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# Heterogeneous reaction kinetics influencing benzo(a)pyrene global atmospheric distribution and related lifetime lung cancer risk

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**Abstract**

Benzo(a)pyrene (BaP) is a ubiquitous and hazardous air pollutant that increases the risk of lung cancer. Heterogeneous oxidation by ozone limits the atmospheric concentrations and long-range transport potential of BaP, but the actual oxidation rates and chemical lifetimes of BaP under varying atmospheric conditions are not yet well constrained. In this study, we employ the ECHAM/MESSy atmospheric chemistry model for the simulation of semivolatile organic compounds (using the SVOC submodel) with coupled surface compartments to compare four different kinetic schemes of BaP oxidation and assess the pollutant's global distribution and associated lung cancer risks. We find that a kinetic scheme considering the temperature and humidity dependence of particle phase state, mass transport, and reaction rate coefficient is

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best suited to reproduce ambient observations, yielding mean global atmospheric lifetime and total environmental residence times of ~5 hours and ~20 days, respectively. Estimates of the BaP-related lung cancer risk surpass $10^{-5}$ (i.e., 10 excess cases per million people) in central and eastern Europe, parts of the Russian Far East, northern India, Pakistan, and western China, and surpass $10^{-4}$ in central, eastern, and northeastern China.

## 1. Introduction

The polycyclic aromatic hydrocarbon benzo(a)pyrene (BaP) is one of the most prominent organic air pollutants and hazardous constituents of fine particulate matter.[1-3] BaP is classified as a human carcinogen by the International Agency for Research on Cancer.[4] The concentration of BaP in particulate matter is regulated in the air quality guidelines of the European Union and other countries.[5, 6] The atmospheric distribution of BaP has been investigated in numerous studies, but the degradation rate in the atmosphere remains a major uncertainty in determining the atmospheric burden and human exposure to BaP.[7-13] Due to its low volatility, BaP resides primarily in the particulate phase of atmospheric aerosols, and the heterogeneous oxidation by ozone is more effective than gas-phase chemistry for its chemical transformation. The degradation rate of BaP depends strongly on both the heterogeneous reaction rate coefficient, which varies across chemical composition of coexisting aerosols, and the accessibility of BaP molecules to oxidants, which is influenced by particle phase state.[9, 12, 14-16] Inhalation exposure to polycyclic aromatic hydrocarbons is known to increase the risk of lung cancer and, recently, global chemistry-transport models have been used to derive lung cancer risk from global atmospheric distribution.[16-19] Although it has been determined that the health burden of PAHs is prominently concentrated in urban areas, investigation into the sensitivity and uncertainty related to the choice of different heterogeneous reaction schemes is lacking in existing studies. Furthermore, the reaction of BaP with $O_3$ can result in the formation of highly toxic oxygenated products such as quinones, epoxides, and hydroxylated BaPs.[20-23] The accumulation of oxygenated BaPs in aerosols results in enhanced bioavailability/bioaccessibility and toxicity.[21, 24-26]

Thus, a quantitative understanding of the heterogeneous reaction between BaP and $O_3$ in the global atmosphere is a major step towards the assessment of the human health risk posed by BaP and its transformation products. In this study, we employ a global atmospheric chemistry model to investigate how different heterogeneous oxidation schemes influence the global

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atmospheric distribution and environmental fate of BaP and how these reflect on lung cancer risk.

## 2. Methods

The global climate and chemistry model EMAC (ECHAM5/MESSy Atmospheric Chemistry)[27, 28] was applied with the SVOC submodel for the simulation of semivolatile organic compounds.[12, 29]

