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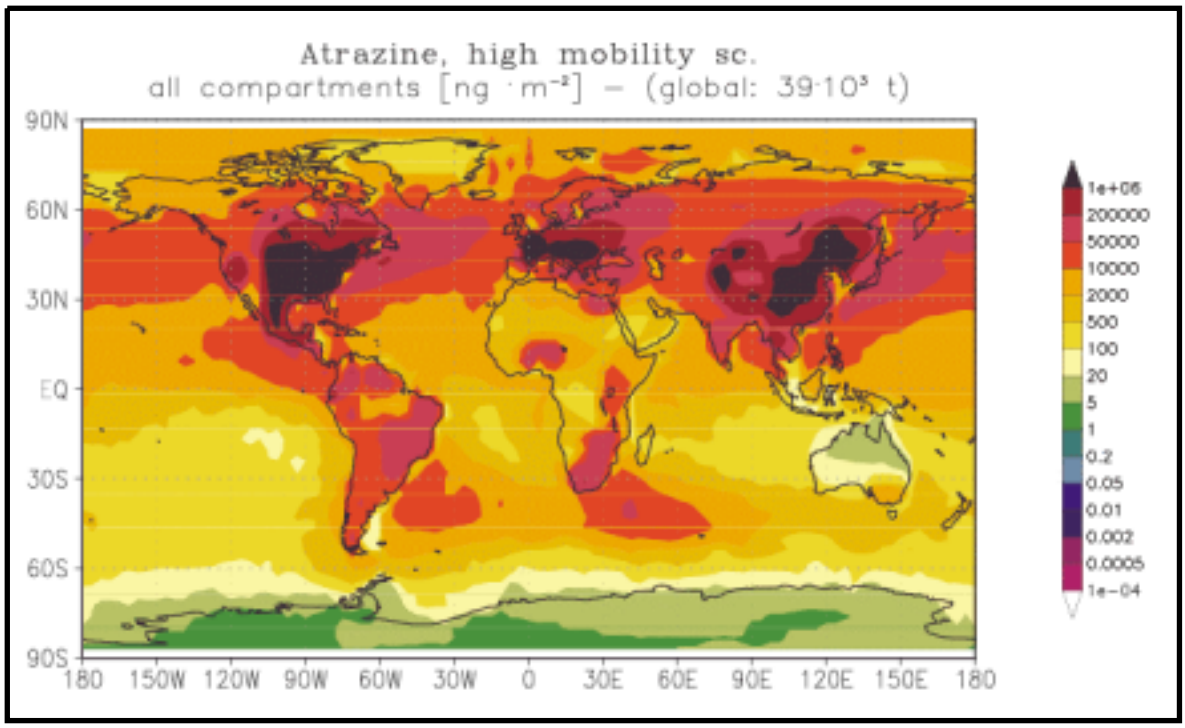

LONG-RANGE TRANSPORT AND MULTIMEDIA PARTITIONING OF SEMIVOLATILE ORGANIC COMPOUNDS: A CASE STUDY ON TWO MODERN AGROCHEMICALS

by

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LONG-RANGE TRANSPORT AND MULTIMEDIA PARTITIONING OF SEMIVOLATILE ORGANIC COMPOUNDS: A CASE STUDY ON TWO MODERN AGROCHEMICALS

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Abstract

The global environmental fate of two modern pesticides was studied using a multimedia model based on a three-dimensional atmosphere general circulation model. The emissions are predicted dynamically based on agricultural application inventories.

The insecticide methyl parathion, when assuming properties at the high mobility end of the respective data uncertainties, was found to be distributed on continental and even global scales. This finding implies that based on present knowledge one cannot exclude that methyl parathion reaches regions as far from the sources as e.g. the Arctic. Two scenarios of the environmental cycling of the herbicide atrazine were studied which reflect a lower and an upper estimate of the substance' mobility. Atrazine largely remains in the source (application) regions and the neighbouring seas. But also atrazine seems to have an albeit limited potential for long-range transport. The findings on substance mobilities are quantified by indicators which address spatial range in the zonal direction in individual media. The seasonal variability of the total environmental burden of both pesticides is governed by the degradation in soil and vegetation which together host 73 % of methyl parathion and 90-99 % of atrazine. Also, the cycling between compartments was studied. Methyl parathion undergoes more deposition and re-emission cycles than atrazine, a characteristics of the environmental fate of semivolatile substances. Persistence is addressed by determination of global total environmental decay times during periods without introduction of new substance into the environment. These are in the range 4-7 months. It is found that the seasonal variability of persistence is pronounced.

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1. Introduction:

The distribution of organic chemicals in the environment is a result of complex mechanisms, as the temporal and spatial patterns of entry into the environment, of the transports in mobile media and the partitioning between media are superimposed. As far as substances are concerned which are slowly degrading and ecotoxic (so-called persistent and toxic substances, PTS) there is a vital interest to study and assess the environmental exposure (Vallack et al., 1998; UNEP, 1999; Klecka et al., 2000). Global chemistry-transport-models have not been used for the description of the transport and the environmental chemistry of semivolatile substances by now, although they are in principle suitable tools for determining the exposition of the environment to these substances. Multimedia environmental fate of chemicals has instead been studied using box models (including series of coupled boxes) with the geospheric transports being represented generically (Mackay and Paterson, 1991; Wania and Mackay, 1995). The long-range transport potential of semivolatile substances is in part due to the 'grasshopper effect' (Vallack et al., 1998, besides others): Through repeated volatilization and subsequent atmospheric deposition cycles such substances can travel long distances, longer than the atmospheric residence time suggests. Note that even longer distances than the distance which would result based on the atmospheric residence time, the mean wind velocity and the number of cycles can be achieved under favourable conditions: If, for instance, re-emission would always occur at the time of the diurnal temperature maximum, say 15:00 h, and deposition would always occur at the time of the diurnal temperature minimum, say 06:00 h, then, because of the diurnal cycle of the main atmospheric sink, the availability of the hydroxyl radical, the effective atmospheric residence time would be longer than the 24 h-mean atmospheric residence time (disregarding the influence of minor sinks for simplicity).

We report first results of an on-going effort to study the regional and global transport and deposition and partitioning between environmental compartments of semivolatile organic compounds using a multimedia model which is based on a general circulation model of the atmosphere.

Many widely used pesticides are subject to considerable volatilization losses upon application and undergo long-range transport as a result of limited environmental degradability (Kurtz, 1990; Unsworth et al., 1999; van Pul et al., 1999). This study is on the environmental fate of two of the globally most important in-use agrochemicals.

2. Model approach

2.1 Mass exchange and chemical transformation within and between compartments

The sources and sinks to the total environment system and the intermedia mass exchange processes which are represented in the model are schematically shown in Fig. 1. The environment compartments freshwater systems and river and ocean sediments are neglected as is the intermedia transport process river runoff. The only substance source to the total system is application in agriculture (to soils and vegetation). Sinks are chemical degradation processes in each compartment and loss from the surface mixed layer of the ocean to the deep sea (Section 2.1.4). Intramedia exchanges are considered in the atmosphere (Section 2.1.1) and the soils (Section 2.1.2).

2.1.1 Atmosphere

Transport and transformation of the compounds are studied using the ECHAM model, version 4, with 19 vertical layers to the height of ca. 10 hPa, with tracer specific modifications. The model is based on the primitive equations (spectral representation), uses the hydrostatic approximation and the pressure levels are terrain following. A realistic interannual climate variability is generated by the model. The model has been described in detail elsewhere (Roeckner et al., 1996). The model has been modified such as to be able to describe the transport, cloud processing, dry and wet deposition and tropospheric chemistry of gaseous and particulate trace substances. Cloud processing of the gas-phase molecules is determined by water solubility, and simple cloudwater chemistry including cloudwater acidity is represented (Feichter et al., 1996). Dry deposition of the gas-phase molecules follows an empiric approach using fixed deposition velocities for various underlying surfaces, i.e. the deposition flux is proportional to the concentration in the lowest level (thickness ca. 65 m). Chemical degradation in the atmosphere is considered through the reactions with the hydroxyl, OH, (day-time) and nitrate, NO_3, (nighttime) radicals. We assume that gas-phase molecules and molecules adsorbed to the particulate phase obey the same chemical kinetics. The spatial and temporal distributions of radicals were taken from a separate simulation of the model with an explicit hydrocarbon-NO_x-HO_x chemistry (Roelofs et al., 1997). This model has been successfully used to study the transport, distribution and atmospheric input of inert tracers and chemically reactive species with an atmospheric lifetime of days (Feichter et al., 1991 and 1996; Dentener et al., 1999). The radical concentrations are monthly mean, three-dimensional fields. The global and annual mean OH concentration is $5.23*10^5$ cm^{-3}. The zonal distributions for January and July are shown in Fig. 2.

