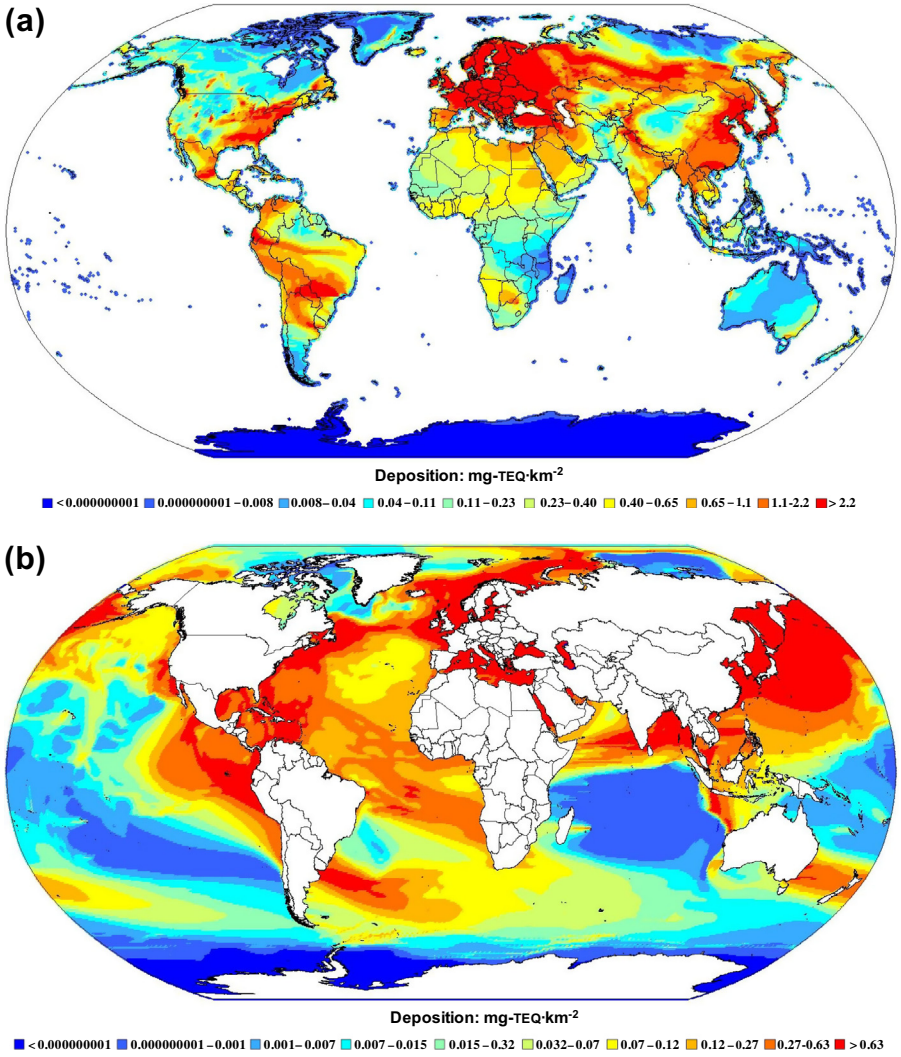

Fig. 4. Deposits of dioxin to land (a) and to the world's oceans (b) presented as toxic equivalents of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin after simulating one year of transport processes of global atmospheric emissions.

Under the assumption that the characteristic travel distance and effective decay rate of dioxins as measured under terrestrial conditions also applied to oceanic conditions, it is suggested that many ocean areas around the world may also have relatively high dioxin loads. These include the northeast and northwest Atlantic, Caribbean, Mediterranean, northern Indian Ocean, and large parts of the north-western Pacific and South China Seas (Fig. 4b). However, several areas of relatively low concentration of dioxins were also identified, specifically parts of the west coast of South America and northern parts of the west coast of North America (Fig. 4b). Marine deposited dioxin ranged from 1×10^{-8} mg-TEQ km^{-2} to 33.5 mg-TEQ km^{-2} and were similar to terrestrial deposits in that lower values were associated with the Antarctic, but the highest values were found in waters off Japan and South Korea. High dioxin depositions were also found in the marine waters of countries around Baltic and Mediterranean Seas.

Dioxin deposited to the oceans results from the production of dioxin on land, and thus the oceans can act as a sink for dioxin. Our initial (monthly) model allocated 38% of annual dioxin production to the ocean, while our final (weekly) model allocated 40% of annual dioxin production. The High Seas receive the largest amount of dioxin (~36 kg-TEQ) as modeled here and, once standardized by area, depositions to the High Seas are approximately 0.16 mg-TEQ km^{-2}. The most impacted countries when comparing the ratio of deposits to emissions were found in Africa and Asia. Of the top 20 impacted countries, 11 are located in Africa and 6 in Asia. The 11 African countries' per capita GDP average less than US$250 person year^{-1}, and the Asian countries average less than US$450 person year^{-1}.

4. Discussion

We have presented the results of a global, dynamic model that describes the annual production, atmospheric dispersion, water basin transport, and depositions of dioxin to marine and terrestrial areas. Specifically, our work provides the opportunity to examine the impacts that dioxin has on marine ecosystems. Coastal shelves provide most of the fish destined for human consumption (Pauly et al., 2002) and some coastal ecosystems (e.g., eastern North America, China, and Europe) receive much larger dioxin loads than other marine areas (e.g. most of South America and Australia). Past research has shown that dioxin levels in fish oils derived from forage fish around Europe and eastern North America have higher concentrations than those sourced from Peru (FAO, 2002; Hites et al., 2004). We would expect a similar relationship for all ecosystem components, with higher concentrations found in places that receive higher inputs of dioxin.

Our model suggests that the oceans are more impacted by dioxin than previously thought. Previously, it was assumed that the ocean only received approximately 5% of the global annual production of dioxin (Baker and Hites, 2000). Here, we have shown that, using spatial and temporal distributions of dioxin emissions in a kinematic model, the oceans receive approximately 40% of the annual deposits. Our first (monthly) model suggested 38% which is very close to our final (weekly) result of 40% and we assume the 2% difference is due to temporal aliasing.

Although much of the ocean depositions are confined to coastal areas, the impacts on the High Seas are not negligible and have consequences for food security. One concern is that dioxin is more likely to partition to plastic particles that are eaten by marine plankton and fishes, an entering point for accumulation (Rios et al., 2010). Thus, human populations with high seafood consumption levels may be exposed to higher levels of dioxin than previously thought.

Seventy-four countries receive more dioxin on land and in the waters of their Exclusive Economic Zones (EEZs) than they produce, including twenty-three African countries (Supplementary material, Table 2). Wind patterns and the fact that Africa is located near Europe and the Arabian Peninsula (two areas of high GDP and thus, dioxin production) combine to affect Africa's food security disproportionately. Thus, Africa and parts of Asia seem to be areas that would benefit from further study of the amount of dioxins found within different ecosystem components. However, these countries may need assistance in the monitoring of dioxin in food products because of their relatively low GDP and capacity for such activity.

This model does not account for direct (i.e., non-atmospheric) releases of dioxin to land or water and this contributes to the lack of mass balance between emissions and depositions for dioxin. However, using the Kuznets curve for dioxin emissions lowers the mass balance discrepancy from 12.5 to 9.7. Polar regions receive little dioxin over the model simulation time of one year, but these areas may be impacted by the accumulation of this toxin over longer time periods. Simulations that were run for a longer duration would show higher levels of dioxin in polar regions as dioxin migrated polewards as a result of the grasshopper effect.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.marpolbul.2013.07.041.

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