EMAC is a numerical chemistry and climate simulation system that includes sub-models describing tropospheric and middle atmosphere processes and their interaction with oceans, land and human influences.[27] It uses the second version of the Modular Earth Submodel System (MESSy2) to link multi-institutional computer codes. The core atmospheric model is the 5th generation European Centre Hamburg general circulation model (ECHAM5).[30] The physics subroutines of the original ECHAM code have been modularized and reimplemented as MESSy submodels and have continuously been further developed. Only the spectral transform core, the flux-form semi-Lagrangian large scale advection scheme, and the nudging routines for Newtonian relaxation are remaining from ECHAM. For the present study we applied EMAC (MESSy version 2.50.0) in the T42L19 resolution, i.e. with a spherical truncation of T42 (corresponding to a quadratic Gaussian grid of approx. 2.8°×2.8° in latitude and longitude) with 19 vertical hybrid pressure levels up to 10 hPa. The applied model setup comprised various submodels including for online ozone chemistry through the MECCA[31] gas-phase chemical kinetics, aerosol microphysics and composition (GMXE)[32], as well as representations for semi-volatile organic compounds. Note that the applied SVOC submodel (and the corresponding model configuration as described in Octaviani et al.[29]) adopts a species-based approach to explicitly simulate the partitioning and fate of organic aerosols in multiple environmental compartments. SVOC is not to be mixed up with the ORACLE submodel[33], which takes a comprehensive bulk-based approach, using volatility and oxygen-to-carbon basis sets to simulate the partitioning and chemical aging of organic aerosols in the atmosphere.

The simulations covered the period 2007-2009, which was preceded by a one-year spin-up period. The emissions of BaP were taken from the global inventory of Shen et al.[34] for the base year 2008 with a total of 4509 Mg per year. We incorporated monthly factors for seasonality, derived from the black carbon anthropogenic emissions in the IPCC's Representative

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Concentration Pathway (RCP) 6.0 emission scenario.[35] Additionally, an entry split of 5% release to the gas phase and 95% to the particulate phase was employed, with re-partitioning occurring for every time step. This choice aligns with BaP's low volatility and is consistent with the approach used in the previous studies.[12, 29]

In the SVOC submodel, the particulate phase of BaP was described using seven lognormal modes, four hydrophilic and three hydrophobic modes.[29] The hydrophilic modes cover the full particle size spectrum (i.e., nucleation, Aitken, accumulation, and coarse mode), while a hydrophobic nucleation mode was omitted. Aerosol microphysical processes and interactions with background aerosol are determined with the help of the GMXe aerosol submodel of EMAC.[32] BaP transported with individual modes are treated explicitly as separate tracers. In the simulations, particulate phase BaP was emitted to the hydrophobic Aitken mode. The SVOC submodel calculates the partitioning of organic compounds between the gas and particulate phases using poly-parameter linear free energy relationships (ppLFER),[36, 37] where the partition coefficient is defined as the sum of individual partition coefficients representing surface adsorption and bulk-phase absorption processes to inorganic and organic aerosols. Besides removal through dry and wet deposition, BaP is subject to heterogeneous oxidation by ozone. Gas-phase oxidation is switched off as BaP predominantly resides in the particulate phase, accounting for at least 90% of the total mass.

In this study, we tested and compared four different kinetic schemes of heterogeneous oxidation by ozone. Firstly, the recently developed Reactive Oxygen Intermediate-Temperature dependent (ROI-T) scheme of Mu et al. 2018[12], which accounts for the formation of ROI upon decomposition of adsorbed ozone[38] and the influence of temperature and relative humidity on the first-order reaction rate coefficient. In ROI-T, BaP is rapidly oxidized under warm and humid conditions due to rapid diffusion in liquid particles, but effectively shielded from degradation under cold and dry conditions caused by slow diffusion in semi-solid or solid particles. The scheme builds on the results of several experimental and theoretical studies.[15, 38-44] The required kinetic parameters are summarized in the Supporting Information Table S1. The other three kinetic schemes are based on laboratory studies of BaP degradation on different substrates without functional dependence on temperature and humidity: the Pöschl et al. 2001[45] scheme represents an upper limit of reactivity based on the surface reaction of ozone with BaP on soot aerosol particles; the Kwamena et al. 2004[46] scheme represents an intermediate level of reactivity based on the reaction of ozone with BaP on organic aerosol particles; and the

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Kahan et al. 2006[47] scheme represents a lower limit of reactivity based on the reaction of ozone with BaP in organic films. The different degradation rates of these laboratory-derived schemes are summarized in Table S2. For the chemical degradation of BaP on ground surfaces (soil and vegetation) and in the ocean surface layer, first-order rate coefficients of $2.55\times10^{-8}$ $s^{-1}$ and $1.30\times10^{-9}$ $s^{-1}$ were assumed, respectively.[48, 49]