Partitioning between the gas and particulate phases is assumed to be described by the empiric relationship between vapor pressure, aerosol surface and adsorbed fraction (Junge, 1977). This approach is justified by field

observations (Patton et al., 1991, besides others). It has been suggested to use the vapor pressure above the substance' super-cooled liquid instead of the vapor pressure above the solid (Pankow, 1987). We refrained from doing so, however, because the results of a flowchamber investigation into the partitioning of atrazine and ethyl parathion in model aerosols (besides other substances; Gath, 1997) suggest that adsorption of these substances would be significantly underestimated. Further conclusions on the phase partitioning of the substances are not supported by this laboratory study, however, they are due to experimental limitations which lead to a considerable data scatter. The particulate-borne fraction of pesticides is treated as bound to sulfate particles only. The global and annual mean sulfate concentration in the boundary layer (> 850 hPa) is 0.38 μg m^{-3} which provides 5 * 10^{-7} cm^2 / cm^{-3} of aerosol surface. The total atmospheric burden is 590 kt with ca. 50 % within the boundary layer and ca. 75 % in the northern hemisphere. The prescribed dry deposition velocities are 0.025 cm s^{-1} to ice and to dry non-forest land and 0.2 cm s^{-1} to the ocean, to forest and to wet non-forest land. Interpolated values are applied to those grid cells which have partly wet soils or are partly covered by forests. The in-cloud and below-cloud scavenging efficiencies of these particles are 100 % and 10 %, respectively.

2.1.2 Soils

Soils are represented with one vertical layer and no explicit depth. Storage of substances in the soils is controlled by the spatial and temporal variabilities of the soil multiphase system: Time and location dependent soil hydrological status and location dependent soil organic matter fraction are, besides the temperature, the controlling parameters. We consider two substance sink processes to the soil compartment, chemical degradation and volatilization, while a third one which exists in reality, loss to the ocean by runoff, is neglected: Chemical degradation of pesticides in the soil is represented by a first-order rate constant and assumed not to be influenced by local conditions other than temperature. It is assumed that a doubling of the degradation rate is caused by each 10 K temperature increase. Such a dependency is a crude estimate. It is justified by the acceleration of biodegradation in soils by temperature and recommended (EC, 2000). Substance loss to the atmosphere is through volatilization. The parameterisation of this process is independent of whether volatilization occurs upon pesticide application or in the form of re-emission following eventual earlier deposition. We assume that the volatilization rate decreases with time obeying an exponential time-law. A parameterisation is used which is based on the experimental determination of losses of a large variety of pesticides from soils in the field and in the greenhouse (Smit et al., 1997). This data set comprises mainly observational data on pesticide loss in soil. The model induced implicitly assumes that volatilization was the only loss process whereas chemical transformation in the soil can be neglected. The rate is dependent on the substance properties (solid-liquid and

gas-liquid equilibria, K_{oc}, K_{gl}, vapor pressure) and on local conditions (soil organic matter content, soil pore space, temperature). The solid/liquid equilibrium constant is assumed to be given by the product of the sorption coefficient, K_{om}, and the soil organic matter content. The latter is taken from a global soil data set (9 classes; Batjes, 1996). Soil density is based on sorptivity (Dunne and Willmott, 1996). Runoff to the ocean is discounted, although pesticides runoff losses occur either as solution in water or through washout of soil material to which the substance is adsorbed to. The first process has been judged to be of only modest significance (< 0.7 % of applied amounts) for the pesticides in use in Germany and for the local climatological conditions (precipitation statistics, besides other; Huber et al., 1998). It is neglected for simplicity. The runoff of pesticides adsorbed to soil material was not covered because the fraction of the substance which ends up mobile in the ocean reservoir would be unknown (soil particle losses to river and ocean sediments, irreversible adsorption to the hydrosol).

2.1.3 Vegetation

Biota are represented as vegetation which covers a fraction of the continental grid cells. Uptake of organic substances by vegetation is incompletely understood. In our model and with regard to trace substance inter-compartmental mass exchange, the vegetation is represented as a surface which allows for reversible adsorption, while other uptake mechanisms are neglected. Atmospheric deposition onto vegetation is influenced by the canopy height. In the model this is only accounted for as far as the dry deposition of particles is regarded (see above).

Similar to the soil, an empirical relationship is used to describe the kinetics of the volatilization loss for both volatilization upon agricultural application or atmospheric deposition. The volatilization rate is determined by the vapor pressure (Smit et al., 1998). Furthermore, the same degradation kinetics is assumed to apply in this compartment as in the soil. Atmospheric deposition to continental grid cells is distributed over the vegetation and soil compartments according to the area fractions covered or not covered by vegetation.

2.1.4 Ocean

The ocean is represented as a surface mixed layer of a depth varying spatially and in time without lateral transports. The geo-referenced depths were taken from a three-dimensional ocean general circulation model simulation based on the criterium of water density not exceeding the surface water density + 0.2 kg m^{-3} (Drijfhout et al., 1996). The global annual mean depth is 80.2 m. Deepest mixing depths are prescribed for February in the northern hemisphere and in September in the southern hemisphere. The maxima of yearly amplitudes of depth variation are located at 60°N (varying between 190 and 600 m) and at 60°S (varying

between 40 and 380 m; Fig. 3). We consider three substance sink processes to the ocean mixed layer compartment: chemical degradation, volatilization and sedimentary loss to the deep sea: Chemical degradation is considered to be a first-order process. Also in this case, a doubling of the degradation rate is assumed for each 10 K temperature increase. This temperature dependence is supported by literature data for methyl parathion decay rates in synthetic seawater ($8.9 * 10^{-8}$ s^{-1} at 277 K and pH 7.8-8.8 (Wade, 1979), $1.10 * 10^{-7}$ s^{-1} at 298 K and pH 7 (Mabey and Mill, 1978), $9.3 * 10^{-7}$ s^{-1} at 313 K and pH 8 (Smith et al., 1978). The flux of trace substances from the ocean to the atmosphere is described based on the stagnant film model (formulation according to Wania et al., 2000) while the dry deposition flux of gaseous trace substances from the atmosphere to the ocean is calculated using fixed dry deposition velocities. Loss to the deep sea is represented as consequence of the seasonal variation of the mixed layer depth: The substances dissolved in the lower part of the mixed layer are considered to be lost to the deep sea when the mixing depth decreases in spring. The substance ocean reservoir is on the other hand not considered to be refilled when the mixing depth increases in autumn.

The atmospheric GCM uses monthly prescribed sea-surface temperatures of the year 1994. The simulation of pesticide transports and transformations starts after 15 years of model spin-up. 5 subsequent simulated years of model output were used. As the studied substances have residence times on the order of months or less in the environmental media, equilibrium with the total environment was achieved within one seasonal cycle. The horizontal resolution used in the here reported simulations was 3.75° and the timestep was 30 min for all compartments.

2.2 Substances studied

The focus of this study is an investigation into the environmental fate of semivolatiles. We chose two important modern agrochemicals, one insecticide, methyl parathion, and one herbicide, atrazine. The criteria for the choice were the environmental residence time of the substances, commercial and environmental relevance and data availability regarding physico-chemical properties, usage and observations in the environment. As usage data were derived from application recommendations and crop distributions (Section 2.3.1), those pesticides of which the major usage is not limited to only few crops could not be addressed. The total environmental residence time, $\tau_{½\ total}$, is decisive for the model tool to choose. For very persistent substances, such as e.g. DDT, $\tau_{½\ total} >> 1$ year would apply. With this study we want to address $\tau_{½\ total}$ on the order of several months.

Methyl parathion, a thiophosphoric acid ester (O,O-dimethyl-O-4-nitrophenyl phosphorothioate; CAS No. 298-00-0), is globally one of today's major insecticides. In 1976 methyl parathion accounted for 13.6 % of all

insecticides applied in the USA (Eichers, 1981). In terms of its application, cotton is by far the most important crop. In the USA ca. 60 % of the substance application is on cotton and ca. 40 % are applied to maize, soybean, fruits, vegetables and others (data for 1991; NASS, 1997; Perkow, 1993). Methyl parathion is very toxic to human and wildlife. It has been reported in environmental and food samples from application areas.

Atrazine is the most important substituted triazine herbicide (6-chloro-N-ethyl-N'-(1-methylethyl)-1,3,5-triazine-2,4-diamine; CAS No. 1912-24-9). It is mainly applied on maize crops (most important maize pesticide in China; in the USA in 1991 ca. 90 % on 66 % of the maize area; other crops: sorghum besides others; NASS, 1997). In 1976 atrazine accounted for 24.2 % of all herbicides applied in the USA (Eichers, 1981). The environmental fate of this herbicide is mostly within the region of application, however, it has been observed in air, precipitation and sea ice besides other compartments several hundred kilometers and beyond from its supposed application (Glotfelty et al., 1990; Chernyak et al., 1996; Goolsby et al., 1997). In maize cropping this pesticide is mostly applied once per year, ca. 1 kg ha^{-1}, in spring-time. Time and dose of application patterns are seemingly quite even throughout climate zones (IAO, 1998; Papasterhiou and Papadopoulou-Mourkidou, 2001). In recent years application has been banned in Germany (1991), the Netherlands, Austria and Scandinavian countries (1994).

