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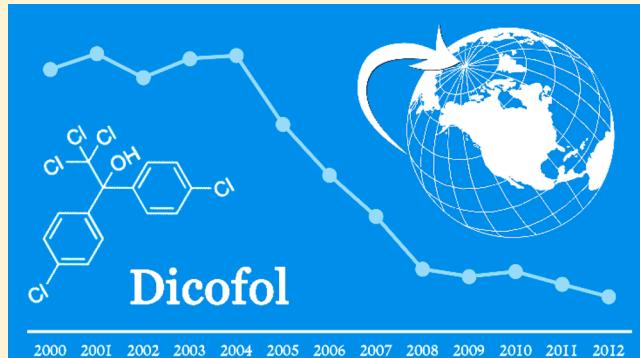
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Supporting Information

ABSTRACT: The uncertainties on whether dicofol can be identified as a persistent organic pollutant (POP) in terms of its long-range transport (LRT) potential and global distribution, are always a controversial topic during international regulation deliberations. The lack of monitoring data in remote background regions necessitates a model-based evaluation approach for assessing the global distribution of dicofol. However, few model simulations are available at present, as there is no inventory available for global historical usage of dicofol that has sufficiently high spatial and temporal resolution. To describe the current status of global emission, we first developed an inventory of global dicofol usage for the period of 2000–2012 at $1^\circ \times 1^\circ$ latitude/longitude resolution. We then assessed the LRT potential of dicofol by calculating its Arctic Contamination Potential using the Globo-POP model. In addition, we simulated the global mass distribution and the fate of dicofol in the environment using the BETR-Global model at $15^\circ \times 15^\circ$ latitude/longitude resolution. Our estimated inventory established that over the period of 13 years, a total of 28.2 kilo tonnes (kt) of dicofol was applied and released into the environment. East and Southeast Asia, the Mediterranean Coast, and Northern and Central America were identified as hotspots of usage and release. Dicofol exhibited a higher Arctic Contamination Potential than several confirmed Arctic contaminants, and a larger current volume of consumption than most existing POPs. The results of our BETR-Global simulation suggest that (i) dicofol can indeed be transported northward, most likely driven by both atmospheric and oceanic advects from source regions at midlatitudes, and (ii) dicofol will be enriched in remote background regions. Continuous use of dicofol in source regions will result in exposure both locally and in remote regions, and the examination of the potential for adverse effects is therefore of paramount importance. Proactive restrictions at the international level may be warranted.



INTRODUCTION

Dicofol, the active ingredient of which is 2,2,2-trichloro-1,1-bis(4-chlorophenyl)ethanol, is an organochlorine acaricide that is applied globally to food, feed and cash crops, such as apple, citrus and cotton.¹ Dicofol is synthesized from technical dichloro-diphenyl-trichloroethane (DDT), a first-generation organochlorine pesticide restricted by the Stockholm Convention as a persistent organic pollutant (POP). As a structurally similar substitute for DDT, dicofol has gained particular favor with the agricultural sector in recent decades. However, now being considered a chemical with potential deleterious effects on both wildlife^{2–4} and human health,^{5–7} together with the fact that its end product often, if not always, contains detectable DDT residuals,^{8–11} dicofol has been restricted or prohibited in most developed countries. In addition, dicofol is listed as a persistent toxic substance in a series of multilateral agreements, such as the Convention on Long-Range Transboundary Air Pollution Protocol on POPs (CLRAP POP Protocol)¹² and the Convention for the

Protection of the Marine Environment of the North-East Atlantic (the OSPAR Convention).¹³ In 2013, dicofol was proposed to be classified as a POP, allowing possible international regulatory action under the Stockholm Convention.¹⁴

However, there is disagreement as to whether the use of dicofol should be regulated at an international level. One of the main arguments against regulation was the lack of evidence that would prove its environmental persistence and long-range transport (LRT). Such absence of irrefutable proof is largely due to insufficient monitoring data on the occurrence of dicofol in remote locations such as the Arctic.¹⁴ To date, a limited number of studies have focused on the occurrence of dicofol, because previously it was only considered to be an indicator for

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DDT and related degradates.^{16–18} The only measurement ever undertaken in a remote location was during an expedition that measured several currently used pesticides (CUPs) along the route from East Asia to the high Arctic Ocean.¹⁵ Otherwise, monitoring data from other locations are mostly confined to urban and agricultural regions because dicofol contamination has long been considered merely a local issue.^{19,20} Due to the insufficient amount of realistic monitoring data, simulation using fugacity models is warranted as a powerful tool complementing existing data in evaluating the potential for the long-range environmental transport of dicofol.²¹ By employing assembled information on usage and emissions, computer simulation is useful to answer (a) whether dicofol travels long distance and accumulates in remote areas and (b) how worldwide dicofol concentrations evolve in response to its global usage.

A detailed inventory of either usage or emissions with high spatial and temporal resolutions is a prerequisite for investigating the global distribution of a chemical.²² However, the precise status of global dicofol usage remains poorly understood. Neither a retrospective nor a contemporary inventory is available for most nations, even for the major dicofol-consuming countries. For instance, with the exception of the United States, almost no country has a year-to-year national record for domestic dicofol usage.²³ At present, the only global estimate of dicofol usage available dates back to the year 2000, the geographic resolution of which is at a low continental scale.²⁴ Given that over the past few years, domestic and multinational, rather than international, restrictions of dicofol usage were implemented, the current geographic pattern of usage and emission is expected to considerably differ from the preregulation pattern. Therefore, in order to identify and evaluate the risk profile of dicofol, it will be important to develop an updated version of a temporally resolved inventory that contains geographic emission hotspots.

In this study, we first developed an inventory of global dicofol usage for the period 2000–2012 at a resolution of $1^\circ \times 1^\circ$ latitude/longitude. Next, we evaluated the LRT potential of dicofol by calculating the Arctic Contamination Potential using the Globo-POP model. Finally, we simulated the global fate and environmental occurrence of dicofol using the BETR-Global model. This study aims to improve our knowledge of dicofol's contemporary global use patterns, environmental distribution and LRT potential. Our results will have implications for ongoing discussions at the international level regarding the possible implementation of risk management actions to regulate the use of this compound.

MATERIALS AND METHODS

Gridded Inventory of Global Dicofol Usage From 2000 to 2012. We combined literature surveys, field surveys and personal communication to develop the global inventory of dicofol usage from 2000 to 2012. Here, we outline the principles used in the inventory development; the details of the approach used are described in Text Section 1 of the Supporting Information (SI).

- (1). National statistics or surveys on dicofol usage, if available, received the highest priority in data collection because they are believed to provide accurate estimates with full consideration of peculiarities and data representativeness. For example, the inventory of the United States was directly compiled from county-level survey records

- (2). Verified spatial- or temporal-specific statistical data on cultivated areas and dicofol application rate were collected to calculate national dicofol usage, when the national usage statistical data were insufficient. For example, China's inventory was prepared based on national statistics on prefectural level cultivated areas of major dicofol-treated crops^{25,26} and field surveys on the application rate and market share of dicofol.^{27,28}
- (3). For the known minor dicofol-consuming nations that lack accurate domestic records, we estimated the entire regional or continental usage as a whole rather than elaborating individual national estimates. The shares of an individual nation's usage in regional or continental totals were assumed to be constant throughout the period. For example, time-course usage was extrapolated for the entire Africa and Middle East region, for which only a single continental record was available for the year 2000.¹³
- (4). All estimates were presented in tonnes of active ingredient. The active ingredient content varies from 20% to 85% in commercial dicofol formulations in various countries. For formulation records in which the active ingredient content is unspecified or too vague for interpretation, a conversion was performed using the common active ingredient contents available on the market in the respective countries.

The assembled usages were continent-by-continent allocated into a $1^\circ \times 1^\circ$ latitude/longitude grid system using the methodology introduced by Li et al.,²⁹ with the exception of the United States and China, for which the available county-level and prefecture-level usage data were used. Here, the $1^\circ \times 1^\circ$ global cropland density database³⁰ (accessible online at <http://www.sage.wisc.edu/iamdata/>) served as surrogate data for gridding in accordance with common practices in previous researches.^{31,32} Geographic constraints of five dicofol-treated crops (SI Figure S1) were also applied to confine the spatial pattern of dicofol usage within the major dicofol-treated regions.

Globo-POP Modeling of the LRT Potential of Dicofol.

The LRT potential of dicofol was assessed by calculating the Arctic Contamination Potential (ACP_{10}^{air}) using the Globo-POP model (version 1.1; courtesy of F. Wania from the University of Toronto at Scarborough). The Globo-POP model is a Level IV (nonequilibrium and nonsteady-state) fugacity model.³³ This model divides the global environment into ten latitudinal climatic zones that circle the earth, each of which consists of six interconnected compartments: atmosphere, agricultural soil, uncultivated soil, freshwater, freshwater sediments, and surface ocean. The northernmost latitudinal climatic zone represents the Arctic region. Apart from atmospheric layers, all compartments are collectively defined as the "surface media". The technical description of the model has been detailed elsewhere,^{33,34} and its structure and scale are schematically illustrated in SI Figure S2.

Zone-specific compartmental parameters and year-specific zonal emission pattern are required as model inputs. In our simulation, we used a generic emission scenario, namely, a hypothetical and standard emission mode that assumes that all dicofol is released into the atmosphere with a zonal emission pattern identical to the global population distribution (details

are provided elsewhere³⁵). The use of this generic scenario aims to avoid simulation differences resulting from distinct emission scenarios, thereby providing results that are comparable with previous simulations on reference substances.³⁶

BETR-Global Modeling of Realistic Global Distribution. Realistic global mass distributions and the temporal evolution of dicofol concentrations for the entire 2000–2012 period were simulated using version 2.0 of the Berkeley-Trent-Global (BETR-Global) model.³⁷ The BETR-Global model is a fugacity-based model that is capable of both steady-state (i.e., Level III) and time variant (i.e., Level IV) calculations.^{37,38} In this study, we performed the Level IV simulation. This model divides the global environment into a set of 288 15° × 15° latitude/longitude grids, each of which consists of seven interconnected compartments: upper air, lower air (planetary boundary layer), vegetation, freshwater, seawater, soil and freshwater sediments. The model allows to generate grid-averaged concentrations using prescribed compartmental characteristics, monthly resolved meteorological and oceanic parameters, and month-specific grid emission inventories. The technical description of the model has been detailed elsewhere,^{37,38} and its structure and scale are schematically illustrated in SI Figure S3.

In this study, we assumed that all used dicofol was released into the environment. We performed five simulations using distinct mode-of-entry scenarios: (I) lower air: vegetation: soil = 2:80:18; (II) lower air: vegetation: soil = 2:90:8; (III) lower air: vegetation: soil = 2:93:5; (IV) lower air: vegetation: soil = 10:80:10; and (V) lower air: vegetation: soil = 50:45:5. These parallel simulations test the sensitivity of the model to the splitting of the emissions into different environmental compartments.³⁹ Our 1° × 1° global annual emission inventories were subjected to the following modifications for input into the model: (1) adjacent 225 grids were merged to create the emission inventory at a 15° × 15° resolution, and (2) the annual emissions into lower air were reallocated into individual months by adopting built-in monthly resolved emission factors.³⁷

We need to consider the initial dicofol concentrations at the commencement of the simulation period, which resulted from the accumulation of the historical emissions of dicofol prior to the simulation period. In this study, a rough emission inventory from 1990 to 1999 (Text section 2 in the SI, Table S1 and Figure S4) was used in a preliminary calculation to establish the initial environmental burden of dicofol ("spin-up" period^{40,41}). A decade is believed to be sufficient for describing the influence of compartmental accumulation, allowing for dicofol's maximum overall persistence of 65 days⁴² that is considerably shorter than the spin-up period.

Physicochemical Information on Dicofol. The two models use the physicochemical properties of dicofol as inputs. Selected measured values (SMVs) from literature were compiled and evaluated with careful consideration of their representativeness and reliability (SI Table S2). For partition coefficients (K_{OA} , K_{OW} , and K_{AW}) and their related variables (water solubility and vapor pressure), the original SMVs were further adjusted to final adjusted values (FAVs) following the methodology of Beyer et al.,⁴³ which ensures the internal thermodynamic consistency between the solubility and partition coefficients.⁴⁴ For the remaining variables, the SMVs were directly adopted in simulations. The SMVs and FAVs are tabulated in SI Table S3.

During the Globo-POP calculation, we conducted a sensitivity analysis to identify the input parameters with the greatest influence on the ACP_{10}^{air} indicator. The simulation was repeated by varying one input parameter at a time to 10% above and below its FAV. The sensitivity (S) is calculated based on the changes in ACP_{10}^{air} with reference to its calculated baseline level using the following equation:

$$S = \frac{[(ACP_{10}^{\text{air}})_{+10\%} - (ACP_{10}^{\text{air}})_{-10\%}]}{20\% \cdot (ACP_{10}^{\text{air}})_{\text{baseline}}}$$

A higher absolute value of sensitivity indicates a greater influence of the corresponding parameter.

RESULTS AND DISCUSSION

Contemporary Global Dicofol Usage Status (2000–2012).