## 3. Results and Discussion

### *Global distribution*

Figures 1 and S1 show the average near-surface concentration and total atmospheric column of BaP, calculated using four different kinetic schemes. With the Mu et al. 2018 (ROI-T) scheme (Figures 1a and S1a), high atmospheric concentrations and column burdens of BaP (>10 pg $m^{-3}$ or >0.1 kg per 2.8×2.8° grid cell, respectively) are predominantly obtained in densely populated and industrialized regions with strong emissions from fossil fuel combustion – such as China, India, Europe, and the eastern US – and in regions with strong biomass burning emissions from vegetation and peat fires, especially in the tropics (Brazil, central Africa, Indonesia). The substantial BaP burden over the Arctic, North Atlantic, and northern Pacific Ocean (~1 pg $m^{-3}$ or ~0.01 kg per grid cell) is caused by long-range transport from North America, Europe, and Asia, and is enabled by shielding effects of highly viscous organic coatings under low temperatures and relative humidity.[50, 51] In contrast, very low near-surface concentrations and atmospheric burden are obtained over the tropical southern Oceans due to short lifetimes and large distances to emission sources. As expected, the lowest burden is seen over Antarctica at large distances from the fossil fuel and biomass burning sources (<$10^{-3}$ pg $m^{-3}$ or <$10^{-4}$ kg per grid cell). This is in agreement with observation-based studies reporting that substantial amounts of BaP are reaching the Arctic[52, 53] but not the Antarctic.[54, 55]

With the Kwamena et al. 2004 scheme (Figures 1b and S1b), we obtain a similar atmospheric concentration and burden of BaP as with the ROI-T scheme, but the spatial distribution patterns are regionally different. This is because the temperature-dependence and humidity-dependence (i.e., shielding effects of organic coatings) are only represented in the ROI-T scheme, but not in the Kwamena et al. 2004 scheme. Consequently, the atmospheric burden in the polar regions is higher with the ROI-T scheme, owing to the low average temperature and humidity leading to a slow BaP degradation rate in a highly viscous particle phase state. On the other hand, the Kahan et al. 2006 scheme represents a lower limit of BaP reactivity and with a long atmospheric

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lifetime due to chemistry of about one week (Table S4). Here, concentrations and burdens are (on average) two orders of magnitude higher than with the ROI-T scheme (Figures 1c and S1c). Accordingly, this scheme enables significant long-range transport of BaP. For example, we see a more pronounced influence of continental sources on marine BaP concentrations, in contrast to other schemes where emissions from shipping lead to clearly defined ship tracks. Furthermore, the Pöschl et al. 2001 scheme, which represents an upper limit of reactivity, yields much lower concentrations (approximately by one order of magnitude on average), with a spatial pattern closely resembling the pattern of BaP emissions (Figure 1d). When ozone concentrations are higher than 150 µg/m3, after one hour, the BaP concentration can be reduced up to 80% in the Kahan et al. 2006 scheme and 20% in the Pöschl et al. 2001 scheme. This reflects a particularly short atmospheric lifetime of only minutes for BaP due to chemistry (Table S4).