The substance properties are incompletely known, i.e. introducing partly significant uncertainty. This would translate into a range of environmental mobilities rather than one. For methyl parathion we study the environmental fate assuming high mobility, i.e. adopting values at the upper mobility end of the data uncertainties. We study the environmental fate of atrazine under two different scenarios: Two sets of the physico-chemical properties and of dry deposition velocities have been compiled such as to design scenarios reflecting a lower and an upper estimate of environmental mobility (Table 1). As the atmosphere is the only mobile compartment in our model, we consider any change in model parameters which enhances the atmospheric residence time or increases the atmospheric source term of the substance a change towards increased mobility.

Note that the substance properties selected suggest that according to presently used definitions (UN-ECE, 1998) atrazine under both scenarios is persistent while methyl parathion is not.

2.3 Substances entry into the environment

No natural sources exist for the substances studied. We assume that agriculture is the only sector of pesticide usage. An application inventory is set up and the compounds' introduction into the environment is then

simulated dynamically as volatilization from soil and vegetation surfaces and determined by the local conditions during and after application.

2.3.1 Pesticide application inventories

Methyl parathion and atrazine are each the most important cotton and maize pesticide, respectively. Cotton and maize are under the five leading crops in terms of the global marketed pesticide volume (IVA, 1997). While 52.3 % of all pesticides applied in the USA in 1976 have been applied on maize cultures and 4.6 % on cotton cultures (Eichers, 1981), worldwide ca. 10 % have been applied on cotton cultures in 1994 (Reller and Gerstenberg, 1997). For the application inventory it is, hence, assumed that the substances are exclusively applied for one crop, atrazine for maize and methyl parathion for cotton. Implicitly, non-agricultural applications (industrial, amenity and forestry, garden and householde uses) are neglected, too. These could account for 10-15 % of pesticide application (PEWG, 2000). In order to account for the uncertainties, a lower and an upper estimate of atrazine application are used in the low and high mobility scenarios, accordingly. Application statistics or recommendations are only available from a few countries on which information the estimates are based. The application time patterns and the receptor media were chosen such as to realistically describe agricultural practices related to the pesticide types (one insecticide, one herbicide) and the crops involved, albeit in a simplified manner. The scenarios are summarized in Table 2.

Each grid cell, 3.75° * 3.75°, on the continents (except of Antarctica) is assigned to one country. For each country, the national crop area (data mostly for 1994 in ha/country; FAO, 1998) is uniformely distributed over the grid cells assigned to this country. Some larger areas without agricultural activities (the Sahara and Gobi deserts, Amazonia, most parts of Western, Northern and Central Australia, parts of Western China and some others) are excluded from this procedure. If such an area is part of a country's area, the national crop area is distributed over the rest of the country's area. The season and frequency of application is assumed to be the same everywhere and is based on application statistics which are available for some countries and for some years: USA 1990-1998 (NASS, 1997), Denmark 1994-1995 (IAO, 1998), New Zealand 1998 (Holland and Rahman, 1999). The pesticide applied per hectar of cropland varies in different countries mainly due to differences in both the cropping characteristics and the intensity of agrochemicals use, i.e. the total area treated by pesticides relative to the total area of cropland and the number of target crops relative to the total number of crops: The world mean value of pesticide application on cropland is 1.45 kg ha^{-1} a^{-1} with regional values of Africa 0.50, Asia 1.16, Europe 1.90, North America 1.70 and Latin America 1.36 kg ha^{-1} a^{-1} (based on 1994 data on cropland and total

amount of pesticide use by country; FAO, 1999). We try to account for the intensity of agrochemical use in the individual countries by applying an intensity of agrochemicals use factor, f_{ac}, defined as:

$$f_{ac\ i} = (u_i / A_i) / (u_s / A_s)$$

with u_i, u_s (kg ha^{-1} a^{-1}) being the total amounts of pesticide use in the country i and the reference country s, respectively, and A_i, A_s the cropland areas of country i and reference country s.

Some countries specializing on fruit and vegetable cropping and/or with significant greenhouse area forming part of the national cropland area apply the highest amounts per unit area (values in kg ha^{-1} a^{-1}): These are Costa Rica (22.4), Israel (18.7), Italy (15.4), Japan (14.6), Republic of Korea (13.0), Belize (12.0), Belgium (11.7), and the Netherlands (11.4). High values of f_{ac} resulting from these high u_i values would be misleading as far as the intensity of agrochemical usage on other crops, else than vegetable and fruits and outside greenhouses is regarded (maize and cotton in this case). To somewhat account for the differences caused by cropping characteristics varying between the countries, we put a ceiling on f_{ac}: It was set $f_{ac} = 8.0$ for all (the above listed) countries with $f_{ac\ i} > 8.0$ when derived according to the definition above. When no data were available it was assumed that the same intensity factor applies as in neighbouring countries.

The application inventories of methyl parathion and atrazine based on global cotton and maize crops, respectively, are shown in Fig. 4. In the model simulation the substances are entried into the vegetation and soil compartments. Hereby we apply a modal split according to the supposedly predominating application situation (cf. Table 2): The maize herbicide atrazine is sprayed in pre- and post-emergence control to the then mostly bare soil (RSC, 1990; Perkow, 1993). We, hence, assume that most of the maize herbicide is received by the soil while a small fraction is received by the leaves of the crop itself or the target organisms, the weeds. The cotton insecticide methyl parathion is sprayed to the fully developed cotton plants mostly prior to harvest (USEPA, 1988; Kidd and James, 1991). We, hence, assume that most of the cotton insecticide is applied to the plant and only a small part is received by the bare soil. Furthermore, in agriculture pesticides will be preferentially applied during daytime and according to the weather conditions. Daytime and weather during and after application has a significant influence on the volatilization and other losses of the pesticide (Kurtz, 1990). We, hence, assume that pesticides are only applied during ‘dry’ (no precipitation) daylight hours of the application season: For each grid cell an average daylight application flux is obtained through division of the total amount of substance to be applied by the number of daylight timesteps (30 min) during the application season. The application flux is set to zero during night-time and timesteps with precipitation, the average daylight application flux is applied during

daylight timesteps without precipitation and a manifold of it, corresponding to the length of the previous precipitation event, is applied on the first 'dry' timestep after a precipitation event. Thus, as a function of the local weather the simulated application periods vary somewhat. The amounts of pesticides which are applied in the first days after the scheduled end of the application season due to persistent precipitation periods towards the end of this season are, however, found to be negligible.

2.3.2 Validation of the application inventory

For some regions and countries information upon pesticide application is available from independent sources (Table 3).

Most of the estimates are within a factor of 2 of the other reportings. These are based on either high-resolution estimates or expert guess. The estimates for Italy (too high) and the Netherlands (too low) deviate more, by a factor of 2.5-6. For consistency reasons the information from independent sources is not used to improve the application inventory.

2.3.3 Pesticide emission: volatilization

We describe pesticide losses from the crop area as determined only by meteorological conditions during and directly after the application (Sections 2.1.2, 2.1.3). In reality, also the type of pesticide formulation used, the species and its leaves, flower and stalk geometry, and eventual conservative measures of soil treatment upon pesticide application play a role. The knowledge of the processes involved and their interactions is incomplete and in part inconclusive. As the pesticides studied here are concerned, it has been found that the species and its geometry is of negligible influence for the volatilization of methyl parathion (Müller, 1993) as are soil conservation measures performed after application for the losses of atrazine (Whang et al., 1993). For simplicity, we assume that the aforementioned influences average out and their overall impact on the volatilization process is reflected by the empirical relationships on which the parameterization is based.

3. Results and discussion

3.1 Substance geographical distributions and partitioning between environmental compartments

By comparison of the distributions in the environmental media (Fig. 5) with the distribution upon application (Fig. 4a), we find that methyl parathion undergoes regional transports and beyond: Non-source regions such as the northern high latitudes are clearly affected. The spatial variation of the total environment load (Fig. 5a) is one order of magnitude over almost the entire northern hemisphere (given the horizontal resolution of this simulation). It is less than that in the atmosphere, i.e. methyl parathion is almost well mixed in the northern hemisphere atmosphere. The environmental distribution is less effective in the southern hemisphere. The reason for this, we believe, is that as a consequence of the moderate water solubility of the substance, the volatilization loss from the ocean is much less significant than from the soils and vegetation. I.e., once deposited into the ocean, methyl parathion would hardly undergo another atmospheric cycle (cf. number of atmospheric cycles, below). The loads in the ocean (Fig. 5e) are highest downwind of the continental source regions (westerly outflows from the Americas, East Asia and Africa in the northern and southern mid latitudes, easterly outflows from equatorial South America and Africa). In these regions and in the entire northern mid latitude oceans 10-100 μg m^{-2} are predicted, which, given the depth of ocean mixed layer (cf. Fig. 3), corresponds to ca. 0.05-2 μg m^{-3}. Relative to the distribution upon entry (Fig. 4a) the annual mean atmospheric distribution (Fig. 5b) is shifted northward in Central Asia and North America and covers non-source regions in North Africa and the Arabian peninsula. The soils and vegetation of the entire Northern Europe and Asia and the non-source regions of North America are affected by the substance distribution (Fig. 5c, 5d). In the northern mid and most of the high latitudes loads of 0.01-0.1 mg m^{-2} in soil are predicted.