Figure 1 provides an overview of the annual trends in

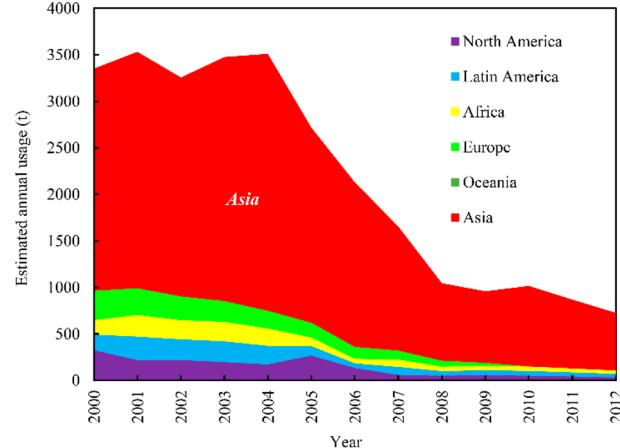


Figure 1. Continental dicofol usage from 2000 to 2012.

global dicofol usage from 2000 to 2012, and SI Table S4 tabulates the numerical data. The global dicofol usage (in terms of active ingredient, which is the same below) decreased from 3.4 kilo tonnes (kt) in 2000 to 0.73 kt in 2012. Of all the 28.2 kt dicofol consumed worldwide during this period, 21.7 kt (76.8%) was from Asia, thus making Asia the largest consumer of dicofol. By using the cropland density as surrogate data together with the geographic constraints of dicofol-treated crops, a gridded spatial distribution for the global cumulative usage at a 1° × 1° latitude/longitude resolution was created (Figure 2a). Figure 2b–d highlight three hotspot regions: East and Southeast Asia, the Mediterranean coast, as well as the Northern and Central America. SI Figure S5 illustrates the changes in the spatial patterns of annual usage for the selected years of 2000, 2005, and 2010. It demonstrates that hotspot regions narrowed sharply in terms of absolute area, and significant shrinkages occurred in the European territories in 2005 and in China and the United States in approximately 2010. SI Table S5 details the dicofol use by tonnage in the major dicofol-consuming countries.

Here, we elaborate on the usage features in individual hotspot regions. In the Far East (Figure 2b), China, India, Japan, and some islands of the Southeast Asia are the major dicofol-consuming countries. China was the largest consumer of dicofol, with a cumulative usage of 19.5 kt (69.1% of the worldwide total) during the study period, although its annual domestic usage was reduced by approximately 75% from 2.0 kt

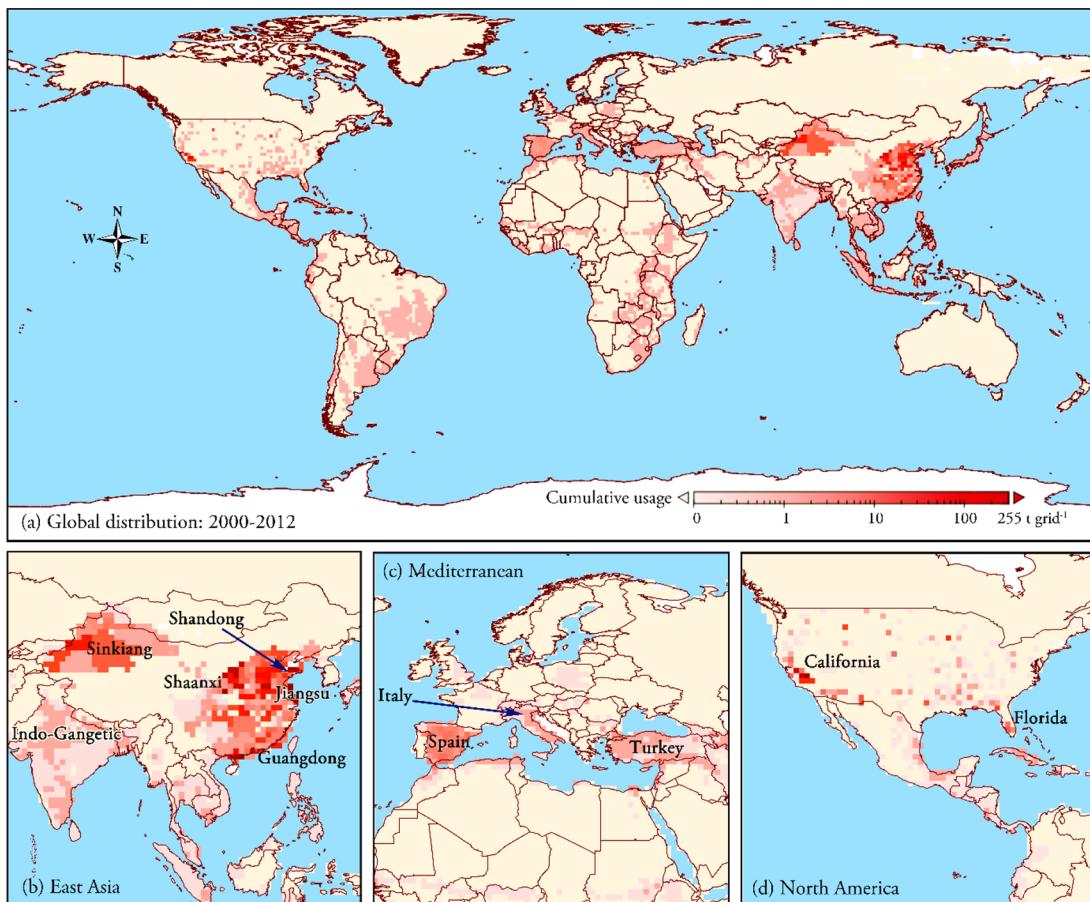


Figure 2. Gridded cumulative dicofol usage from 2000 to 2012 at a $1^\circ \times 1^\circ$ latitude/longitude resolution for the globe (a) and three hotspots East Asia (b), the Mediterranean coast (c), and North America (d).

in 2000 to 0.53 kt in 2012. Major intensive usage occurred in the central and eastern provinces of China, such as Shandong, Jiangsu, Hebei, and Shannxi, as well as in northwest China, including some regions in Sinkiang. Our estimate regarding the geographic distribution of hotspot regions is consistent with the survey results of China's top 10 dicofol-consuming provinces.²⁷ In addition, our estimate (2.09 kt) for the year 2002 is close to that of Qiu et al.⁸ (2.75 kt) in terms of the national total amount; however, it differs in terms of the geographic distribution of hotspot regions because Qiu et al.⁸ highlighted southern provinces like Guangdong and Guangxi as the heaviest consumers. A further comparison at the provincial level (SI Figure S6) shows that the two estimates are in satisfactory agreement for most provinces; the exceptions are Guangdong and Guangxi, where the estimated dicofol usage on tropical fruits such as litchi and longan are responsible for the major discrepancy between the two estimates. For instance, in contrast with our low estimates of 24 and 21 t of dicofol used on litchi in Guangdong and Guangxi, respectively, the estimates of Qiu et al.⁸ were more than 5-fold higher (230 and 90 t; personal communication). There appears to be an overestimation of the amount of dicofol usage, because a recent survey in Guangdong revealed that most dicofol has been used for controlling mites on citrus rather than on litchi;^{45,46} in fact, litchi have been treated more frequently with cypermethrin than with dicofol.⁴⁷

China's leading position in global dicofol usage is manifested in its heavier monitored dicofol level than in other countries.

For example, Fujii et al.⁴⁸ reported higher dicofol levels in breast milk collected from Chinese mothers (geometric mean of 9.6 ng g^{-1} lipid) than that from Japanese (0.32 ng g^{-1} lipid) and Korean (1.9 ng g^{-1} lipid) mothers. Zhong et al.⁴⁹ reported higher dicofol concentrations in the Bohai and Yellow Seas of China (mean of $63 \pm 65 \text{ pg l}^{-1}$) than in the North Pacific and the Arctic ($9 \pm 23 \text{ pg l}^{-1}$). Moreover, DDT impurities were common in commercial dicofol formulations in Chinese market.⁸ As circumstantial evidence, the geographical distribution of the changes in the monitored DDT levels is consistent with the geographical distribution of dicofol usage, allowing us to approximately locate the hotspot of dicofol usage on the map of China. An upward trend in DDT concentration was observed in the provinces that the use of dicofol continued, such as Fujian⁵⁰ and Guangdong,⁵¹ although the production and use of DDT have been completely prohibited since the Stockholm Convention was enacted in China in 2004. In contrast, a downward trend in DDT concentration was observed in northeast provinces in which negligible dicofol was applied; for instance, the DDT concentration in the Heilongjiang River Basin decreased from an average of $3.4 \mu\text{g kg}^{-1}$ dw (dry weight) in 1997–1999⁵² to $0.87 \mu\text{g kg}^{-1}$ dw in 2005.⁵³

India is another major consumer of dicofol in Asia. In India, annual dicofol usage decreased from 145 t in 2000 to 45 t in 2012. Most dicofol was applied in the Indo-Gangetic Plain (Figure 2b), which is the large and fertile area drained by the Indus and Ganga Rivers that stretches over northern and

Table 1. Calculated Arctic Contamination Potentials and Either Cumulative Usage or Emissions of Dicofol During 2000–2012 for Selected Chemicals Confirmed As Arctic Contaminants

chemicals	mACP ₁₀ ^{air} (%)	eACP ₁₀ ^{air} (%)	cumulative usage (U)/emissions (E) for 2000–2012 (t)
dicofol	3.70 (this study)	0.06 (this study)	(U) 28,200 (this study) (E) 0
heptachlor		0.004 ⁶²	(E) 0
aldrín		0.04 ⁶²	(E) 0
hexabromocyclododecane		0.05 ⁶²	(U) 336,000 ⁶³
polychlorinated biphenyl-8	3.17 ⁶⁴	0–0.25 ³⁶	(E) 91.7 ⁶⁵
γ-hexachlorocyclohexane	3.39 ^a	0.42 ^a	(U) 0 ⁶⁶
DDT	2–3 ³⁶	0.25–0.5 ³⁶	(E) 0 ^b
chlordane	3–4 ³⁶	0.25–0.5 ³⁶	(U) 2,067 ^c
polychlorinated biphenyl-138	2.08 ⁶⁴	0.72 ^a	(E) 3.71 ⁶⁵
α-hexachlorocyclohexane	3–4 ³⁶	0.5–1.0 ³⁶	(U) 0 ⁶⁶
perfluorocarboxylic acids		1.08–1.92 ⁶⁷	(E) 2,010–5,470 ^{68d}

^aThe built-in default examples of the Globo-POP model, version 1.1. ^bDuring the period, no DDT was used for the prohibited purpose by the Stockholm Convention, i.e., direct agricultural spraying for plant protection; meanwhile, an average of 15 kt a⁻¹ DDT was used for the acceptable purpose,⁶⁹ i.e., indoor walls spraying against the anopheles mosquito to control malaria. ^cGlobal usage was assumed to equate to the production in China, as China is the only chlordane producer during this period. The total production was compiled from previous studies.^{28,70,71} ^dThe results of the “plausible scenario” for the period 2003–2015 in ref 68.

eastern India. India asked for an exemption to the Stockholm Convention to produce and use DDT as an intermediate in the production of dicofol prior to May 17th, 2009; currently, an Indian state-owned enterprise still manufactures dicofol with an average annual production output of approximately 50 t.⁵⁴

In Europe, dicofol usage was estimated to decrease from 317 t in 2000 to 32 t in 2009. Dicofol usage has basically been banned since 2010,¹² although minor usage was still permitted in some regions for a full year after the prohibition.¹⁹ The highest volumes of dicofol usage were located in the coastal countries on the northern shore of the Mediterranean Sea (Figure 2c). Our estimates (SI Table S5) are in acceptable agreement with those of Denier van der Gon et al.⁵⁵ for the major European dicofol-consuming countries, such as Spain (150 and 125 t in 2000 for our and their estimates, respectively), Italy (87 and 95 t) and Turkey (33 and 24 t).

Spain has long been the only manufacturer and the leading consumer of dicofol in Europe.¹² Historical usage has resulted in serious local dicofol contamination in Spain.⁵⁶ As a recent example, Hart et al.¹⁹ and Coscollà et al.²⁰ separately reported airborne-carried dicofol concentrations in Valencia (a city in eastern Spain) with respective means of 19.8 and 25.0 pg m⁻³ in 2010. These local extremes are almost 5-fold higher than the regional mean in the air of the Bohai and Yellow Seas (3.8 ± 2.3 pg m⁻³), the waters adjacent to the heaviest dicofol-consuming districts in China.⁴⁹ Besides, our estimate captured the geographic distribution of atmospheric concentration of dicofol in the European domain that are covered by the European Monitoring and Evaluation Programme (EMEP),⁵⁷ in which the atmospheric concentration in France and its neighboring countries was approximately a thousand times higher than that in other regions.