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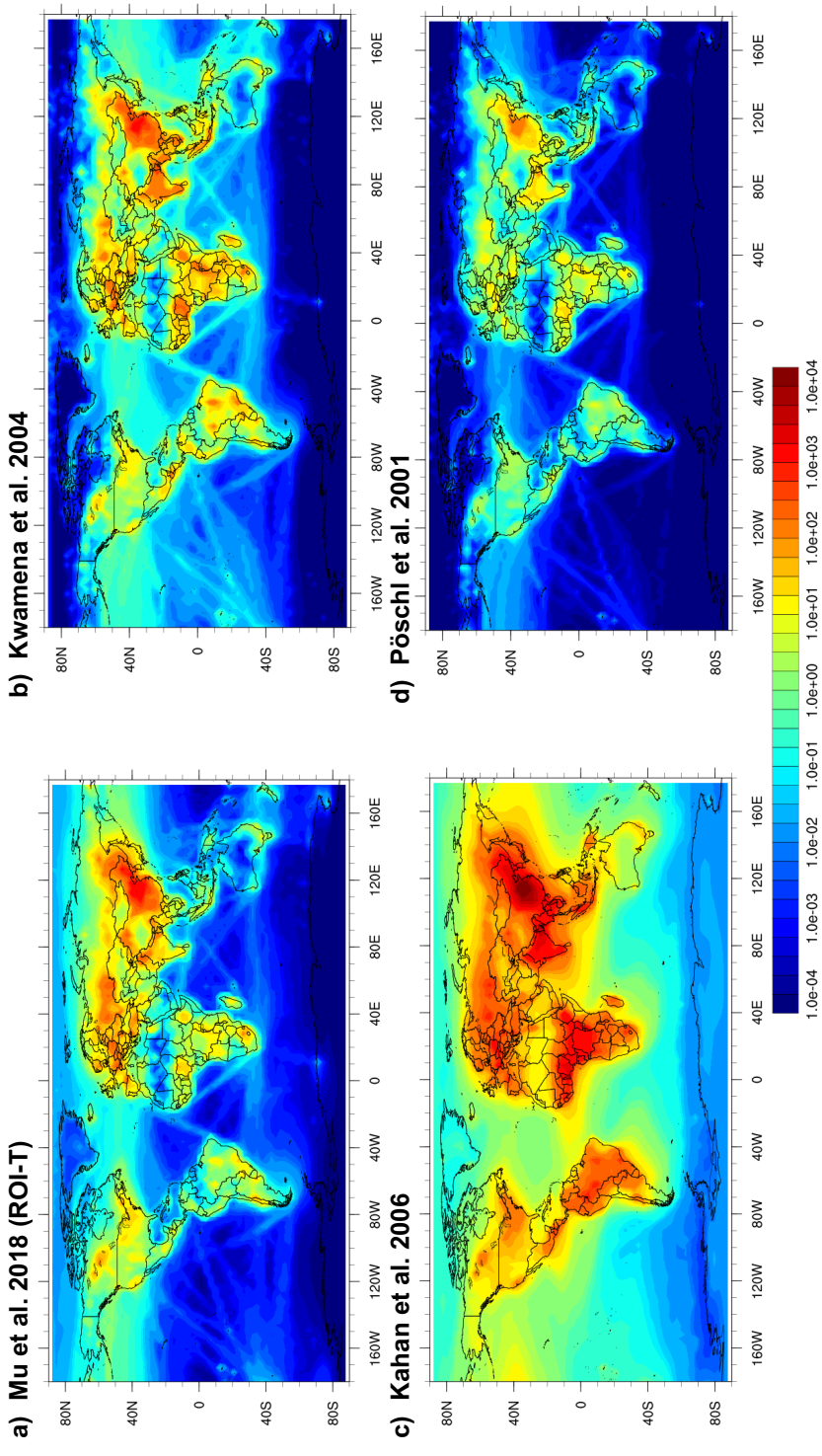


**Figure 1.** Global near-surface atmospheric concentrations of BaP (pg $m^{-3}$) averaged over 2007-2009 using different kinetic schemes of heterogeneous oxidation: (a) Mu et al. 2018 (ROI-T), (b) Kwamena et al. 2004, (c) Kahan et al. 2006, (d) Pöschl et al. 2001.

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The comparison of field measurement data with the ROI-T scheme demonstrates improved agreement between global model results and observations in both source and remote regions (Figures S2-S3), also discussed in Mu et al.[12]. The model results obtained with the ROI-T scheme come much closer to observations at Arctic stations compared to the Kwamena et al. 2004 and Pöschl et al. 2001 schemes (Figures S2-S3), enabling better treatment of the long-range transport. Although the Kahan et al. 2006 scheme comes closest to the mean and median observations at the Arctic stations, it generally overestimates BaP concentrations in other locations and during Arctic summer months. A conservative overall estimate of uncertainty follows from the lower and upper limit values obtained with the Pöschl et al. 2001 and Kahan et al. 2006 schemes. As a more realistic estimate of uncertainty, however, we suggest using the difference between the ROI-T scheme (which is physicochemically more realistic and in better agreement with global observations[12]) and the Kwamena et al. 2004 scheme (an alternative estimate of intermediate reactivity and has been used in many regional/global modeling studies[8, 29, 56-59]).