Methyl parathion is fairly homogeneous distributed over the environmental compartments: In the annual mean the atmosphere, soil, vegetation and ocean compartment host 7, 53, 20 and 19 % of the total burden. In the atmosphere the substance is mostly in the gas-phase: At ground level 2 % are found in the particulate phase while in the height of the top of the boundary layer this fraction is 33 %.

By comparison of the distributions in the environmental media (Fig. 6) with the distribution upon application (Fig. 4b), we find that atrazine undergoes regional transports but not beyond that: The gradients in the northern hemisphere total environment are steeper than those of methyl parathion and the source distribution is recognizable. Most of the atrazine is stored in the soils (Fig. 6c). In the source regions loads exceeding 1 mg m^{-2}

soil are predicted. Obviously, the distribution in the vegetation compartment extends also to non-source regions in the western part of North America and throughout the northern high latitudes (Fig. 6d). Even in the atmospheric distribution the main source regions are retained (Fig. 6b). It is clearly less homogeneous than the atmospheric distribution of methyl parathion. The reason for that is not in the atmospheric lifetime itself: Removal of atrazine is less efficient than for methyl parathion, because the hydroxyl rate constant, k_{OH}, and the water solubility which favors washout, both, have smaller values in the case of atrazine (Table 1). Atrazine is less mobile in the atmosphere, because once deposited the most probable fate is degradation in the ground compartments while re-emission through volatilization is less likely than in the case of methyl parathion (cf. vapor pressures, Table 1). We come back to that point in Section 3.4. Hence, the source region of atmospheric atrazine, unlike methyl parathion, is almost limited to the pesticide application regions. In the ocean, then similar to the methyl parathion distribution, there are 'plumes' visible which stretch out from the continental source regions (Fig. 6e and 4b). 50 μg m^{-2} is predicted as a typical load for the northern mid latitude oceans which, given the depth of the ocean mixed layer (cf. Fig. 3), translates into 0.2-0.5 μg m^{-3}. These tendencies are even more pronounced under the low mobility scenario (not shown): The difference of atrazine load between the total environment in the main source regions and in remote areas of the northern hemisphere covers 4 orders of magnitude instead of 2 as for methyl parathion in the annual mean. The same applies to the oceanic load in both hemispheres. A typical concentration in the ocean surface waters of the northern mid latitudes would be ca. 0.01 μg m^{-3}. Hot spots, with concentrations as high as 0.1-1 μg m^{-3} (loads 10-50 μg m^{-2}), limited by steep gradients, are identified in the Bay of Biscay, the Mediterranean and Japan Seas.

Most of atrazine is found in the soils: 90 % under the low mobility scenario and 70 % under the high mobility scenario. This difference between the scenarios is seen as at the expense of the vegetation (storing only 7 % instead of 20 %) and the ocean (storing only 2 % instead of 9 %). Due to its low vapor pressure and high water solubility atrazine only to a small extent partitions into the atmosphere: In the model simulation, 0.2 % (low mobility) and 0.7 % (high mobility) are predicted. As a global mean, at ground level 20 % of atrazine in air are found in the particulate phase while in the height of the top of the boundary layer this fraction is 90 %.

We stated that atrazine is regionally distributed. But it is found in the vegetation in the northern non-source regions, besides others. Having in mind that atrazine due to its high water solubility and low vapor pressure has a limited tendency to partition to the atmosphere, this result is remarkable. We conclude that this herbicide has an albeit limited potential for long-range transport.

The substance distributions of the low and high mobility scenarios of atrazine are very different. The concentrations in the non-application regions differ by 1-2 orders of magnitude (see also Fig. 8-10). 280 and 3500 t of atrazine are stored in the atmosphere and ocean, respectively, under the high mobility scenario, whereas only 21 and 190 t are stored in these compartments under the low mobility scenario. These scenarios mostly reflect the uncertainties resulting from lack of knowledge of the degradation processes (e.g. k_{OH}, cf. Table 1) and of intercompartmental exchange (dry deposition velocity, Table 1). Based on the validation of the application estimates (Section 2.3.2) we believe that the uncertainties which propagate from these are less influential and cannot account for more than a factor of 2-3 in the concentration distributions. The conclusion is that due to data uncertainties the concentration in the atmosphere or ocean cannot be predicted better as to the order of magnitude.

3.2 Comparison of model results with observations in air and in ocean surface water

In order to account for interannual variability preferred observational data would be multi-annual means, e.g. from monitoring programs. Such data are not available for the substances studied, but from episodic measurements in air and in ocean water. The observational data represent, furthermore, only part of the globe, namely the northern mid latitudes and are biased towards the application areas of the substances.

Methyl parathion: Only few observations of methyl parathion in the environment have been reported. The time series of observations in air of Rolling Fork in the Mississippi Valley (Foreman et al., 2000) is shown in Fig. 7. Methyl parathion was determined during June-September while the levels were below detection limit during April-May. The model predictions under the high mobility scenario match very well the seasonal cycle and the absolute concentration level.

Atrazine: Highest levels of this herbicide in air are observed during the application season, April-July, and close to the areas of application. The on-site temporal and spatial variability is very high, in particular in the source areas. For comparison with model results in particular those measurement sites are relevant which are presumably not influenced by nearby application of the substance. The observations were not continuous, but monthly values are based on 2-5 days of sampling time, while the model results are represented as monthly means (Fig. 8).

The concentration levels agree with the observed ones within an order of magnitude or less with both over- and underestimations occurring. The reason why underestimation or overestimation is found are not known. For the European sites (Fig. 8) emission overestimates could account for a factor of 2 (Table 1). The model - mostly as a consequence of the difference in altitude - suggest higher concentration for the Wank mountain site (800 m a.s.l.)

than for the Aubure mountain site (1100 m a.s.l.) while in fact higher concentrations were reported from the higher site. Atrazine was measured during low altitude flights over forests and agricultural fields in the application season over Southern Ontario (Zhu et al., 1998; cf. Fig. 9). In this case monthly mean model results are compared with only a few hours (ca. 4 h in June 1993 and ca. 2 h in July 1994) of total sampling time but averaged over a larger area, ca. 800 km^2. The model results suggested under the low mobility scenario agree quite well with these observations.

There are a few observation of atrazine in ocean water: 1-7 ng l^{-1} were observed in the German Bight (North Sea; Bester and Hühnerfuss, 1993). However, due to the coarse resolution of the model there is no basis to compare observations from this marginal sea with model results. An upper limit, < 9 pg l^{-1}, was reported from surface water of the Bering and Chukchi seas in summer, Chernyak et al., 1996). 1-20 and 20-400 pg l^{-1} are predicted by the model under the low and high mobility scenarios, respectively, for these areas and the same season. < 1 – 32 ng l^{-1} have been measured in surface waters of the Atlantic, in the South Atlantic Bight, in July 1994 (Alegria and Shaw, 1999). The model results for atrazine concentrations in this area of the Atlantic ocean in July are 0.14 and 3.5 ng l^{-1} under the low and high mobility scenarios, respectively (three-year average; Fig. 10). Highest concentrations were observed in a sea area which was affected by a major storm event that deposited significant rainfall some days before and the authors believe that pesticide enrichment resulted from rain scavenging. The model results match the observations at the lower end of the data range. The model results, taking a multi-year average are, however, meant to reflect typical not extreme weather situations.

Because of the episodic character of the observations these comparisons cannot provide a sufficient means for model validation. Also, an unambiguous decision whether the low or high estimate of the substance (atrazine) mobility is closer to reality cannot be based on these comparisons. Given the limitations of comparability and the coarse resolution of the model we judge the agreement between the observations and the model results satisfactory for both the atmosphere and ocean compartments.

3.3 Seasonal variation of the substances burdens in the environment

The annual variation of the total environmental burden reflects the dynamics of pesticide application and degradation in the environmental compartments: it reaches the maximum value in the month following the entry into the environment and the minimum value in the month prior to application. The seasonal variation of the total environmental burden of both methyl parathion and atrazine is governed by the dynamics in the soil and vegetation burdens (which together host 73 % of methyl parathion and 90-99 % of atrazine).

Due to its high volatility, methyl parathion readily leaves the vegetation, which is the major compartment of entry into the environment in our scenario and undergoes re-distribution. The annual increase of the substance burden in the atmosphere starts in the month of application while this is observed one month after the entry in the soils and in the ocean. Only a small fraction of atrazine is cycling in the atmosphere (see above, partitioning between environmental compartments) which is a consequence of its significantly lower volatility (cf. Table 1, vapor pressures). Therefore, the delay of the annual increase of the oceanic atrazine burden as compared to the major compartment of entry (soils) is longer, 2 and 3 months in the high and low mobility scenarios. Once the sources are switched off, the burdens are removed with different dynamics in the various compartments. The removal is fastest in the atmosphere for both substances. Atrazine returns, however, for a second time in the year to the atmosphere and reaches an albeit small maximum in November and October under the low and high mobility scenarios, respectively. The reason for this behavior is the superposition of the seasonal variability of the atmospheric sinks (dominated by precipitation and photochemistry) and the source, volatilization. Obviously, the sources prevail in those months where volatilization is still relatively high due to high temperatures of the soils and vegetation which store the substance (northern hemisphere summer and autumn) and photochemistry yet started to decline (northern hemisphere autumn).