In North and Central America, the United States was responsible for the greatest dicofol usage (Figure 2d). Annual dicofol usage in the United States decreased by 90% from 323 t in 2000 to 32.7 t in 2012. Most of the dicofol usage was located along the West Coast, the Gulf Coast, and in the Florida peninsula. California contributed approximately 40% (705 t) to the total national dicofol usage from 2000 to 2012, followed by 15% (270 t) from Georgia and 14% (257 t) from Florida. Likewise, based on the historical data from 1987 to 1996, a similar conclusion was drawn by the United States Environ-

mental Protection Agency (USEPA)¹ that California and Florida were the major consumers. The application rates of dicofol were considerably higher in the United States than other nations. For instance, the average application rate reached 1.3 kg per hectare (kg ha⁻¹) in the United States,¹ whereas it was only 0.44 kg ha⁻¹ in Europe¹³ and 0.31–0.45 kg ha⁻¹ in China (Text Section 1 in the SI).

A worldwide descending trend in dicofol usage appeared for the most recent decade (Figure 1). This trend may be attributed to two factors. First, the awareness of environmental concerns about dicofol and its residual DDT impurities has triggered voluntary restrictions, phase-outs and eliminations under a variety of regional multilateral agreements.¹² Dicofol has no longer been authorized for use in Japan since 2004, in the European Union member states since 2009 and in Canada since 2012.^{12,58} Furthermore, alternative mite-controlling technologies, for example, the environmentally sound integrated pest management (IPM), have also been introduced as agricultural substitutes.²⁷ Second, the preference for dicofol has diminished in many nations due to the drug resistance as a result of the abuse of dicofol,⁵⁹ thus, its market share has decreased. For example, due to the competition of emerging products such as pyridaben, abamectin and propargite,⁶⁰ dicofol has lost its dominance in China's acaricide market. In China, the market share of dicofol decreased from 27% in 1999 to less than 8% after 2008 (calculated from the statistical data provided by China's National Agro-tech Extension & Service Center).

The LRT Characteristic of Dicofol. Using the Globo-POP model, we evaluated the LRT potential of dicofol by calculating the absolute and relative Arctic Contamination Potentials (eACP₁₀^{air} and mACP₁₀^{air}) (Table 1), two intensive properties that are independent of the rate of emission. Based on the simulated total dicofol mass that resides in the Arctic surface media (M_{Arctic}) after a decade of continuous emission, eACP₁₀^{air} is defined as the percentage of M_{Arctic} in the cumulative global emission (E_{TG}), and mACP₁₀^{air} is defined as the percentage of M_{Arctic} in the total dicofol mass remaining in the entire global environment by end of the tenth year (M_{TG}).³⁶ For illustrative comparison, the eACP₁₀^{air} and mACP₁₀^{air} of a number of Arctic contaminants are also summarized in Table 1. The eACP₁₀^{air} of dicofol (0.06%) is close to the low end of the values presented in Table 1, and higher than the values of three legacy POPs:

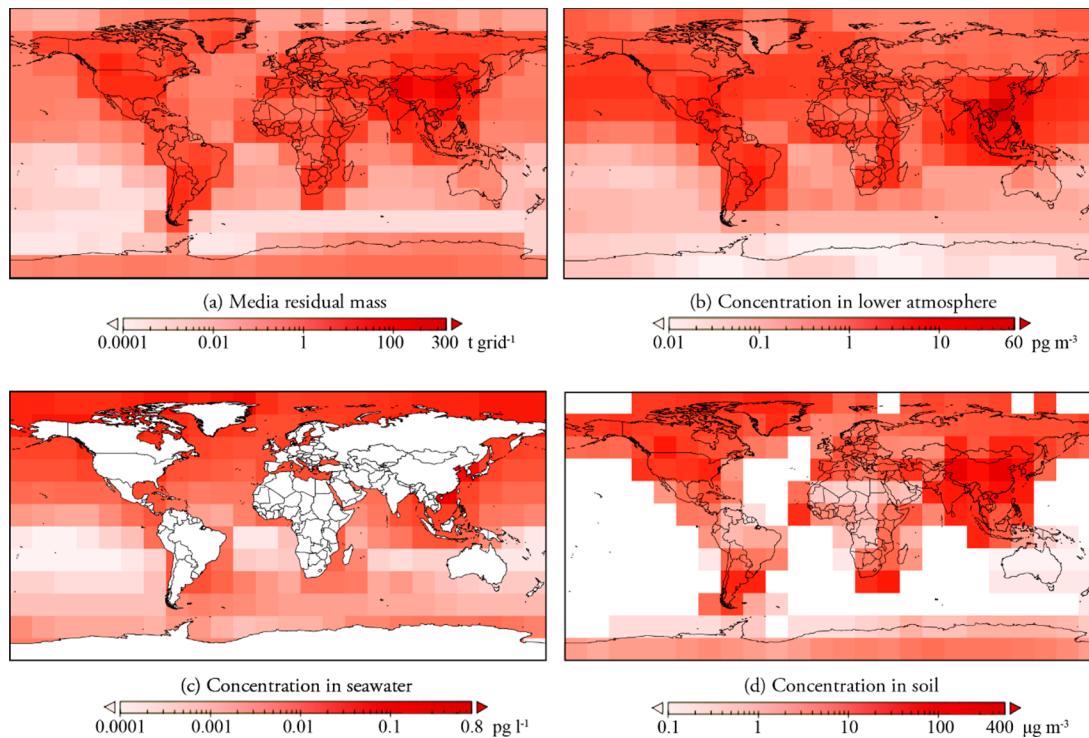


Figure 3. Geographic distributions at a $15^\circ \times 15^\circ$ latitude/longitude resolution of simulated compartmental residual mass (a) and, concentrations in the lower atmosphere (b), seawater (c), and soil (d) at the end of 2012. Note: the continent outline does not represent the gridded land-sea distribution in the BETR-Global model.

heptachlor, aldrin and hexabromocyclododecane (HBCDD). The model output demonstrated that dicofol can be transported from source locations to remote regions with moderate efficiency. Furthermore, dicofol possessed the highest $mACP_{10}^{\text{air}}$ value (3.70%) among the known Arctic contaminants, suggesting that it has the strongest relative enrichment in the Arctic environment. Note that dicofol remains in use and is also emitted into the environment at a high volume, whereas most of the Arctic contaminants have been drastically curbed as a result of implementing the Stockholm Convention (Table 1). As the occurrence (i.e., measurement above detection limits) of any chemical in remote regions is also a function of emission strength, the implications of these findings are not discussed here. Model simulations using the BETR-Global model incorporate the estimated emissions of dicofol are presented below. Likewise, dicofol has been identified as an Arctic contaminant in an automatic screening with the criteria of atmospheric LRT and bioaccumulation.⁶⁷ In fact, dicofol has an atmospheric oxidation half-life of 81 h, and is therefore eligible to be classified as an LRT substance, exceeding a half-life greater than 48 h, which is the criteria for LRT substance under the CLRAP POP Protocol.

Relative to other Arctic contaminants, dicofol exhibits a moderate $eACP_{10}^{\text{air}}$ and the highest $mACP_{10}^{\text{air}}$. This suggests that the persistence of dicofol is more influenced by temperature, with cold temperatures within the Arctic circle favoring slow degradation and relative enrichment; whereas warm temperatures near the equator favoring fast degradation, even faster than the degradation of the Arctic contaminants. In addition, because of its intermediate water solubility (0.8 mg L^{-1}) and $\log K_{\text{AW}}$ (-4.091), a great amount of dicofol is prone to be trapped or sequestered by water bodies during air–water exchanges along the meridional transport.³⁵ The water-

captured fraction is less persistent (half-life of 82 h) than that in other compartments, thus reducing the overall environmental persistence of dicofol before reaching the Arctic. As a corresponding example, γ -hexachlorocyclohexane experiences similar water sequestration in air–water exchanges ($\log K_{\text{AW}} = -3.96$), but its particular inertness in water (half-life of 8760 h) renders its $eACP_{10}^{\text{air}}$ nearly septuple that of dicofol. Our model sensitivity analysis shows that $eACP_{10}^{\text{air}}$ is sensitive to the half-life in uncultivated soil, and $mACP_{10}^{\text{air}}$ was most strongly influenced by $\log K_{\text{AW}}$ (SI Table S6).

Global Distribution and Chemical Fate of Dicofol. To provide more realistic insights into its global distribution and accumulation in remote regions, we simulated the chemical fate and transport of dicofol using the BETR-Global model. Before that, the reliability of the simulation was evaluated by testing its performance during the spin-up period and validating the consistency between simulated and observed environmental concentrations. First, the time series of the global mass during the spin-up (1990–1999) and simulation (2000–2012) periods (SI Figure S7) demonstrates that, since 1992, the response to the annual emission change of the worldwide dicofol mass was fast, which is evident from the simulations of all five scenarios. This quick response means that the mass transfer in the simulated global environment was well balanced by the end of the decadal spin-up period, thus there was negligible bias although we did not consider the emission of dicofol occurring prior to 1990. Second, the comparison between the simulated grid-averaged and observed concentrations¹⁵ (SI Figure S8) indicates that most of the simulated concentrations were within a factor of 4 (between the dashed lines) with reference to the observed levels. As indicated by the correlation coefficients (r) and root-mean-square errors (RMSEs) in SI Table S7, an increased initial emission fraction to lower air, or a decreased

initial emission fraction to soil, improved the simulation performance of marine concentrations but worsened that of atmospheric concentrations. These results indicate scenarios II and III performed better in describing the occurrence of dicofol in both marine and atmospheric environments. Hereinafter, we will only present the results from scenario III to illustrate the global circulation of dicofol. A further investigation shows that the discrepancy between the simulation and observation is mainly due to the underestimation of both the marine concentrations in grid no. 93 (the Yellow Sea and the Sea of Japan), and the atmospheric concentrations in grid nos. 25 and 72 (northern Bering Sea and Chukchi Sea). One possible reason for this is that the simplified simulation generates grid-averaged results and, therefore, underestimates some extreme marine concentrations that resulted from riverine discharges from heavily polluted subgrid areas such as Eastern China.^{15,49} At the same time, our simulation fails to represent the observed spatial variability in the concentration within a grid (see the leftmost horizontally aligned points in individual subplots of SI Figure S8).

Figure 3 shows the spatial patterns of simulated compartmental residual mass, as well as lower atmospheric, oceanic and soil concentrations by the end of 2012. Figure 4 presents the latitude-specific statistical results. The spatial pattern of the residual mass (Figure 3a) was more diffusive than that of emissions (Figure 2); a smaller fraction of dicofol was found to be distributed at low latitudes (between 30°N and 30°S)

whereas a larger fraction at mid- and high latitudes (above 30°N and 30°S; Figure 3a). As indicated in Figure 4a, by the end of 2012, 7.1% (52.2 t) of residual dicofol resided at mid- and high latitudes of the Northern Hemisphere (north of 45°N) where only 2.2% of the global dicofol has been used over the past 12 years; in contrast, merely 15.3% (112 t) of the global residual dicofol was located at low latitudes (between 30°N and the equator) where 29.8% of the global dicofol has been used. Importantly, 1.9 t (0.3%) and 2.2 t (0.3%) of dicofol has traveled to and settled in the Arctic and Antarctic regions, respectively, although almost no dicofol usage occurred in these regions. As shown in Figure 4b, larger fractions of global lower atmospheric residual amounts are observed to be located at lower latitudes (between 30°N and 30°S), whereas larger fractions of global oceanic residual amounts at higher latitudes (north of 45°N). The opposite accumulation latitudes indicate that the net lower atmospheric and oceanic LRTs convey dicofol toward different directions.

In general, relatively higher dicofol concentrations appeared at mid- to high latitudes, except for some extremes in hotspot regions such as the west shore of the Pacific and the Mediterranean coast (Figures 3b–d). For example, the latitudinal average oceanic concentrations of dicofol increased with elevated latitudes from 0.021 pg l^{-1} near the equator (0–30°N) to 0.23 pg l^{-1} within the Arctic (north of 75°N; Figure 3c). In some grids representing remote areas in the Arctic Circle, such as Alaska, Siberia, and North Canada, the simulated dicofol concentrations in soil were comparable to those in tropical dicofol-treated areas, like the Gulf of Mexico (Figure 3d). The latitudinal concentration gradient is clear evidence of the potential of dicofol for LRT, condensation and enrichment in locations distant from its sources.⁷²

Most of the released dicofol disappeared during the LRT, generating a moderate global environmental budget in comparison with its considerable usage volume. By the end of 2012, a total of 731 t of dicofol remained in the environment, compared with a total usage of 28.2 kt during the simulation period, plus 5.2 kt of undecomposed dicofol remained after the spin-up period. It is common that only a relatively small fraction of the total amount of a contaminant released into the environment persists. For example, after a 50 year release period, > 99.0% of released α -HCH degraded, whereas 0.22% survived in the global environment.⁷³ Figure 5 shows the mass distribution of dicofol among environmental compartments in individual latitudinal zones, suggesting that dicofol spreads across multicompartmental from vegetation and soil where 98% of it had been originally applied. For instance, in the 24 northernmost grids representing the Arctic, 9.1% of the zonal dicofol mass resided in aquatic compartments. The soil compartment dominated the global dicofol environmental budget (413 t; 56.5%), followed by vegetation (311 t; 42.6%); whereas 5% and 93% of dicofol had been applied in soil and vegetation, respectively. As shown in Figure 5, at higher latitudes, dicofol was inclined to stay in soil, whereas at lower latitudes, it was found predominantly in vegetation (Figure 5). Vegetation is a dominant, persistent, and slow-release source of dicofol to the global environment, because the largest fraction (93%) of the total released dicofol was applied to the foliage surfaces, and dicofol possessed the longest half-life (17520 h) in vegetation among all compartments. Furthermore, the foliage uptake from the reactive atmosphere compartment was the major route that dicofol re-entered the less reactive vegetation compartment (dicofol meets the criterion of chemicals with log