***Vertical profiles***

Figure 2A shows vertical profiles of BaP mass mixing ratio averaged globally. All schemes except the Kahan et al. 2006 scheme demonstrate a steep decrease in BaP concentrations with increasing altitude across the planetary boundary layer (up to ~3 km/~700 hPa). In the free troposphere (up to ~15 km, ~100 hPa), temperature and humidity are generally lower. As a result, the ROI-T scheme yields a more gradual decrease in concentration, while the temperature and humidity-independent Kwamena et al. 2004 and Pöschl et al. 2001 schemes show a stronger decrease. On the other hand, the low reactivity of the Kahan et al. 2006 scheme results in an overall much smaller BaP decrease with altitude. Differences between the schemes for different parts of the world are discussed in the Supporting Information S4.

***Burden and lifetime***

The global and regional total atmospheric column burden of BaP are presented in Table S3 as absolute and relative values. The global BaP burden obtained with the ROI-T scheme is ~1.6 Mg (Table S3a), of which 84% is concentrated in the northern mid-latitudes (Table S3b) and 42% in the planetary boundary layer below ~1.5 km altitude (850 hPa). With the other kinetic schemes, the global atmospheric burdens of BaP range from a 16 times lower limit of ~0.1 Mg (Pöschl et al. 2001) via a 50% lower value of ~0.8 Mg (Kwamena et al. 2004) to a 40

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times higher upper limit of ~64 Mg (Kahan et al. 2006). Most of the BaP burden predicted by these schemes is found to reside in the tropics (47-66%). The much lower fraction of the BaP burden predicted for the tropics under the ROI-T scheme (~14%) is due to faster degradation at high temperature and humidity.

The atmospheric (photo-)chemical lifetime of BaP, in the following just referred to as atmospheric lifetime, is calculated as the ratio of atmospheric burden (in pg $m^{-2}$) to its chemical loss rate (in pg $m^{-2}$ $h^{-1}$). These lifetimes are calculated on both the global and regional scale as well as annual and seasonal means (Table S4). Lammel et al.[7] previously estimated a global atmospheric lifetime for BaP of ~48 h without considering heterogeneous degradation and ~0.17 h when accounting for it. On the other hand, Shrivastava et al.[16] considered coating of BaP containing aerosols with organics, providing viscosity-dependent shielding from ozone oxidation and resulting in an atmospheric lifetime estimate of ~5 days (120 h), as opposed to ~2 h without shielding. These estimates significantly differ from our estimated global atmospheric lifetime (mean value from 2007-2009) using the ROI-T scheme of about 5 h. The difference to Lammel et al.[7] can be attributed to differences in the scheme for heterogeneous chemistry. Their study employed reaction rate coefficients independent of temperature and humidity for particulate BaP oxidation, only allowed for reaction with OH and $NO_3$, and used a different method for gas-particle partitioning i.e., considering interaction with black carbon and organic matter. Our study implemented the ppLFER method, which not only considers interactions with black carbon and organic matter, but also considers interactions with various other particulate matter constituents. The differences with Shrivastava et al.[16] arise because the BaP heterogeneous kinetics are fully turned off at $T \leq 296$ K or relative humidity ≤ 50% in their study, whereas in the ROI-T scheme they are gradually slowed down as a function of temperature and humidity. The differences in atmospheric burdens and lifetime as well as their spatial distribution patterns highlight the importance of temperature- and humidity-dependent treatment of aerosol phase and heterogeneous reaction rate coefficients in determining global atmospheric transport and distribution of hazardous pollutants.[3, 12, 16, 42]

Across latitudinal zones, atmospheric lifetime varies by more than an order of magnitude i.e., 1.8 h in the Tropics and 43.5 h in the Antarctic (ROI-T; Table S4). The Kahan et al. 2006 and Pöschl et al. 2001 schemes yield the longest and shortest lifetimes, respectively, i.e., 155.5 and 0.08 h as the global annual means, 164.2 and 0.1 h in the Arctic, and 224.2 and 0.12 h in the