3.4 Substance mobility: Shifts of distributions

We address the spatial scale of the environmental fate of the pesticides using indicators for the substance distributions movements in the individual media and in the total environment, namely the north-south movement of the center of gravity (Table 4a) and the changes of the zonal distributions (Table 4b). Whether non-source regions are affected is certainly the most important aspect of investigations into the spatial scale of substances. In particular the high latitudes and the interhemispheric transports are of prime interest. We refrain here from discussing the respective changes in east-west direction.

The centers of gravity of the global cotton (methyl parathion) and maize (atrazine) crop distributions and, therefore, the application distributions (50%-percentiles) are close to each other at 35.1°N and 37.7°N, respectively. Relative to these, the annual mean distributions in the soil and vegetation compartments are distorted towards north (by 4.6-15.4 °; Table 4a) while in the atmosphere and ocean compartments distortions towards north and south are predicted. Despite the partitioning between media of atrazine, which would suggest that the substance is not very mobile, the center of gravity of the substance in the environment is significantly more northerly than upon emission: While the 50% percentile of the cumulative zonal distribution of the

application pattern is at 37.7°N, it is found at 42.6±0.3°N in the soils and at 46.9±0.3°N on the vegetation (annual means, range under both mobility scenarios). Methyl parathion, which partitions more to the atmosphere, is found at 48.4-50.5°N in the soils and on the vegetation, while the 50% percentile of the cumulative zonal distribution of the application pattern of this substance is at 35.1°N. The seasonal variability of these migrations is mostly governed by the application: In the soils, vegetation and ocean compartments both substances migrate northward during non-application months until the more southerly entry in the following year causes a new start. Zonal shifts as large as +21.2°N, +8.9°N and +10.9°N relative to the distribution upon entry are reached in the pre-application month in the vegetation. Under the two scenarios the migration patterns of atrazine hardly differ. In the ocean, however, the smaller amount of the pesticide which is found there under the low mobility scenario (2 % = 0.3 kt of atrazine) appears to be more mobile than the higher amount found there under the high mobility scenario (9 % = 3.8 kt; Table 4a). The decisive difference is the residence time in the atmosphere: The distribution of atrazine deposited into the ocean in the first 1-3 months after application zonally centers at the equator when short-lived in the atmosphere (low mobility scenario), because only coastal waters are reached in both hemispheres. It centers at ca. 20°N when longer lived in the atmosphere (high mobility scenario), because then the plumes cover coastal waters and the open oceans according to extension of the application areas in both hemispheres (larger in the north). Furthermore, under both scenarios in this season (northern summer) the atmospheric residence time of atrazine is longer in the south because of the zonal distribution of the main atmospheric sink, the OH radical (a factor of 3-4 higher at 30°N than at 30°S; cf. Fig. 2). The fraction of atrazine deposited prior to degradation is therefore larger in the south, which, partly, compensates for the zonal distribution of the atmospheric source, volatilization (higher in the north).

The zonal distributions in the atmosphere move northward and southward with the season, as the source, volatilisation, is strongly influenced by temperature. When the substance volatilizes from vegetation surfaces (which is the prevailing situation for methyl parathion) temperature alone determines the process, while other factors are involved when the substance volatilizes from the soils (cf. Section 2.1; which is the prevailing situation for atrazine). In consequence, this movement of the distribution is much more pronounced for methyl parathion (zonal amplitude 27°; Table 4a) and less for atrazine (6.5 and 5.9° for the low and high mobility scenario, respectively). Substances having short atmospheric residence time (low mobility scenario) are more sensitive to the seasonal movement of the source term.

In conclusion, when refering to the north-south movement of the center of gravity as an indicator for spatial range, we find that methyl parathion mobility exceeds atrazine mobility in most of the media and in the total environment. This applies when based on annual mean movements as well as on seasonal variability. As far as

reflected by this indicator, the two scenarios of the environmental fate (meant to account for lack of knowledge) of atrazine are quite similar.

The annual mean widths of the zonal distributions in the media relative to the situation upon application are quantified in Table 4b. The numbers reflect the superposition of several processes in space and time, i.e. spatial distributions of source and sink terms and their chracteristic time difference: Large positive values reflect a spreading of the distribution over the latitudes while large negative values reflect a narrowing. The indicator is meant to represent a large majority of the distribution and, hence, is based on the distance between the 5%- and 95%-percentiles. Significant spreading is found for methyl parathion in most of the media. It is largest in the ocean and is not found in the soils. Atmospheric transports and deposition provide an all-year source for oceanic methyl parathion which, however, in different seasons is located in different latitudes (cf. seasonal range of center of gravity in the atmosphere, Table 4a). The residence time in the ocean is long enough (characteristic times for degradation are 45 d at 298 K and 180 d at 278 K and the sinks to the deep sea and to the atmosphere are not very limiting) to sustain a broad latitudinal distribution. The same applies for oceanic atrazine, albeit less pronounced.

In the receptor media upon entry of the substances into the environment, the vegetation (receiving 90% of methyl parathion and 0-10% of the applied amount of atrazine) and the soils (receiving 10% of methyl parathion and 90-100% of the applied amount of atrazine), the fringes of the cumulative zonal distributions are almost exclusively moving northward by various distances, the northern fringes by 2-21° and the southern fringes by 21-49°. Only in the case of methyl parathion in the vegetation, the southern fringe of the zonal distribution moves southward by 9°. This leads to spreading or narrowing (Table 4b). Movements of these two distributions are resulting from the same source and sink processes, i.e. atmospheric deposition, re-emission by volatilization and compartmental degradation. There are, nevertheless, systematic differences: In the low and mid latitudes the vegetation covered areas prevail. Therefore, the source process, atmospheric deposition will in these latitudes mostly refill the vegetation compartment. This favors the mobility within this compartment relative to the mobility of the soils compartment. Volatilization from the vegetation is steered by temperature whereas from the soils it is steered by several parameters, soil hydrological status and organic matter content besides temperature. Therefore, one of the sink processes, volatilization, is determined by the seasonal and latitudinal temperature distribution as far as the vegetation compartment is considered, but it's spatial and temporal pattern differs when considering the soils. Why are the north-south movements more pronounced in the southern hemisphere ? It is important to remind that large fractions of the pesticides degrade: Only 51, 18 and 26 % of the entried amount is

stored in the total environment as an annual mean for methyl parathion and the low and high mobility scenarios of atrazine, respectively (cf. Table 2 and Fig. 4 for amounts entried and stored). As a consequence of the higher temperatures, the degradation in the soils and on the vegetation in the tropics and subtropics is faster than in the mid-latitudes. The southern fringe of the application are in the tropics and in the subtropics of the southern hemisphere. (The same tendency, but less pronounced, is delivered by this indicator when based on the the 1% and 99 %-percentiles instead of the the 5% and 95 %-percentiles of the zonal distributions.) Furthermore, in the southern hemisphere much of the potential source to the ground compartments, the atmospheric depositions, are received by the ocean. In consequence, the southern fringe of the distributions appears to be more mobile.

The differences between the mobilities of atrazine in the ground compartments under the two scenarios are determined by the difference in the atmospheric residence time: The mass fraction of atrazine which returns to the ground compartments prior to atmospheric degradation is higher under the high mobility scenario. That is why under the high mobility scenario the vegetation compartment in the south can be refilled substantially.

In conclusion, when referring to the north-south spreading or narrowing of the distributions as an indicator for spatial range, we find that the substances studied can show both tendencies in environment media. Again, methyl parathion mobility surmounts atrazine mobility in all media. As far as reflected by this indicator, the two scenarios of the environmental fate (meant to account for lack of knowledge) of atrazine differ significantly in the atmosphere and vegetation media.

3.5 Substance mobility: Number of atmospheric cycles

Methyl parathion, due to ist higher vapor pressure, has a higher tendency to re-evaporate from the ground compartments and this leads to a higher tendency to cycle through the atmosphere and refill the ground compartments than atrazine. As the repeated cycling through the atmosphere is a key process for the understanding of the environmental fate of semivolatile substances, we make an attempt to quantify this process for the substances studied: We trace the number of atmospheric cylces the compound is undergoing, N_{ac}, by deriving a respective measure from the model results: The total depositional flux, $F_{tot.\ dep.}$, divided by the total agricultural application flux, $F_{appl.}$, per unit time provides obviously a measure of the mean number of atmospheric cycles of a compound.

$$N_{ac} = F_{tot.\ dep.} / F_{appl.}$$

As a consequence of competing losses volatilization into the atmosphere and chemical degradation within the receptor medium, a fraction of the amount applied would not enter the atmosphere at all. Therefore, $N_{ac} < 1$ would result for compounds which do not undergo re-emission and $N_{ac} < 1$ or $N_{ac} > 1$ are possible results for substances which are re-emitted into the atmosphere. The results are listed in Table 5. The relatively small numbers suggest that the substances studied have a limited tendency for intercompartmental cycling.