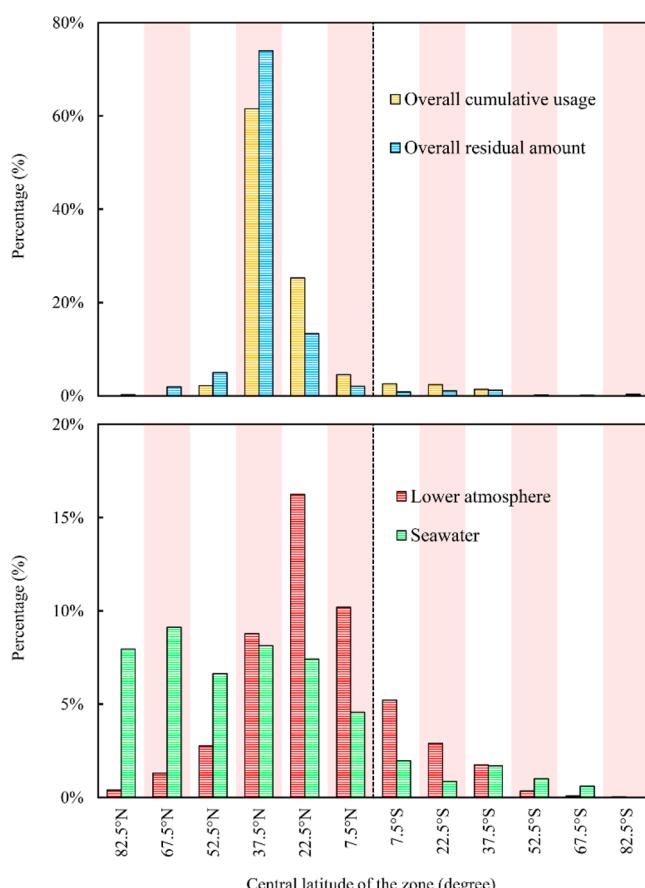


Figure 4. Latitudinal zonal distributions of (a) overall cumulative dicofol usage (2000–2012) and overall residual dicofol amount at the end of 2012, and (b) lower atmospheric and oceanic residual dicofol amounts at the end of 2012.

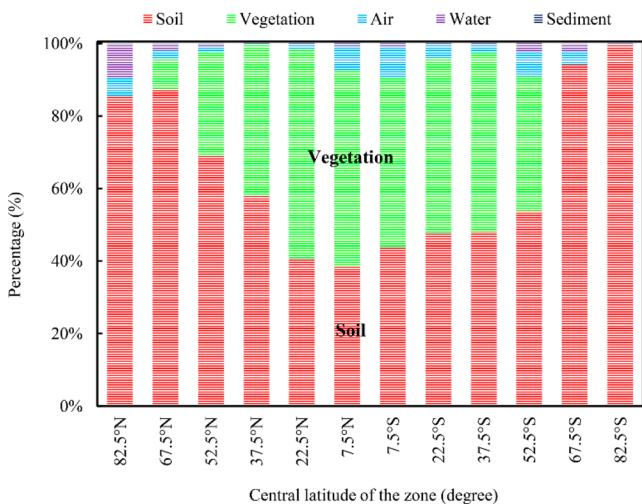


Figure 5. Mass distribution of dicofol among environmental compartments at the end of 2012 in individual latitudinal zones.

$K_{OA} > 6$ and $\log K_{AW} > -6$ in ref 74); this lowered the LRT potential but increased the overall persistence of dicofol.⁷⁴

Figure 6 shows the temporal changes in concentrations in several selected locations of interest. In general, dicofol concentrations declined in response to the reduction of global loading during the period 2000–2012, with the sole exception of soil concentration in the Antarctic (Figure 6b). Even though this region is void of dicofol emissions, its concentration in soil was found to increase before 2005 mirroring the advective inflow of dicofol being higher than the degradation loss, because the global dicofol usage stayed high at that time. Ever since, however, its total concentration has been reduced because the advective inflow of dicofol was subdued relative to the degradation loss. The concentration trends in remote regions, such as the Arctic (Figure 6e), Antarctic (Figure 6f) and Pamir (Figure 6g), resembled the trends of global usage (red line in Figure 6), indicating that they were affected by the global circulation of dicofol. High average concentration levels were found in some hotspot regions, such as central and eastern China (Figure 6h and 6i), California (Figure 6j) and the Mediterranean Coast (Figure 6k). Considering the *Precautionary Principle*⁷⁵ throughout the international management of chemicals, quantitative, and comprehensive assessments on the possible risks to inhabitant health and local ecosystems in these hotspot regions are needed in future studies. The common trends of reduction in concentration in recent years suggests

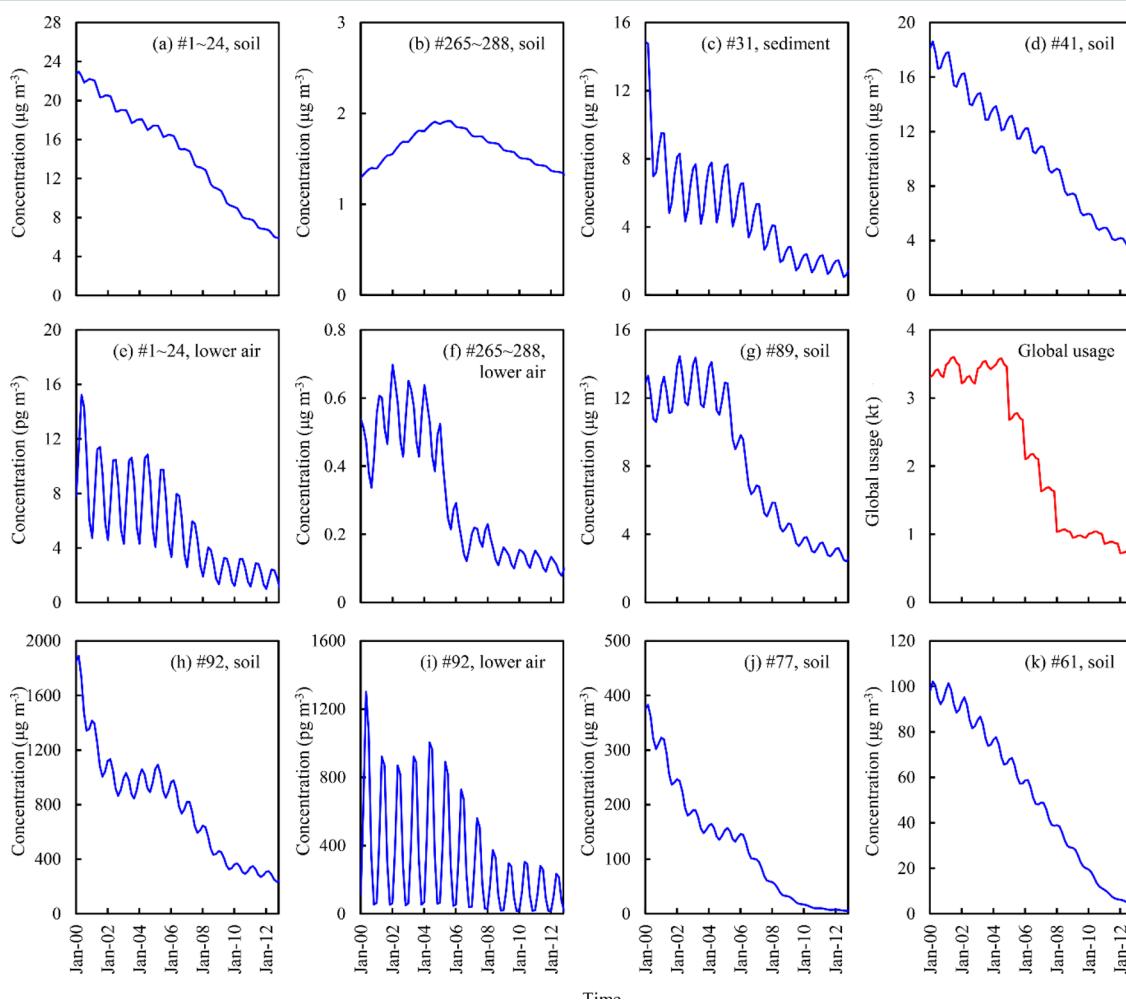


Figure 6. Trends in dicofol concentrations in selected grids from 2000 to 2012. Different grid numbers represent different regions: (no. 1–24) the Arctic, (no. 31) the Great Lakes, (no. 41) the West Siberian Plain, (no. 61) the Mediterranean coastal countries, (no. 89) the Pamir, (no. 92) central and eastern parts of China, and (nos. 265–288) the Antarctic. Global annual usage is also presented for comparison.

that progress has been made toward moderating the global environmental burden of dicofol by existing phase-out actions. However, the rate of decline in concentrations (especially in nongaseous compartments) in remote subpolar or polar regions is less promising than that in global usage. For example, the soil and sediment concentrations in the Arctic have declined from 2000 to 2012 by factors of 3.9 and 3.5, respectively, despite a larger decline in global annual usage by a factor of 4.6. The delayed decline suggests an apparent accumulation of dicofol in the frigid remote regions where the temperature-dependent degradation was substantially slowed down.⁷² This accumulation hinders the instant alleviation of dicofol contamination for decades to come even if global usage is ceased, thereby prolonging the exposure of the Arctic wildlife and ecosystem to dicofol.

■ ASSOCIATED CONTENT

S Supporting Information

Detailed preparation of inventory of global dicofol usage, SMVs and FAVs of dicofol properties, model sketches, modeling spin-up and validation, and simulation results. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

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Notes

The authors declare no competing financial interest.

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Supporting Information

**Global inventory, long-range transport
and environmental distribution of dicofol**

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Text Sections

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Text Section 2 Preparation of rough estimation of the global dicofol usage for the spin-up period
1990 ~ 1999

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Text Section 1 Preparation of inventories of continental dicofol usage for the period 2000 ~ 2012

Here, we describe the development of inventories of dicofol usage in each continent. All mass units appearing in this section are in tonnes of activated ingredient (a.i.).

1. North America

In North America, the United States and Canada are both dicofol-consuming countries.

For **the United States**, the annual information for the years of 2000 ~ 2009 was collected from a county-level estimate of dicofol usage by the United States Department of the Interior and the United States Geological Survey.¹ The estimate was prepared by combining county-level harvested-crop acreage data (from the United States Department of Agriculture National Agricultural Statistics Service) and Crop-Reporting-District-level pesticide-use data (from GfK Kynetec, Inc.), as described in its methodology document.² The data were electronically available in the form of tab-delimited files at <http://pubs.usgs.gov/ds/752/>. We assumed that the annual dicofol usage for the post-2009 period was in a linear decline, for convenience's sake, from the level in 2009 to zero in 2016, because dicofol is anticipated to be prohibited in the United States after October 31st, 2016.³

For **Canada**, approximately 1 t dicofol has been annually consumed since 2000, and the usage was not permitted after December 31st, 2011.⁴ Therefore, we assumed that the annual usage to remain constant at 1 t for each year from 2000 to 2011, and to be zero after 2012.

2. Asia

We adopted different approaches in estimating the dicofol usage in Asia: (1) country-

specific estimates were made for the major Asian consumers, including China, India and Japan; (2) spatial extrapolation, based on gross application rate of dicofol in India, was applied to estimate the dicofol usage in the rest part of Asia that lacks sufficient available information.

For **China**, we used a “bottom-up” method develop inventories of prefectural* dicofol usage allowing for the adequate information available. Dicofol usage on j^{th} crop in i^{th} prefecture in the year t was estimated by eq S1:

$$U_{ijt} = A_{ijt} \times f_i \times r_j \quad (\text{S1})$$

where, A_{ijt} is the cultivated area (kilo hectare, kha) of j^{th} crop in i^{th} prefecture in the year t , f_i is the unitless proportion of dicofol-treated cultivated area in all acaricide-treated cultivated area in i^{th} prefecture (it is assumed to remain constant for all dicofol-treated crop species in a given prefecture), r_j is the application rate (or referred as formulation rate, in tonnes of active ingredient applied per kilo hectare, t-a.i. kha⁻¹) in unit cultivated area of j^{th} crop. The estimated national total was generated by summing up individual estimates of five major dicofol-treated crops (apple, citrus, cotton, litchi and pear) in all 345 Chinese prefectures (Taiwan was excluded) were summed up.