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Antarctic. This 50% increase from the global mean to the Antarctic lifetime under the Pöschl et al. 2001 scheme is caused solely by the reduced regional $O_3$ concentration, as the scheme neglects the effects of temperature and humidity. The ROI-T scheme demonstrates that the atmospheric lifetime is significantly enhanced due to the lower temperature and humidity in the Antarctic (43.5 h) compared to the Arctic (~12 h). For other climatic regions, the calculated lifetime increases from the tropics to higher latitudes (Table S4). These lifetime trends imply that BaP will accumulate more in the polar regions and thus endanger vulnerable marine ecosystems. The seasonal signal, i.e., the atmospheric lifetime in winter over lifetime in summer, ranges from 10-13 in northern high- and mid-latitude regions and is ~2 in the tropics and southern hemisphere.

More than 99% of BaP mass is stored in soils, oceans, vegetation, snow, and glaciers (Table S5). Therefore, in the following, we will investigate the total burden in these surface compartments. We find that the total surface burden and distribution are highly dependent on the atmospheric degradation scheme (see Supporting Information S5 for more details). This implies that the selected atmospheric degradation scheme has a major impact on BaP's environmental fate, overall environmental persistence, long-range transport potential, and consequently human and ecosystem exposure in remote environments. Thus, it is important to use an accurate representation of the reactivity of BaP in air for environmental and human health risk assessment. Compared to the global atmospheric burden of ~1.6 Mg BaP (Table S3), the total burden in surface compartments is ~249 Mg under the ROI-T scheme (Table S5). This total environmental burden (atmosphere and surface) is fed by ~4500 Mg per year of global emissions, hence, corresponds to an environmental residence time of the pollutant of ~20 days.

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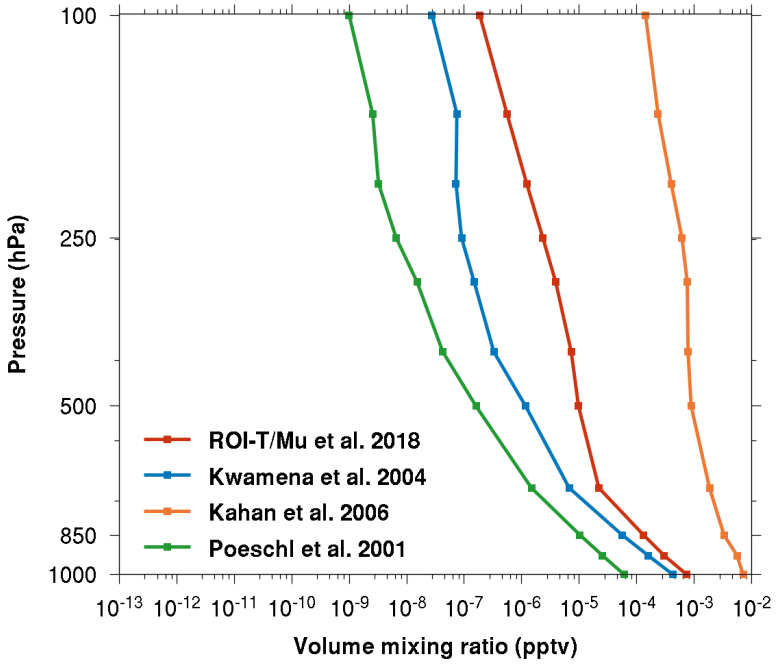
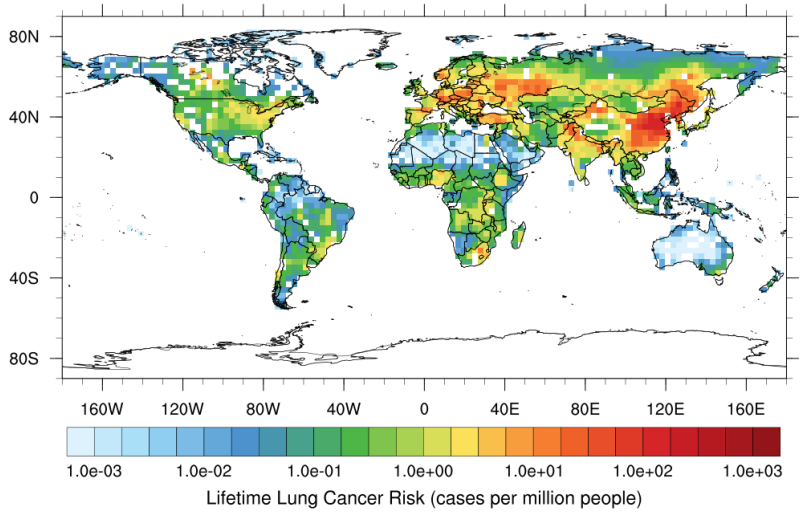
**A. Vertical profile of global mean BaP concentration**