Atrazine definitely does not belong to the substances undergoing the so-called grasshopper effect. The low numbers determined for the number of atmospheric cycles reflect that a large part of the pesticides studied here remains in the soil or vegetation or is degraded in these compartments or in the atmosphere during transport and prior to deposition. N_{ac} can be described as $N_{ac} = \Sigma\ p_i\ N_i$, with i = 0, 1, 2 ... and p_i denoting the fraction of molecules undergoing 0, 1, 2... atmospheric cycles. Assuming that the mass transfer between the ground compartments and the atmosphere can be described as a phase equilibration process, constant in time (Poisson distribution), we estimate $p_{i,}$ i = 0, 1, 2 ...$_,$ for the various N_{ac} (cf. Table 5). For atrazine this figure $p_0 = 91\%$ and 84% for the low and high mobility scenarios, respectively. Nonetheless, it is estimated that 13% (8%) of the material in the high mobility scenario (low mobility scenario) re-deposits once and 2% (ca. 1%) twice. Those numbers are reflected also by the high ratio of pesticide present in the land surface compartments (soil and vegetation) compared to atmospheric values.

In the case of methyl parathion, half of the amount entried into the environment does not undergo atmospheric deposition, 25% once and 13% twice. 5% of the methyl parathion molecules applied onto vegetation and soils will hop at least four times.

3.6 Total environmental persistence

We define a measure of persistence, the total environmental halftime, $\tau_{½\ total}$, which is the time period until 50% of the global burden (sum over all compartments) of the compound is degraded based on a first-order exponential decay during periods of undisturbed decay in the system, i.e. upon switched off sources (agricultural application in the case of pesticides). In reality, the total environmental decay as resulting from the superposition of very different and in part temporally variable degradation rates in the individual media cannot be a first-order process. We prefer a halftime which is linked to a first-order rate coefficient as the measure of persistence. Such a measure is derivable largely independent of the type of model used and therefore is common in environmental chemistry. The decay rate is determined by fitting a first-order exponential function to the time series of the global multimedia burden, m. The total environmental halftime, $\tau_{total\ ½}$, is then given by:

$$\tau_{½\ total} = \ln 2 / \ln (m_{i-1}/m_i) * \Delta t$$

with m_{i-1}, m_i representing the burdens of subsequent time steps Δt . In consistency with the time resolution of the application scenario a time-step of Δt = 1 month was used. The results are shown in Fig. 12 and are listed in Table 5.

The annual mean persistence of the methyl parathion and atrazine under the high mobility scenarios is almost the same, ca. 7 months. It is less, ca. 4 months, for atrazine under the low mobility scenario. (Note, that the definition for persistence applied here does not allow to determine persistence during the 1-2 months of application, such that the annual mean value is based on only 10-11 months.) The seasonal variability of persistence is remarkably pronounced with a maximum in the northern winter. It is stronger for atrazine than for methyl parathion: A factor of 1.9, 5.5 and 7.2 are between the minimum and maximum monthly means of persistence of methyl parathion and atrazine under the low and high mobility scenarios, respectively. This result is also visible in Fig. 11a. It reflects the temperature dependence of the degradation in soil and vegetation and the multimedia partitioning.

4. Conclusions

4.1 Results vs. input data uncertainties

The purpose of this study is an investigation into the environmental fate of important in-use agrochemicals on the global scale using a multimedia model which has been developed based on an atmosphere general circulation model. Such a model is geo-referenced and capable to simulate a realistic climate. Hence, it should be in principle more suitable to study environmental chemistry and transports than using generic models. As inherent to any modeling study, many simplifications of the processes which in reality influence the environmental fate of semivolatiles had to be made (cf. Section 2.1). Several elements of the total environment system are not represented, i.e. sediments, freshwater systems and horizontal transports in the ocean. (As a consequence of the characteristic transport and decay times, the latter is not relevant for the substances studied.) Data uncertainties related to the sources and sinks of the substances limit the applicability of the results: For instance, the degradation rates and their temperature dependencies are very uncertain (Table 1). Given these limitations, we found that the predicted concentration levels are in satisfying agreement with the observed levels. There is, however, only insufficient observation data available for proper model validation. For methyl parathion we studied an upper estimate of environmental mobility and for atrazine we studied both a lower and an upper estimate of environmental mobility. We found that methyl parathion undergoes regional to global and atrazine

undergoes regional distribution. Having in mind that these substances due to their high water solubility have a limited tendency to partition to the atmosphere this result is remarkable. As we studied methyl parathion only assuming properties at the high mobility end of the respective knowledge, we identify the regional-global distribution as the upper limit of the global environment exposure to this pesticide based on current application. This finding implies that based on present knowledge one cannot exclude that methyl parathion reaches regions as far from the sources as e.g. the Arctic. No efforts to measure the substance far from the application areas have been undertaken to our knowledge. The spatial range of atrazine, which means a more than modest potential for long-range transport is in particular noteworthy. This finding is in agreement with observations of this herbicide far from the appliaction areas (Section 3.2). Another conclusion from the distributions predicted for the two scenarios of atrazine environmental cycling is that due to current data uncertainties the concentration in the atmosphere or ocean cannot be predicted better as to 1-2 orders of magnitude. The differences in the substance distributions of the low and high mobility scenarios are mostly attributed to the uncertainties resulting from lack of knowledge of the degradation processes while the uncertainties which propagate from the source estimates (application inventories) are less influential. The removal of the pesticides from the environment, i.e. the seasonal variability of the total environmental burdens, is governed by the degradation in the soil and vegetation which host most of the substances (73 % of methyl parathion and 90-99 % of atrazine; cf. Fig. 11). The degradation rates in the soil and vegetation compartments are in particular uncertain. In reality, these rates are supposedly highly variable in space and time. In the model, the same rate has been applied for all soils and this value was selected out of a broad range of experimental findings (mostly model soils) spanning 1-2 orders of magnitude (cf. Table 1). The degradation rate in vegetation, in lack of better knowledge, was taken to be given by the rate in soil. A conclusion from this deficiency is that the substance dynamics in the total environment is quite uncertain. This points to the research need to improve knowledge of the biotic and abiotic degradation processes in the soils, in the ocean (including their spatial variability as far as the biotic processes are concerned) and also in the atmosphere – in fact of many environmentally relevant substances. This has been recognized (van Pul et al., 1999; Klecka et al., 2000; besides others) and tends to even gain importance in the future. As related to degradation in the atmosphere it is not only the gas-phase reaction rate coefficient with the hydroxyl radical which is essential to predict the atmospheric lifetime (which is not known for the pesticides studied here), but it is also necessary to gain knowledge of photodegradation rates of substances adsorbed to or absorbed in particles, because semivolatiles to a large extent are partitioning to the atmospheric aerosol. Only few such data are available (e.g. Palm et al., 1998).

4.2 Multimedia environmental fate and respective indicators

There is an albeit limited tendency of the two semivolatiles studied for intercompartmental cycling. The relatively large water solubility is, we believe, the reason why the soil compartment tends to retain the substances and the probability for volatilization is much larger from the vegetation compartment. Repeated atmospheric cycling is more pronounced for methyl parathion than for atrazine. For the interpretation of this finding, it has to be kept in mind that any result on spatial and compartmental distributions is specific for the chosen scenario of substance entry into the environment. In the present study we did not systematically study these influences, but assumptions were made which were chosen with the aim to be as close as possible to reality. Each one scenario of time and location of the entry was studied for each substance and the receptor medium was varied in the two scenarios of atrazine environmental fate. The higher tendency for atmospheric cycling of methyl parathion is the result of several features, vapor pressure and preferential medium upon entry (vegetation and not soil) being the most important. The significance of the modalities of pesticide application on the environmental fate has been subject of research on the local level, e.g. in the context of pesticide regulatory processes (Gottschild et al., 1995; besides others). Regional or even beyond regional implications may also be relevant. The knowledge of the time, location and mode of entry of the substance into the environment will always be incomplete. It depends primarily on the temporal and spatial resolution of the model used, to what extent these uncertainties will propagate into the results. To know the sensitivity of the results to these characteristics is essential for the understanding of environmental behavior of xenobiotics and for the application of results of exposure analyses in the context of substance risk assessments.

By choice of suitable indicators, we derived characteristics of the compounds to address the total environmental persistence and the scale of the long-range transport potential. A total environmental decay time was determined. As an average for the periods without entry of the substances into the environment these were in the range 4-7 months. The seasonal variability of this decay time is dominated by the temperature dependence in various media and is found to be remarkably pronounced: Monthly means differ up to a factor of ca. 2 for methyl parathion and up to 5.5-7 for atrazine under the low and high mobility scenarios, respectively. Results of model-based exposure analysis depend on the model used, i.e. complexity of processes represented, temporal and spatial resolution. The indicators are descriptors of the environmental behavior and their main application is in the field of substance risk assessments in the context of international chemicals policies (e.g. UNEP, 1999). A large variety of adequate indicators is in principle at hand as a consequence of the complexity of multimedial and spatial cycling. Whether or not or to what extent the same indicator derived from different model types tells the same should be clarified.