Here are the sources of data: (i) The cultivated area data (A_{ijt}) of apple, citrus, cotton, litchi and pear were gathered from national or provincial annual statistics.^{5, 6} For a few years that lack available data, a linear interpolation was made using the data of two adjacent years. (ii) The proportions of dicofol-treated cultivated area (f_i) of several major dicofol-consuming provinces has been surveyed for the year of 2002.⁷ For other provinces without available

* In Chinese, prefecture is a general term of city, municipality and autonomous prefecture.

data, the number of their neighboring provinces was adopted to estimate the provincial proportion in 2002; eq S2 was adopted to simply extrapolate the provincial proportions in other years:

$$\frac{\text{Provincial Proportion (year } t\text{)}}{\text{Provincial Proportion (year 2002)}} = \frac{\text{National Market Share of Dicofol (year } t\text{)}}{\text{National Market Share of Dicofol (year 2002)}} \quad (\text{S2})$$

where, national market share of dicofol in all acaricides declined linearly from 26.6% in 1999 to 7.3 % in 2009 and maintained steady after that, which was calculated from statistic data provided by China's National Agro-tech Extension & Service Center. (iii) The national generic crop-specific application rates (r_j) were estimated based on realistic survey results in three selected demonstration counties,⁸ and adjusted or localized in accordance with the field survey results for several provinces in which dicofol has been abuse quite often (X. Qiu, personal communication). Here, we adopted the realistic application rates, instead of optimal and rational ones recommended by distributors or administrators, because it is common that pesticides were in excessive and uncontrolled application in most rural regions of China⁹ – the recommended maximum usage limits seem to be invalid in most agricultural practices.

In the three demonstration counties, a total of 9.5 t, 27.5 t and 9.5 t of dicofol, with an average market share (f_i) of 49% among all acaricides, were recorded to be applied to citrus (with the overall acaricide-treated field of 13,000 ha), apple (33,300 ha) and cotton (30,000 ha) during the period 2005 ~ 2009.⁸ The gross application rates (i.e. $f_i \times r_j$ in eq S1) were therefore estimated to be 0.15, 0.17 and 0.22 kg ha⁻¹ for citrus, apple and cotton; the net application rates (r_j) were further adjusted to be 0.31, 0.35 and 0.45 kg ha⁻¹ by dividing

dicofol's national average market share ($f_i = 49\%$) during the five-year period. For some eastern provinces, including Jiangsu, Zhejiang, Anhui and Jiangxi Provinces, dicofol was more intensively used on cotton at a net application rate of 0.58 kg ha^{-1} around 2002 (data were provided courtesy of X. Qiu). For southern provinces like Guangdong, dicofol was more intensively used on citrus at a net application rate of 1.14 kg ha^{-1} (320 t applied on 280 kha of citrus crops).¹⁰ Therefore, adjustments were made to above provinces. In addition, the application rates on litchi and pear were assumed equal to those on cotton and apple in each province.

For **India**, Hindustan Insecticide Ltd. is the single enterprise producing dicofol for the recent decade. The annual sales records for the period 2005 ~ 2011 were available in its official annual reports.¹¹ The annual production volumes for the period 2000 ~ 2004 were available from *Ref. 12*. No export was recorded. In this study, we assumed the annual usage from 2000 to 2011 to equate to the respective sales or production volumes that year.

For **Japan**, an available document¹³ records that, in 1994, 88 t dicofol water powder and 105 t dicofol emulsifiable concentrate formulation were produced, together with 98 t dicofol active indigent and 89 t commercial formulation were imported. Here, we converted all commercial dicofol products into active indigent and then combined them, by assuming that 20% of active indigent presents in water powder, emulsifiable concentrate formulation and commercial formulation. The result suggests that a total of 154.5 t of active indigent was used in Japan in 1994. Note that dicofol usage has been banned in Japan since 2004.¹⁴ Therefore, we assumed the annual usage to decline linearly from 154.5 t in 1994 to zero in 2004, and no longer occur since 2005.

For **Russia**, the annual dicofol usage was unavailable except for a record of ~ 4 t for the year 2000.¹⁵ In this study, the usage volume was assumed to constantly equate to 4 t from 2000 throughout 2012.

For **the rest part of Asia (mainly Southeast Asia)**, most dicofol was applied for foliar spraying on field crops and ornamentals at low latitudes. Notably, the plants with intensive dicofol treated in China and Japan (e.g. cotton or deciduous orchards like apple and citrus) cannot survive in southeastern Asian region because of the dominant tropical climate. Therefore, it is anticipated that limited amount of dicofol usage happens in the Southeast Asia. For example, only 0.3 t dicofol (2,084 liters of 42% dicofol emulsifiable concentrate formulation was consumed from 1988 to 1992) was annually used in Sri Lanka.¹⁶ Considering the similarity in crop species and agricultural practices between India and Southeast Asia, we assumed the gross application rates of dicofol equate in both India and Southeast Asia. Therefore, we obtained the annual dicofol usage in the rest part of Asia by the cropland area ratio of India to the rest part of Asia (around 163.6 : 158.4 read from global cropland map¹⁷) and the annual usage in India.

3. Latin American, Africa and Middle East

In general, countries in Latin American, Africa and Middle East are light dicofol users. For instance, in 2000, continental dicofol usages were reported to be 166.49 t Latin American, and 177.64 t for Middle East.¹⁸ Therefore, instead of elaborating the specific national usages, efforts were made to obtain the regional or continental estimates as a whole in this study.

In Latin American, some of dicofol demand was once self-sufficient. For instance, Brazil produced 209 t commercial formulation (~20% activated ingredient) and imported another

111 t for its own domestic market in 2000.¹⁹ Dicofol was produced by the only manufacturer (Dow AgroSciences) located in Brazil, but the production was claimed ceased in 2003 ~ 2004 (<http://www.pops.int/documents/registers/closedsys.htm>), even though some sales remained.²⁰ Since then, most of the dicofol demand depended exclusively on the import from the only Chinese producer, Jiangsu Yangnong Chemical Group Co. Ltd.²¹

Given this, the annual import of dicofol in Latin American was assumed to be in proportion to the annual export volume from China, which was further assumed to be in proportion to the annual output of Jiangsu Yangnong Chemical Group Co. Ltd. Therefore, the annual usage in Latin America for any given year was estimated by eq S3:

$$\frac{\text{Usage in Latin American (year } t\text{)}}{\text{Usage in Latin American (year 2000)}} = \frac{\text{Production Volume in China (year } t\text{)}}{\text{Production Volume in China (year 2000)}} \quad (\text{S3})$$

The usage in Africa and Middle East was estimated likewise.

4. Europe

In 2000, the **European Union** member states used 317 t of dicofol,¹⁵ of which 100 ~ 150 t was consumed in **Spain**,¹⁸ 120 t in **Italy** and **Turkey**¹⁸ and 14 t in **France** (2001 data).²² Therefore, 50 ~ 100 t dicofol was supposed to be used in the rest part of the European Union. In addition, dicofol was not registered in Finland, Iceland and Ireland,²² so the usages in the three countries were assumed to be zero for the whole estimation period. After 2009, dicofol was no longer permitted to be registered nor used in the European Union,²⁰ therefore, the dicofol usage in each European consuming country was assumed to linearly decrease between 2000 and 2009, and not to take place since 2010.

5. Oceania

At present, there is no current dicofol production in **Australia**, as shown in websites of Nufarm Australia Ltd., the only former manufacturer in Australia. Most dicofol was applied for foliar spraying on cottons, leafy vegetable, garden fruit and tea, at a relatively intensive application rate of $0.03 \sim 0.06 \text{ kg hectoliter}^{-1}$ (i.e., $1.2 \sim 2.4 \text{ kg ha}^{-1}$).²³ Dicofol was listed as one of “the most important insecticides in use” in Australia, because its annual national usage was higher than 1 t per year.²⁴ However, the exact usage volume was not available. For a conservative purpose, the annual dicofol usage was supposed to be ~1 t per year in Australia from 2000 to 2012.

The dicofol usage in **New Zealand** was ignored in this study, because of a lack of available information,.

Text Section 2 Preparation of rough estimation of the global dicofol usage for the spin-up period of 1990 ~ 1999.

Given that available records of the global dicofol usage is quite rare prior to 2000, we adopted a rough extrapolation in estimation for the spin-up period. Stretching back to 1957, the year that dicofol was first commercialized, we define the following key time-points in entire dicofol usage history to facilitate the extrapolation:

(1) *start year*, the year dicofol was first adopted in a territory, was assumed to be the year of retrievable earliest field application records in the given territory unless there was a

clear record;

(2) *cease year*, the year dicofol usage is projected to stop in a territory, was decided based on the regulation timetable of dicofol in the territory; and

(3) *data available years*, refer to several isolated key years that accurate dicofol consumption information was documented.

Table S1 lists information for the key time-points. For each continent, we presumed that its dicofol usage linearly increased from zero in *start year* to the reported known level in *data available years*, and then linearly declined to zero in *cease year*. Accordingly, the global dicofol usage was aggregated from individual continental usage estimates (Figure S4).

Table S1 The start year, cease year and selected data available years for the major nations in each continent.

Region	Country	Start year	Cease year	Data available year
North America	US	1957 ²⁵	2016 ³	Usage records for the years of 1966, 1971, 1976, 1982, 1989 and 1992 are available at Guidechem.com (available online at: www.guidechem.com/reference/dic-2413.html).
	Canada	N.A.*	2012 ⁴	1.06 t was reported used in 2003. ²⁰
Asia	China	1976 ²¹	2020**	Surveyed information was available on production volumes for the years of 1984~1999. ²¹ Here, we assumed the annual domestic usage to equate to the annual production volume that year.
	India	1961 ²⁶	N.A.	Production record for the year of 2000 was available. ¹² Here, we assumed the annual domestic usage to equate to the annual production volume that year. Usages for the years of 1961, 1965, 1973, 1978, 1988 ~ 1993 and 1995 were extrapolated from the reported domestic pesticides production volume (available online at: www.indiastat.com).
	Japan	N.A.	2004 ¹⁴	Calculated 154.5 t was used in 1994 (see Text Section 1 in this document).
Europe	Italy	1958 ²⁷	2009 ²⁰	The usage record for the year of 2000 was available. ²⁰
Latin America and Africa	Brazil	1958 ²⁸	N.A.	The usage record for the year of 2000 was available. ¹⁸

Note: * N.A.= not available.

** On May 17th, 2014, China stopped the production of technical dicofol product (a.i. = 80%). However, at present, the formulation and processing of stockpiled technical product is still allowed for producing emulsifiable concentrate (a.i. = 20%), soluble concentrate (a.i. = 20%) and pesticide mixtures (a.i. = 22.5%). Therefore, it is expected that the domestic dicofol usage will remain until the official registration of dicofol expires Jan. 14th, 2020.

Table S2 Compiled literature reported values and selected measured values (SMVs) of physical-chemical properties of dicofol.

Notes: All literature reported values were retrieved from peer-reviewed articles, official reports and online chemical databases. For a particular physical-chemical property, only typical experimentally-measured values were chosen for further evaluation, whereas model estimates were excluded unless no measured values were available. Different measured values were chosen in the following priority order: commercial dicofol formulation > *p,p'*-isomer (major content (> 80%) in commercial formulation²⁹) > *o,p'*-isomer. Inferior values were excluded unless no prior values were available. The selected data were adjusted to standard temperature (25 °C) and converted into identical units. Obvious faulty data and identifiable outliers were discarded. Selected measured values (SMVs), also referred as literature-derived values (LDVs), were summarized from the eligible and representative measured data.

Partition coefficients (unitless)

log K_{ow}

Number	Value	Reference	Comments
(1)	5.02	30	Measured value recommended by KOWWIN in EPI suite TM .
(2)	4.18	31	Logarithmic mean of measured values (4.08 ~ 4.28) for <i>p,p'</i> -dicofol.
(3)	4.40	31	Logarithmic mean of measured values (4.32 ~ 4.48) for <i>o,p'</i> -dicofol.
(4)	6.06	25	Measured value provided by the pesticide registrant without original reference.
SMV	4.92		Mean of (1), (2), (3) and (4)

log K_{aw}

Number	Value	Reference	Comments
(1)	-5.005	30	Measured value recommended by KOAWIN in EPI suite TM .
(2)	-7.641	32	For <i>o,p'</i> -dicofol; Stated as the maximum reported value, but no reference is provided, not used.
(3)	-5.005	32	For <i>p,p'</i> -dicofol; Stated as the maximum reported value, but no reference is provided, not used.
(4)	-3.472	33	Cited by Ref. ³⁴ ; Reported measured value although temperature is unavailable.
SMV	-4.239		Mean of (1) and (4).

log K_{oa}

Number	Value	Reference	Comments
(1)	9.29	35	Estimated representative value.

(2)	10.025	—	Calculated value by KOAWIN in EPI suite™ using measured K_{OW} and K_{AW} values ³⁰ .
(3)	7.95	33	Cited by Ref. ³⁴ ; reported measured value although temperature is unavailable. However, the reported vapor pressure (1.87×10^{-3} Pa) corresponding to K_{OA} differs substantially from other reported values; this value is thus identifiable as outlier. Not used.
SMV	9.66	Logarithmic mean of (1) and (2).	

Degradation Half-life (h)

Agricultural Soil

Number	Value	Reference	Comments
(1)	1440	35	Representative value for modelling, but no reference is provided for this value thus it cannot be checked for validity; not used.
(2)	528	25	For <i>o,p'</i> -dicofol in strawberry fields. Not used since data for commercial dicofol formulation was given highest priority.
(3)	1728	25	For <i>p,p'</i> -dicofol in strawberry fields. Not used since data for commercial dicofol formulation was given highest priority.
(4)	2712	35	For commercial formulation in citrus groves fields.
(5)	1200	31	For 42% a.i. formulation in grain barley fields.
(6)	1320	31	Average of values (1200~1440) for <i>p,p'</i> -dicofol. Not used since data for commercial dicofol formulation was given highest priority.