**B. Estimated lifetime lung cancer risks**

**(i) Additional cancer cases per million people exposed**



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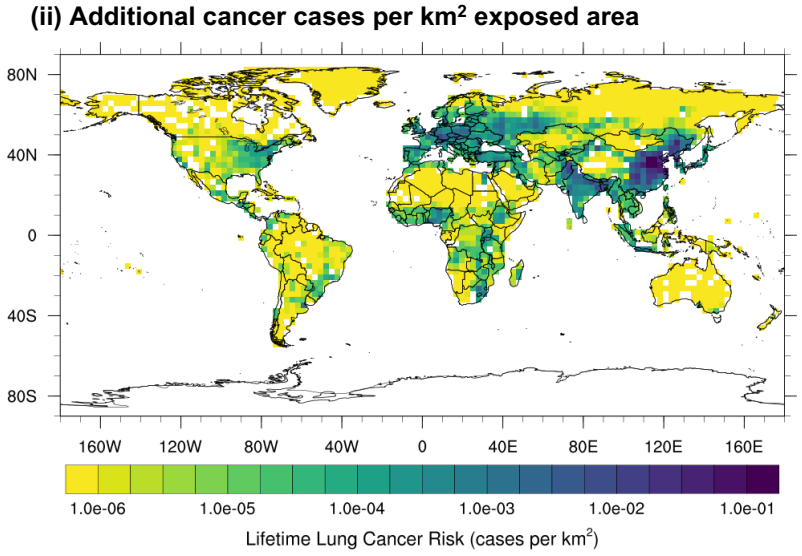


**Figure 2.** A: Vertical profiles of global mean BaP volume mixing ratio (pptv) averaged over the period 2007-2009 and obtained with different kinetic schemes (Mu et al. 2018 (ROI-T), Pöschl et al. 2001, Kwamena et al. 2004, Kahan et al. 2006). B: Estimated lifetime lung cancer risks (LLCR) for BaP as additional cancer cases (i) per million people exposed over a lifetime of 70 years, and (ii) per km$^2$ of exposed area based on BaP concentrations obtained with the ROI-T scheme.

***Lifetime lung cancer risk***

Figure 2B shows the lifetime lung cancer risk (LLCR) estimates due to the exposure to BaP alone. LLCR is derived from the ROI-T predicted near-surface BaP concentrations and a unit-risk (UR) for lung cancer upon chronic exposure to 1 ng m$^{-3}$ BaP over a lifetime of 70 years. The US EPA[60], cited by WHO[61], estimated a UR of $8.7\times10^{-5}$ per ng m$^{-3}$, which is comparable to the estimate produced by the National Institute for Public Health and the Environment of the Netherlands[62] (UR = $10\times10^{-5}$ per ng m$^{-3}$). The WHO unit risk is used to estimate the LLCR value according to the following equation.

$$LLCR = UR \times [\mathrm{BaP}]$$

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where [BaP] is the 3-year average (2007-2009) near-surface concentration of BaP (ng $m^{-3}$). Note that this calculation of lifetime cancer risk assumes steady near-surface concentrations over the entire lifetime and does not consider the cancer risk by exposure to chemical transformation products of BaP, as discussed further below. Moreover, the LLCR due to BaP alone, as presented in this study, only represents a fraction and at most a lower estimate of the LLCR due to total air pollution. BaP is co-emitted with other carcinogenic polycyclic aromatic compounds of various atmospheric lifetime and carcinogenicity of photochemical products, and does not dominate carcinogenicity of polluted air[63, 64].