In this study we refrained from investigating also the environmental fate of secondary xenobiotics, such as the main metabolites of atrazine, desethylatrazine and hydroxyatrazine. Whenever an exposure assessment is undertaken with the aim to address the overall risk posed by the entry of a xenobiotic, daughter substances should be covered, too, as these might be even more ecotoxic and persistent (Fenner et al., 2000).

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Figure captions

Fig. 1: Schematics of the compartments, sources, sinks and intercompartmental mass exchanges. Intramedia mass exchanges (not shown) are considered in the atmosphere (gas, aerosol particles, cloud and rain droplets) and the soils (air, soil water, soil organic matter). Intramedia transports are only considered in the atmosphere. V = volatilization, DD = dry deposition, WD = wet deposition, CD = chemical degradation, AA = agricultural application, LD = loss to the deep sea.

Fig. 2: Zonally and vertically averaged atmospheric OH concentration in January and July (cm^{-3}).

Fig. 3: Zonally averaged seasonal minimum and maximum monthly mean depth of ocean mixed layer (m).

Fig. 4: Applications of (a.) methyl parathion and (b.) atrazine based on global cotton and corn crops, respectively (see text). Lower estimates corresponding to 0.047 Tg a^{-1} and 0.090 Tg a^{-1}, respectively, data given as mean application rate (kg m^{-2} s^{-1}) during the month of application, August and May, respectively. Resolution 2.8° * 2.8°.

Fig. 5: Annual mean spatial distributions of methyl parathion, high mobility scenario, in (a.) the total environment and in the (b.) atmosphere, (c.) soils, (d.) vegetation and (e.) ocean compartments.

Fig. 6 Annual mean spatial distributions of atrazine under the high mobility scenario in (a.) the total environment and in the (b.) atmosphere, (c.) soils, (d.) vegetation and (e.) ocean compartments.

Fig. 7: Predicted (solid line) and observed (crosses) levels of total (gaseous + particulate) methyl parathion in air Rolling Fork/MS/USA (1995; Foreman et al., 2000). Observed values are pseudo-weekly samples (5 min out of every hour).

Fig. 8: Predicted (low and high mobility scenarios, dashed and full lines, respectively) and observed (crosses) levels of atrazine in air at Wank/Alps (Germany, 800 m a.s.l., 1989 and 1990, particulate fraction only; Herterich, 1991), at Aubure/Vosges Mtn. (France, 1100 m a.s.l.), at Strasbourg/Rhine Valley (1993 and 1994; both: Sanusi et al., 2000) and at Colmar/Rhine Valley (1992; Millet et al, 1997). Observed values are given as

data ranges from 2 consecutive years, each year's value based on 2-4 weekly samples (Wank) or as means based on 1-4 24 h samples per month (Aubure, Strasbourg, Colmar).

Fig. 9: Predicted (low and high mobility scenarios, results area averaged over ca. 800 km^2, dashed and full lines, respectively) and observed levels (stars) of atrazine during low-level flights, 160-170 m altitude, over Southern Ontario in 1993 and 1994 (Chatham-Midland-Ottawa triangle; Zhu et al., 1998). Observed values are 1 h samples.

Fig. 10: Predicted (low and high mobility scenarios, dashed and full lines, respectively) and observed levels (stars) of atrazine in the ocean surface waters of the South Atlantic Bight in 1994 (Alegria and Shaw, 1999). Model results area averaged over ca. 290000 km^2 (2 grid cells). Observed values are probed from 17 sites in an area of ca. 21500 km^2. The error bar reflects $\pm$ 1 σ (n = 17).

Fig. 11: Temporal variation of the global burdens of methyl parathion (solid line) and atrazine (low mobility scenario: dotted line, high mobility scenario: dashed line) in (a.) the total environment and in the (b.) atmosphere, (c.) soils, (d.) vegetation and (e.) ocean compartments. In consistency with the time resolution of the application scenario a time-step of Δt = 1 month was used.

Fig. 12: Seasonal variation of the total environmental decay time, $\tau_{½\ total}$ (definition see text), of methyl parathion (solid line) and atrazine (low mobility scenario: dotted line, high mobility scenario: dashed line) during the periods without introduction of the compounds into the environment.

Table 1: Substance physico-chemical properties and values adopted for the model scenarios. All values refer to T = 298 K. Estimates when no measured values were available (see footnotes). The radical rate coefficients k_{OH} and k_{NO3} are applied for both the gaseous and particulate-bound compounds.

	Methyl parathion		Atrazine		
	Value	Value adopted under the high mobility scenario	Value	Value adopted under the low mobility scenario	Value adopted under the high Mobility Scenario
Vapor pressure p_{sat} (mPa) [a]	1.5	1.8	0.038	0.038	
Water solubility s_{water} (mg l^{-1}) [b]	57.5	57.5	33	33	
Sorption coefficient K_{om} (l kg^{-1})	141 [c]	141	70 [c]	70	
OH radical rate coefficient k_{OH} (cm^3 $molec^{-1}$ s^{-1})	No data available	$1.67 * 10^{-11}$ [d]	No data available	$3.8 * 10^{-11}$ [e]	$1.5 * 10^{-12}$ [e]
NO_3 radical rate coefficient k_{NO3} (cm^3 $molec^{-1}$ s^{-1})	No data available	0 [f]	$1.5 * 10^{-16}$ [g]	$4.5 * 10^{-16}$	$0.75 * 10^{-16}$
Degradation rate in the soil k_{soil} (s^{-1}) [h]	$(2.8–170)* 10^{-7}$ [c]	$1.4 * 10^{-7}$	$1.45 * 10^{-7}$ [i]	$1.3 * 10^{-7}$	$1.6 * 10^{-7}$
Degradation rate on vegetation k_{veg} (s^{-1}) [h]	No data available	Same as k_{soil}	No data available	Same as k_{soil}	
Degradation rate in the ocean k_{ocean} (s^{-1}) [h]	$(8-84) * 10^{-7}$ [j]	$2.64 * 10^{-7}$ [k]	No data available	$5 * 10^{-9}$ [l]	
Deposition velocity of gaseous molecule over sea $v_{dep(sea)}$ (cm s^{-1})		0.05		0.5	0.05
Deposition velocity of gaseous molecule over land $v_{dep(land)}$ (cm s^{-1})		0.1		1.0	0.1

[a] Temperature dependence is controlled by the enthalpy of vaporization, 95 and 146 kJ mol^{-1}, for methyl parathion and atrazine, respectively.

[b] Temperature dependence is controlled by the enthalpy of solution, which in lack of better knowledge is assumed to be 27 kJ mol^{-1}.

[c] Halftimes between 1 and 60 days have been reported (Wauchope et al., 1992; EXTOXNET, 2000; FAO, 2000)

[d] estimated using a value attained by application of a strucure-reactivity relationship of similar compounds (Kwok and Atkinson, 1995) and then divided by a factor of 3

[e] lower and upper estimate, respectively, to account for the uncertainty (cf. $14 * 10^{-12}$ cm^3 $molec^{-1}$ s^{-1}, based on an extrapolation from a high-temperature measurement; Klöpffer and Kohl, 1990)

[f] estimate

[g] based on QSAR (Güsten et al., 1984; Sabljic and Güsten, 1990)

[h] Temperature dependenc: It is assumed that a doubling of the degradation rate is caused by each 10 K temperature increase.

[i] Halftimes corresponding to $0.7-4.1 * 10^{-7}$ s^{-1} were reported. Selected value (Breitkopf et al., 2000; Smit et al., 1997)

[j] Range of rates derived from halftime values in freshwater aquatic ecosystems or artificial systems (FAO, 2000). No measured value available for the non sterile seawater. Hydrolysis rate constant at pH 7 and 298 K: k_{hydr} = 9.6-11 * 10^{-8} s^{-1} (Mabey and Mill, 1978; WHO, 1993)

[k] Estimate: Applying a factor of 3 to account for less biological activity in the ocean compared to freshwater aquatic ecosystems.

[l] Assumed to be given by the hydrolysis rate coefficient (Widmer, 1993).

Table 2: Characteristics of the pesticide application inventories.

	Methyl parathion	Atrazine	
	High mobility Scenario	Low mobility scenario	High mobility scenario
Crop, global crop area (ha) [a)]	Cotton, $5.52 * 10^7$	Maize, $1.33 * 10^8$	
Application rate per hectar (kg ha^{-1} a^{-1}) (globally (kt a^{-1}))	1.21 (51) [b)]	0.96 (90) [c)]	1.28 (148) [b)]
Application time, diurnal pattern	Dry (i.e. precipitation free) daylight hours		
Application time, seasonal pattern	July-August	May	
Media receiving pesticide application	Soil 10%, vegetation 90% [d)]	Soil 100% [e)]	Soil 90%, vegetation 10% [e)]

[a)] (FAO, 1997 and 1998)

[b)] 110 % of the application in the USA, in 1991 (NASS, 1997)

[c)] 90 % of the application in Denmark, in 1993 (IAO, 1998)

[d)] This insecticide is mostly formulated as wettable powder or emulsifiable concentrate and applied foliar (sprayed to the fully developed cotton plants; USEPA, 1988; Kidd and James, 1991).