(7)	1680	31	Average of values (1488~1872) for 35% a.i. formulation in strawberry fields.
(8)	112.8	31	For 42% a.i. formulation in rotated cotton, lettuce, barley and carrot fields. Not used since the result is calculated from the dispassion of total degradation residues of dicofol.
(9)	216	25	For <i>p,p'</i> -dicofol in cotton fields. Not used since data for commercial dicofol formulation was given highest priority.
(10)	1464	25	For <i>p,p'</i> -dicofol in citrus crops fields. Not used since data for commercial dicofol formulation was given highest priority.
(11)	2160	35	For commercial formulation in apple orchards.
(12)	1392	35	For commercial formulation in irrigated soil of California cotton fields.
SMV	1830		Mean of (4), (5), (7), (11) and (12). The figure is rounded to the nearest 10.

Uncultivated Soil

Number	Value	Reference	Comments
SMV	3660	—	Estimated value. At present, there is no specific, quantitative measurement on dicofol's half-life in uncultivated soil, although the degradation was revealed to be slower in uncultivated land than planted land due to a lack of rhizosphere microorganisms in uncultivated soil. ³⁶ In previous laboratorial pot experiments, dicofol's half-life in unplanted soil was approximately 1.7 ~ 2.0-folds that in soil planted with <i>Ageratum conyzoides</i> ; ³⁷ dicofol's half-life in sterilized soil without rhizosphere microorganisms was 1.6 ~ 2.0-folds that in soil planted with pepper. ³⁸ However, the

half-life varies with the application rate of organic fertilizer, agrotype, and sterilization treatment.³⁷

³⁸ In this study, a factor of two was assumed to convert dicofol's half-life in agricultural soil to that in uncultivated soil, based on the conservative but reasonable worst cases above. The figure is rounded to the nearest 10.

Freshwater

Number	Value	Reference	Comments
(1)	720	35	Stated as the representative value for modelling, but no reference is provided for this value thus it cannot be checked for validity; not used.
(2)	2040	31	For <i>p,p'</i> -dicofol at pH = 5 in abiotic system; not used.
(3)	82	31	Average of values (64 ~ 99) for <i>p,p'</i> -dicofol at pH = 7 in abiotic system.
(4)	0.43	31	For <i>p,p'</i> -dicofol at pH = 9 in abiotic system; not used.
(5)	1128	31	For <i>o,p'</i> -dicofol at pH = 5 in abiotic system; not used.
(6)	8	31	For <i>o,p'</i> -dicofol at pH = 7 in abiotic system; not used.
(7)	0.15	31	For <i>o,p'</i> -dicofol at pH = 9 in abiotic system; not used.
SMV	82		Directly taken from the pH = 7 case. Freshwater pH ranges from 5.6 to 7 if the equilibrium between unpolluted precipitation and atmospheric CO ₂ dissolution is considered. Besides, it ranges from 6.5 to 8.5 if it allows aquatic life to survive. ³⁹ Therefore, an ideal pH between 6.5 to 7 was taken into account in this study.

Seawater

Number	Value	Reference	Comments
(1)	82	31	Average of values (64 ~ 99) for <i>p,p'</i> -dicofol at pH = 7 in abiotic freshwater system.
(2)	0.43	31	For <i>p,p'</i> -dicofol at pH = 9 in abiotic freshwater system.
(3)	1	40	Hydrolysis at pH 8.2. Not used since only hydrolysis was considered.
SMV	82		Directly taken for the pH = 7 case in freshwater system due to no available seawater data. The average pH of ocean surface waters is 8.1. ⁴¹ For most chemicals (e.g., ref. ⁴²), their half-lives get prolonged, if not remain equal, with increasing ionic strength (salinity), i.e., larger in seawater than freshwater at the same pH values. Also considering that dicofol's half-life decreases with the increasing pH value, ²⁹ the half-life (82 h) at the pH value smaller but nearest to 8.1 in freshwater was chosen therefore in this study.

Vegetation

Number	Value	Reference	Comments
(1)	17520	43	For dicofol residues on treated plant tissues.
SMV	17520		Directly taken.

Freshwater Sediment

Number	Value	Reference	Comments
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(1)	696	44	Reported measured value although temperature is unavailable.
			From the FOOTPRINT Pesticide Properties Database (http://sitem.herts.ac.uk/aeru/iupac/223.htm)
(2)	333	34	Reported measured value although temperature is unavailable.
(3)	720	35	In anaerobic system.
SMV	583		Mean of (1), (2) and (3).

$k_{(OH)}$ (cm³ molecules⁻¹ s⁻¹)

Number	Value	Reference	Comments
(1)	3.43×10^{-12}	45	
SMV	3.43×10^{-12}		Directly taken.

Energies of Phase Transfer (J mol⁻¹)

Item	Value	Reference	Comments
$U(K_{ow})$	-20000	46	Corresponding posterior value of DDT.
$U(K_{aw})$	74400	46	Corresponding posterior value of DDT.
$U(K_{oa})$	-94400	—	Calculated from $U(K_{ow})$ and $U(K_{aw})$.

Table S3 Selected measured values (SMVs), final adjusted values (FAVs), uncertainty degrees, and the adjustment percentage from SMVs to FAVs for the physical-chemical properties of dicofol as inputs in the Globo-POP and BETR-Global model.

Notes: (a) A subjective uncertainty degree ranging from 0 (highest accuracy) to 5 (highest uncertainty), which reflects the measurement reliability of a variable, was assigned to each variable. A higher uncertainty degree integer was assigned to the variable with fewer experimentally-measured values available and/or varying in a larger span of orders of magnitude.

In adjusting SMVs to FAVs, we used an iteration approach⁴⁷ to converge the values of individual physical-chemical properties to a final set that is simultaneously consistent with the several constraining equations given in Beyer et al.;⁴⁷

(b) The adjustments to partition coefficients refer to the non-logarithmic values;
(c) For an indiscriminate overall soil half-life used in the BETR-global model, we deduced a combined value (~ 3300 h) from soil half-lives in uncultivated (3660 h) and agricultural lands (1830 h), and weighted by their respective default global areas defined in the Globo-POP model;

(d) According to the *IPCC Fourth Assessment Report on Climate Change*⁴⁸, globally weighted average concentration of hydroxyl radical (OH) in the troposphere is 10^6 molecules cm⁻³;

(e) Here, we use the built-in activation energies of DDT recommended by the BETR-Global model, due to a lack of dicofol-specific data; and

(f) Vapor pressure and water solubility are included here for use in calculating FAVs, but not in the model stimulation.

Physical-chemical property	SMV	FAV	Uncertainty degree ^(a)	Adjustment percent (%)
Molecular weight	370.5			
Partition coefficient				
$\log K_{\text{ow}}$	4.92	5.517	4	-295 ^(b)
$\log K_{\text{AW}}$	-4.24	-4.091	1	-41 ^(b)
$\log K_{\text{OA}}$	9.66	9.958	2	-99 ^(b)
Half-life at 25 °C (h)				
Uncultivated soil	3660 ^(c)			
Agricultural soil	1830 ^(c)			
Freshwater	82			
Seawater	82			
Vegetation	17520			
Freshwater sediment	583			
Air	81 ^(d)			
Reaction rate of vapor with OH (cm ³ molecules ⁻¹ s ⁻¹)	3.43×10^{-12}			
Energies of phase transfer (J mol ⁻¹)				
$U(K_{\text{ow}})$	-20000			
$U(K_{\text{AW}})$	74400			
$U(K_{\text{OA}})$	-94400			

Activation energies in degradation reactions (J mol⁻¹)^(e)

E_a (Air)	10000			
E_a (Vegetation)	30000			
E_a (Freshwater)	30000			
E_a (Seawater)	30000			
E_a (Soil)	30000			
E_a (Freshwater sediment)	30000			
<i>Vapor pressure (Pa)</i> ^(f)	5.35×10^{-5}	1.06×10^{-4}	2	-98
<i>Water solubility (mol m⁻³)</i> ^(f)	2.1×10^{-3}	2.96×10^{-3}	1	-41

Table S4 Estimated annual continental dicofol usage (in tonnes) from 2000 to 2012

Year	Asia	Europe	North America	Latin America	Africa	Oceania
2000	2,387	317	325	166	155	~1
2001	2,542	285	218	251	234	~1
2002	2,353	254	218	223	208	~1
2003	2,622	222	196	225	209	~1
2004	2,763	190	171	200	186	~1
2005	2,096	159	266	101	94	~1
2006	1,770	127	132	51	48	~1
2007	1,333	95	60	85	79	~1
2008	833	64	48	51	48	~1
2009	769	32	58	51	47	~1
2010	865	0	50	51	48	~1
2011	740	0	42	45	42	~1
2012	619	0	33	38	36	~1

Table S5 Estimated annual dicofol usage (in tonnes) in selected major consuming countries within the hotspot regions from 2000 to 2012.

Year	China	United States	India	Spain	Italy	Turkey
2000	2,013	324	145	150	87	33
2001	2,222	217	120	135	78	30
2002	2,088	217	102	120	69	27
2003	2,366	195	105	105	61	23
2004	2,562	170	87	90	52	20
2005	2,010	265	36	75	43	17
2006	1,651	131	56	60	35	13
2007	1,211	59	56	45	26	10
2008	732	47	47	30	17	7
2009	669	57	32	15	9	3
2010	775	49	43	0	0	0
2011	650	41	43	0	0	0
2012	530	33	43	0	0	0

Table S6 Sensitivity at $\pm 10\%$ variation for physical-chemical properties of dicofol in the Globo-POP model.

Physical-chemical parameters	S (mACP ₁₀ ^{air})	S (eACP ₁₀ ^{air})
Partition coefficient		
$\log K_{OW}$	-0.014	0
$\log K_{AW}$	0.257	0
$\log K_{OA}$	-0.041	0
Half-life at 25 °C (h)		
Uncultivated soil	0.122	0.833
Agricultural soil	-0.041	0
Freshwater	0	0
Seawater	-0.014	0
Freshwater sediment	0	0
Reaction rate constant (cm ³ molecules ⁻¹ s ⁻¹)		
Reaction rate of vapor with OH	0.041	0

Table S7 Statistical evaluation between the BETR-Global simulations and observations.

Scenarios		I	II	III	IV	V
Seawater	r	0.7713	0.7706	0.7705	0.7673	0.7547
	$RMSE$ (pg l ⁻¹)	19.2	19.0	18.9	18.9	17.7
Air	r	0.7060	0.7060	0.7060	0.7068	0.7104
	$RMSE$ (pg m ⁻³)	10.7	11.3	11.6	11.7	11.8

Figure S1 General geographic distribution of the growing regions of five major dicofol-treated crops. This figure was created based on the information from *Ref.*⁴⁹ for apple, USDA database⁵⁰ for cotton, *Ref.*⁵¹ for citrus, and *Ref.*^{52, 53} for litchi. The growing region of pear is assumed to be identical as that of apple.

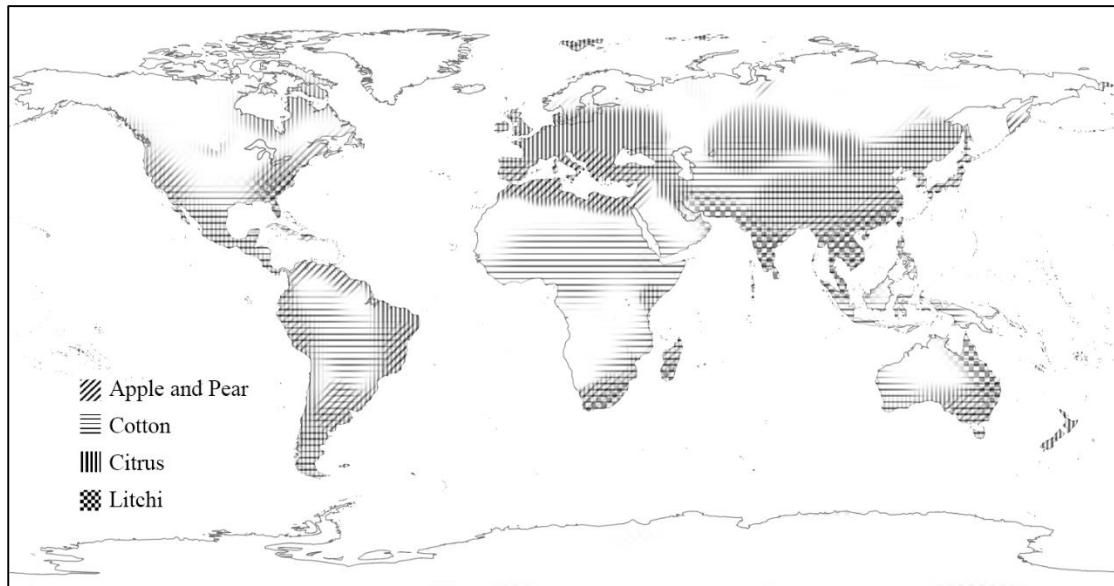
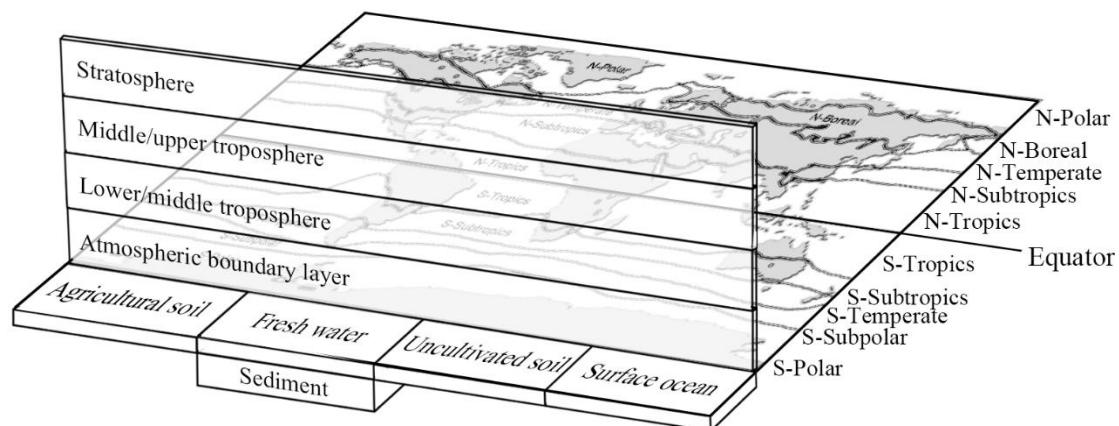