The estimated LLCR from BaP exposure is very low ($<1\times10^{-8}$) in parts of North Africa and Australia, while we find the highest risk in Central, Eastern, and Northeastern China, exceeding $1\times10^{-4}$, or 100 excess cases per million people. Elevated risk (1-100 excess cases) is seen in northeast America, central, eastern and southeastern Europe, parts of Eastern and South Africa and Nigeria, parts of Brazil, Argentina and Chile, western southern parts of the Russian Far East, China, and the Indus and Gangetic Plains (Southern Asia). Due to its influence on BaP distribution in air, the choice of degradation scheme has a pronounced influence on the estimated lung cancer risk (SI S6). When combined with population density[65] (Figure 2B(ii)), higher risks ($>1\times10^{-2}$ additional cases per $km^2$) are observed in densely populated of regions, notably in China, India, Pakistan, central and eastern Europe, Nigeria, South Africa and eastern US (between $1\times10^{-4}$-$1\times10^{-2}$ cases per $km^2$). In remote regions, the lung cancer risks are usually below $1\times10^{-6}$ additional cases per $km^2$. Considering population density and its correlation with LLCR is crucial for formulating effective public health policies and interventions to mitigate BaP-related health implications.

A limitation related to the model's spatial resolution is related to the spatial variability of BaP concentrations at scales smaller than the model grid size, also known as subgrid variability (SGV). As BaP is a primary pollutant, its near-surface SGV is caused by the spatial heterogeneity of the emission sources, which can be large in polluted areas[66]. In such areas, where both population density and emission sources are concentrated, i.e., urban environments, SGV can lead to a systematic underestimation of LLCR. Conversely, in regions where population centers and emission sources are evenly distributed across a grid cell, the error

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introduced by SGV will be small. A possible approach to address this constraint involves spatial downscaling, using high-resolution population data to disaggregate emissions onto a finer resolution grid.

## 4. Implications & Outlook

The atmospheric degradation, persistence, long-range atmospheric transport potential, and compartmental distribution of BaP are very sensitive to temperature and relative humidity. This study improves our understanding and prediction of the atmospheric fate and large-scale distribution of BaP and other organic pollutants which are carried by aerosols and subject to heterogeneous reactivity. The efficiency of shielding from photochemistry, which can vary significantly between regions, shapes the pollutant's distribution and long-range transport potential. These factors, already more sensitive than previously anticipated,[67] are expected to change under a changing climate. The effect of future climate on BaP reactivity and, hence, lifetime in various parts of the atmosphere, remains to be investigated. Oxygenated BaPs, which are formed during the oxidation reaction of BaP with $O_3$, are known to have toxicological and physicochemical properties that can contribute to, or even enhance, the overall adverse effects of BaP on human and ecosystem health. To achieve a more comprehensive health risk assessment, future research could explore and incorporate the toxicity of these products. The dependence of BaP reactivity on temperature and relative humidity demonstrated in this study suggests that individuals living in warm and humid climates may be exposed to air with a comparatively higher fraction of BaP oxidation products (that have been formed from photochemical reaction of BaP). Further quantitative estimates of the global distribution of BaP oxidation products will require data on photochemical yields and degradation kinetics, which are currently lacking. The distribution of oxidation products of BaP in near-surface (i.e., inhaled) air should be used to study the related cancer risks for exposed populations. This will also require an estimate of the unit risk of BaP oxidation products. Apart from BaP, other PM constituents contribute to the carcinogenicity of ambient air.[68, 69] Little is known about these substances' reactivity. As a number of suspects are polycyclic aromatic compounds,[70, 71] the here presented implications on atmospheric fate may apply for a range of hazardous pollutants.

## Supporting Information

Descriptions of different parameterization schemes of BaP multiphase degradation rates (Tables S1-S2), spatial distribution of BaP atmospheric column burden (Figure S1), model

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performance evaluation (Figures S2-S3), vertical profiles of regional-mean BaP (Figure S4), global and regional mean of BaP atmospheric burdens and their respective lifetimes (Tables S3-S4), global and regional mean of BaP burden across soil, vegetation, and ocean compartments (Table S5), spatial distributions of lifetime lung cancer risks (Figure S5).

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