Figure S2 Schematic climate zones and environmental compartments in the Globo-POP model



Geometry of the model: The Globo-POP model divides the entire global environment into ten multimedia latitudinal bands (climatic zones) circling the earth surface, according to the climate division by Troll.⁵⁴ They are northern polar (the Arctic), northern boreal, northern temperate, northern subtropic, northern tropic, southern tropic, southern subtropic, southern temperate, southern subpolar and southern polar zones, respectively.⁵⁵ Each climate zone consists of six discrete, homogenous environmental compartments: atmosphere (stratosphere, middle/upper troposphere, lower/middle troposphere and atmospheric boundary layer), agricultural soil, uncultivated soil, freshwater, freshwater sediments, and surface ocean. Readers are suggested to refer to Ref.56-58 for more technical details.

Dynamics of the model: The inter-zonal advective mass flows of atmosphere, freshwater and seawater, as well as inter-compartmental advective and diffusive mass flows like gas-adsorption, volatilization and so on, are considered to connect individual

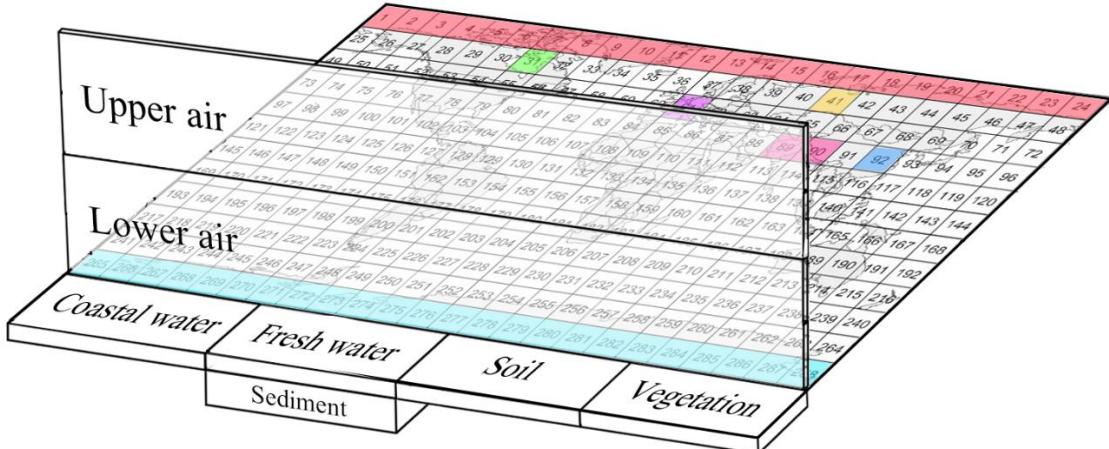
regional environments and compartments. They are represented by fugacity-based mass equilibrium equation set, as following:

$$\frac{d(f_x Z_x V_x)}{dt} = \text{Emission}_x(t) + \sum_{y=1}^n [D_{y \rightarrow x}(t) f_y(t)] - f_x(t) \sum_{y=1}^n [D_{x \rightarrow y}(t)] - f_x(t) D_{x \rightarrow \text{loss}}(t)$$

Reaction Rate = Emission + Transport in – Transport out – Loss

where, subscript x and y denote the target compartment of our interest and other surrounding compartments, respectively. Subscript "loss" represents the dissipating processes, including degradation through geobiochemical reactions, fresh water sediment burial and settlement into the deep ocean. Variable f represents fugacity, the concept describes the escaping tendency of a chemical from a certain compartment. Variable D represents D -value, the constant describes the rate of transport and degradation of the chemical within or between compartments. Variable V represents compartment volume.

Figure S3 Schematic grids and environmental compartments in the BETR-Global model



Geometry of the model: The BETR-global model divides the entire global environment into 288 $15^{\circ} \times 15^{\circ}$ multimedia grids. Each gridded region consists of seven discrete, homogenous environmental compartments: atmosphere (upper and lower air), soil, vegetation, fresh water, and coastal water. Inter-regional advective mass flows of atmosphere, fresh water and coastal water, as well as inter-compartmental advective and diffusive mass flows, are considered to connect individual regional environments and compartments. Readers are suggested to refer to Ref.59-61 for more technical details.

Dynamics of the model: The mechanism of the BETR-Global model is similar to the Globo-POP model. See notes below Figure S2 for details.

Here, we present the time series of dicofol concentrations in several selected grids of interest, which were denoted in color in Figure S3 as well:

Grid nos. 1 ~ 24 (red): the Arctic;

Grid no. 31 (green): the Great Lakes;

Grid no. 41 (orange): the West Siberian Plain;

Grid no. 61 (lilac): the Mediterranean coastal countries;

Grid no. 89 (pink): the Pamir;

Grid no. 92 (blue): central and eastern parts of China;

Grid nos. 265 ~ 288 (bright blue): the Antarctic.

Figure S4 Rough estimate of global dicofol usage for the spin-up period (1990 ~ 1999).

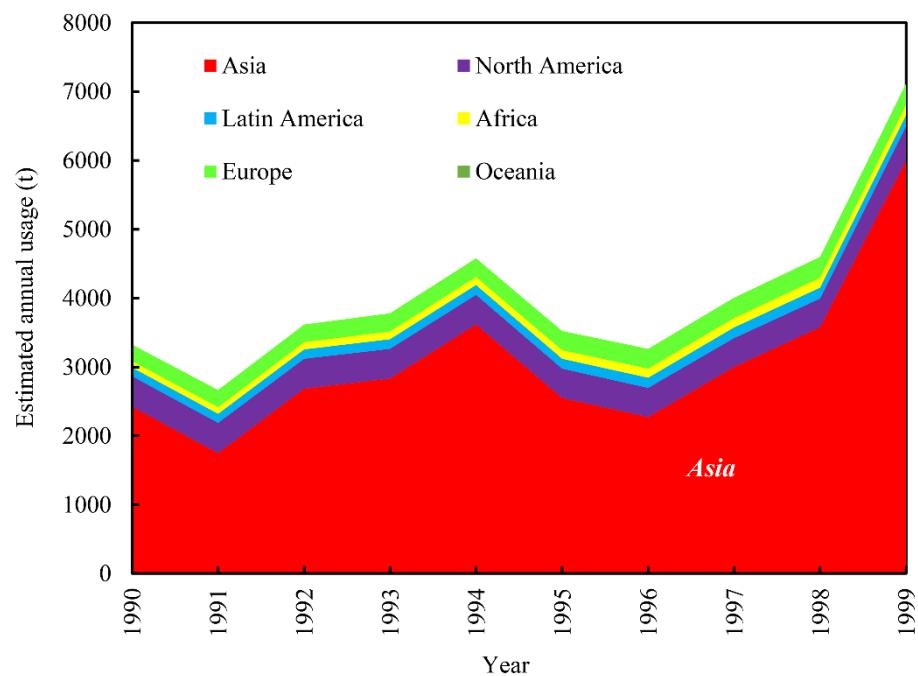


Figure S5 Gridded map of global dicofol usage at $1^{\circ} \times 1^{\circ}$ latitude/longitude resolution for the years 2000 (a), 2005 (b) and 2010 (c).

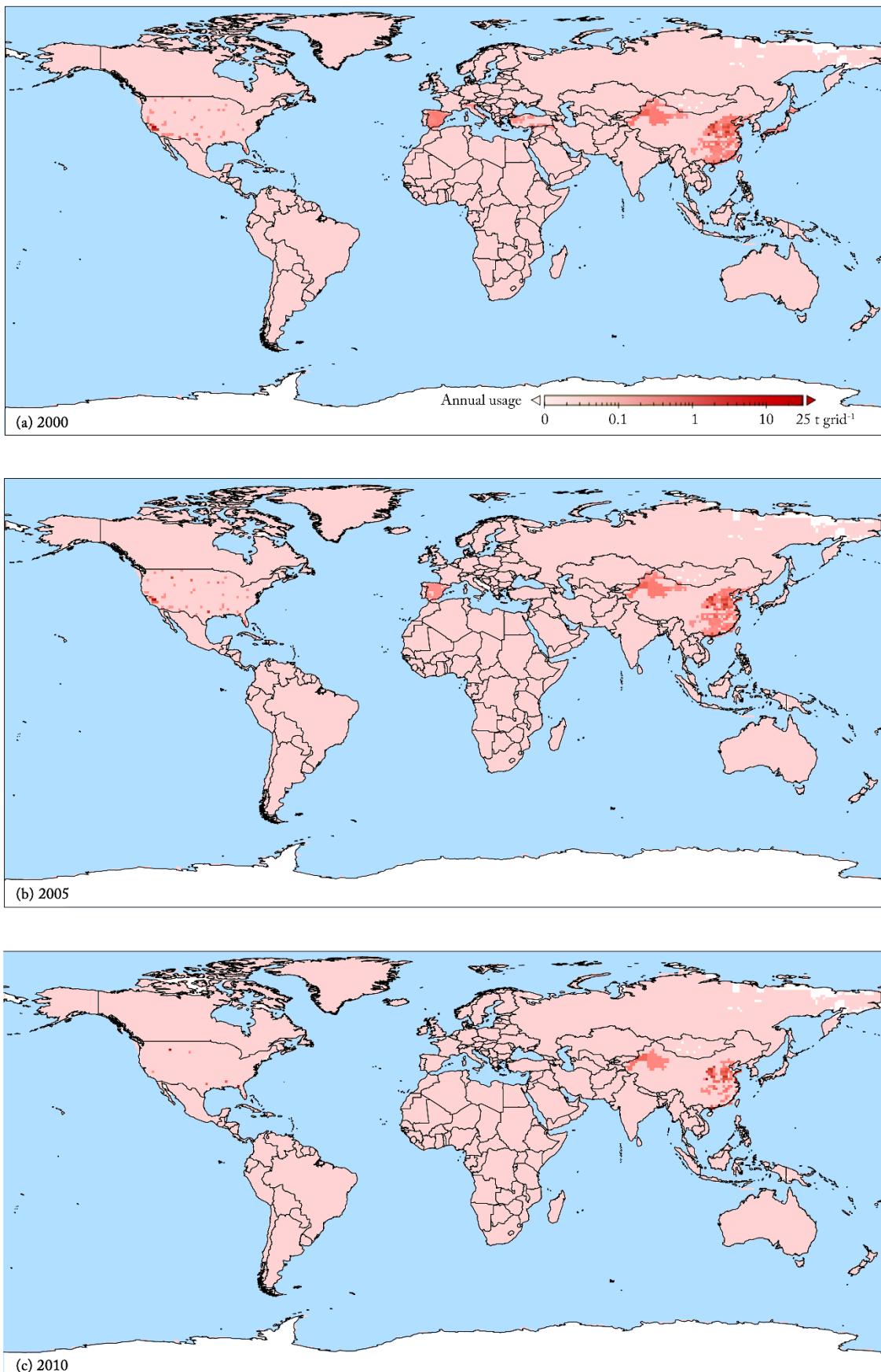


Figure S6 Comparison of provincial dicofol usage in China between this study and the results from Qiu et al.⁶²

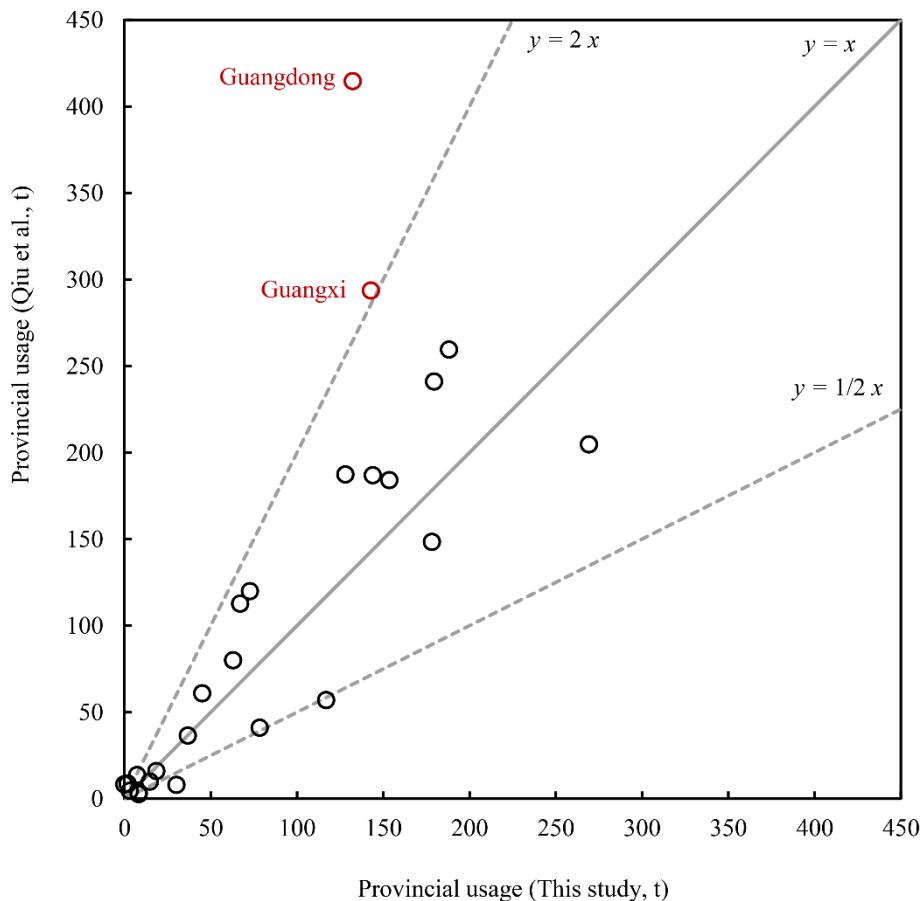


Figure S7 Trends in annual global dicofol usage (i.e., environmental release) and simulated media residual mass during the model spin-up (1990 ~ 1999) and simulation (2000 ~ 2012) periods for five scenarios.

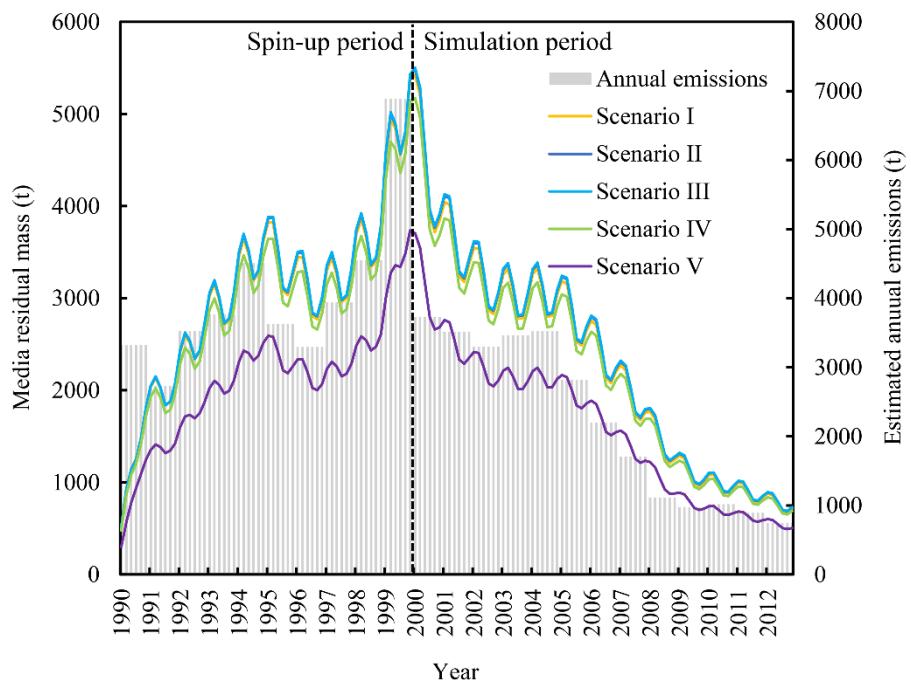


Figure S8 Comparison between simulated grid-averaged and observed marine and atmospheric concentrations in five mode-of-entry scenarios.

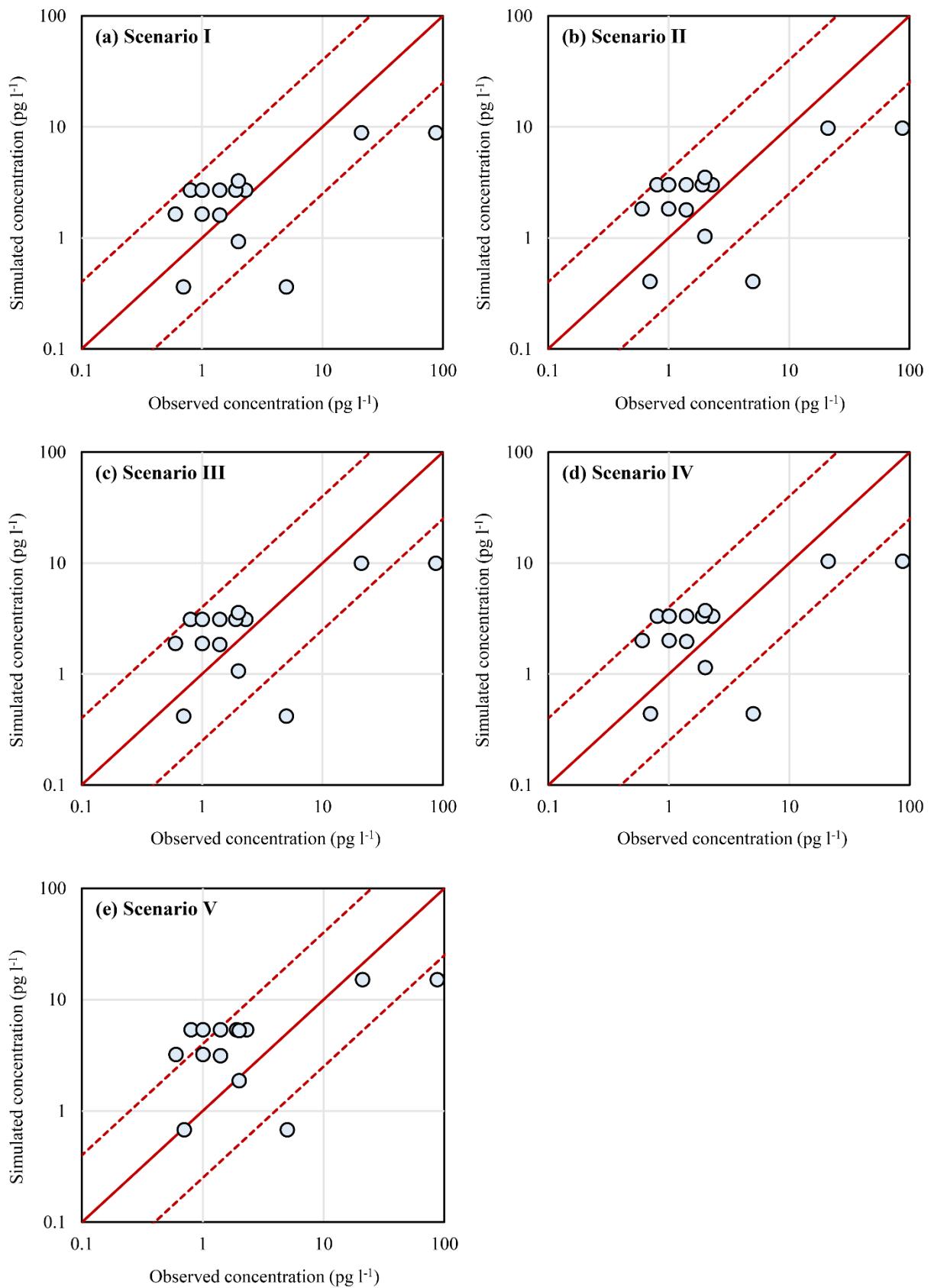
Notes: (a) The observed data are gathered from *Ref.63*, which is composed of 18 surface seawater samples and 17 air samples from ten different BETR grids that encompass East Asia through Bering and Chukchi Seas.⁶³ It is noteworthy that a few observed samples were taken from the same BETR grids; the spatial variability of observed concentrations at sub-grid level cannot be represented by grid-averaged results of the BETR-Global simulation at $15^{\circ} \times 15^{\circ}$ latitude/ longitude resolution;

(b) Because most of the seawater samples are collected offshore and interferences from riverine freshwater are reported to be difficult to differentiate,⁶³ simulated grid-averaged freshwater concentrations, if any, were used to compare with the seawater observation;

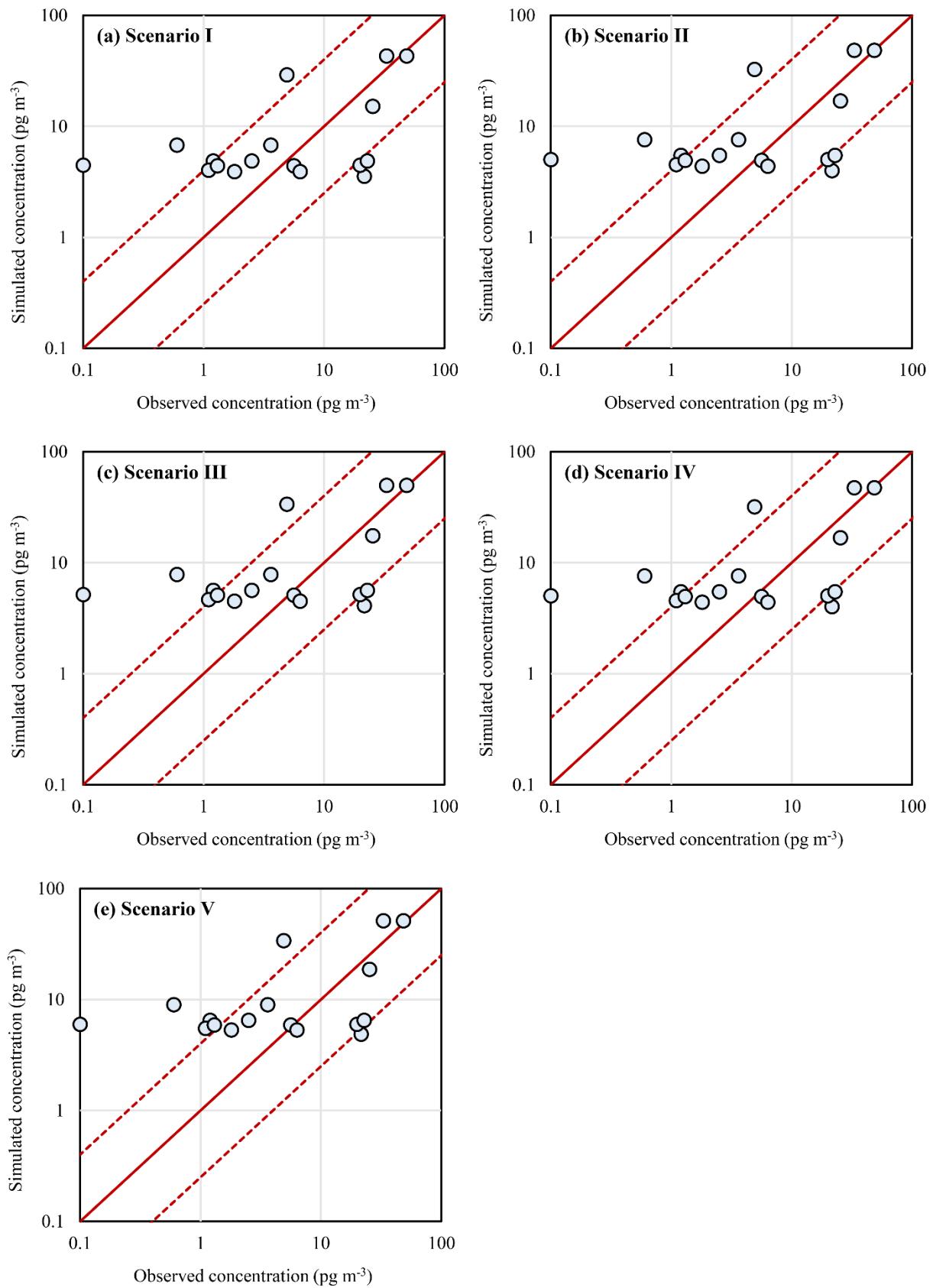
(c) The five scenarios with distinct entry modes of intinal emissions (in percent) are:

- | | |
|---|--|
| (I) lower air: vegetation: soil = 2:80:18; | (II) lower air: vegetation: soil = 2:90:8; |
| (III) lower air: vegetation: soil = 2:93:5; | (IV) lower air: vegetation: soil = 10:80:10; |
| (V) lower air: vegetation: soil = 50:45:5. | |

Simulated concentrations in seawater



Simulated concentrations in lower air



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