[e)] This herbicide is mostly formulated as wettable powder, emulsifiable concentrate or granulate and sprayed to the bare ground or after plant growth begins (pre- and post-emergence control; RSC, 1990; Perkow, 1993).

Table 3: Comparison of reported and estimated (application inventory, range given by low and high mobility scenarios, see text) pesticide application amounts (unless otherwise stated) for several countries and regions.

Substance	*Country or region*	f_{ac}	*Estimated (kt a^{-1})*	*Reported (kt a^{-1})*	*(year(s))*	*Reference*
Methyl parathion	China	1.28	27-33	7.5 [a)]	(1990)	[1]
	USA	1.00	28-38	29	(1991-93)	[2]
	World	0.74	90-148	90 [a)]	(1976-85)	[3]
Atrazine	Austria	1.32	0.22-0.30	0.28-0.41	(1991-93)	[4]
	Netherlands	4.08	0.045-0.057	ca. 0.19	(1990)	[5]
	Italy	4.08	3.6-4.7	0.72	(1990)	[6]
	EU-15	1.02	9.6-12.8	6.4 [b)]	(1992-94)	[7]
	USA	1.00	24-32	29	(1991-93)	[2]

a) Production volume

b) Most important crops considered only

[1] Liu (2000).

[2] USGS (1998)

[3] Rippen (2000)

[4] UBA (1996)

[5] Teunissen-Ordelman and Schrap (1997)

[6] Halfon et al. (1996)

[7] European Statistical Bureau, Brussels, personal communication.

Table 4: Characterization of geographical distributions of methyl parathion and atrazine in the total environment and in individual media by indicators: (a.) Annual mean zonal shifts of centers of gravity relative to the distribution upon entry into the environment (latitude (°N)). The values in brackets refer to the range in individual months. (b.) tendencies of zonal spreading (values > 0) or narrowing (values < 0). The values refer to the distance between the 5 and 95 % percentiles of the zonal distributions.

	Total Environment	Atmosphere	Soil	Vegetation	Ocean
a.	(°N)	(°N)	(°N)	(°N)	(°N)
Methyl parathion (high mob.)	+11.8 (+6 - +17)	-5.5 (-17 - +10)	+13.3 (+9 - +17)	+15.4 (+4 - +21)	+7.3(+0- 11)
Atrazine (low mob.)	+4.9 (+2 - +6)	+5.0 (+2 - +8)	+4.6 (+2 - +6)	+8.8 (+7 - +10)	-10.4(-38 - +3)
Atrazine (high mob.)	+5.7 (+2 - +7)	+3.3 (±0 - +6)	+5.2 (+2 - +7)	+9.4 (+5- +11)	-3.3 (-17 - +2)
b.	(°)	(°)	(°)	(°)	(°)
Methyl parathion (high mob.)	+21	+37	-1	+29	+69
Atrazine (low mob.)	-37	-29	-37	-44	+32
Atrazine (high mob.)	-23	- 7	-37	+1	+30

Table 5: Characteristics describing the fate of methyl parathion and atrazine in the total environment: Mean number of atmospheric cycles, N_{ac}, estimated fraction of molecules, p_n, undergoing n = 0, 1, 2 and 3 atmospheric cycles (%; assuming a Poisson type distribution, see text) and total environmental decay time, $\tau_{½\ total}$, given as: annual mean (minimum monthly mean – maximum monthly mean). Mean values based on three simulated years.

	N_{ac} (p_0, p_1, p_2, p_3) - (%/%/%/%)	$\tau_{½\ total}$ (d)
Methyl parathion (high mobility)	1.03 (49/25/13/7)	201 (142-264)
Atrazine (low mobility)	0.10 (84/13/2/0)	128 (40-218)
Atrazine (high mobility)	0.19 (91/8/1/0)	203 (54-387)

Fig. 1

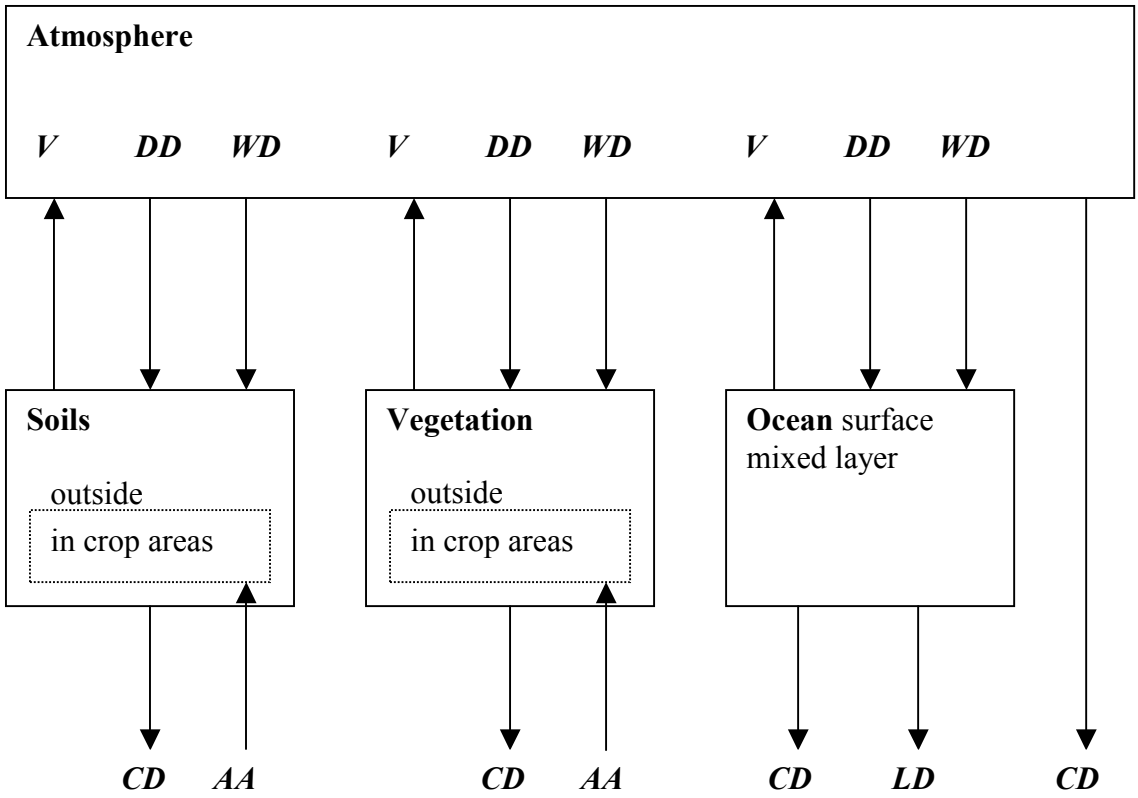
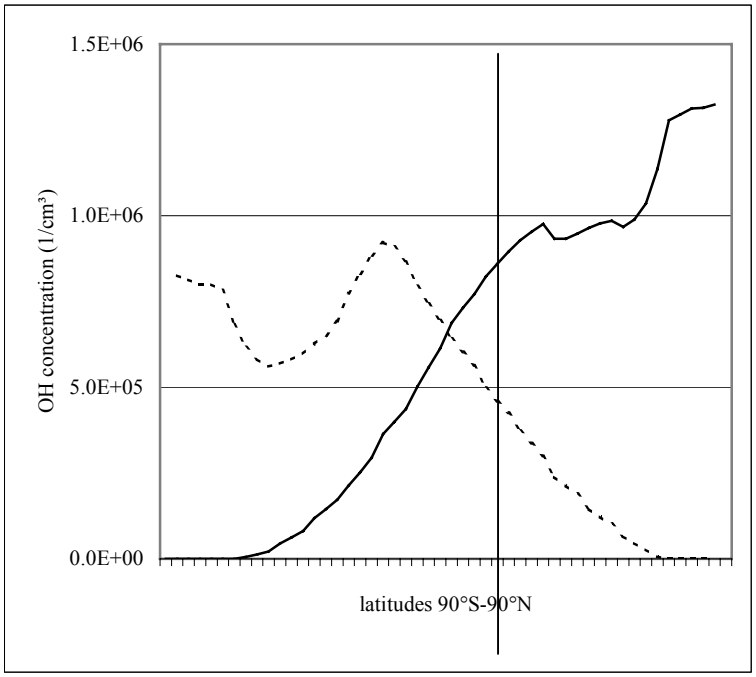

Atmosphere
V
DD
WD
V
DD
WD
V
DD
WD
Soils
outside
in crop areas
Vegetation
outside
in crop areas
Ocean surface
mixed layer
CD
AA
CD
AA
CD
LD
CD

Fig. 2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1.0E+06
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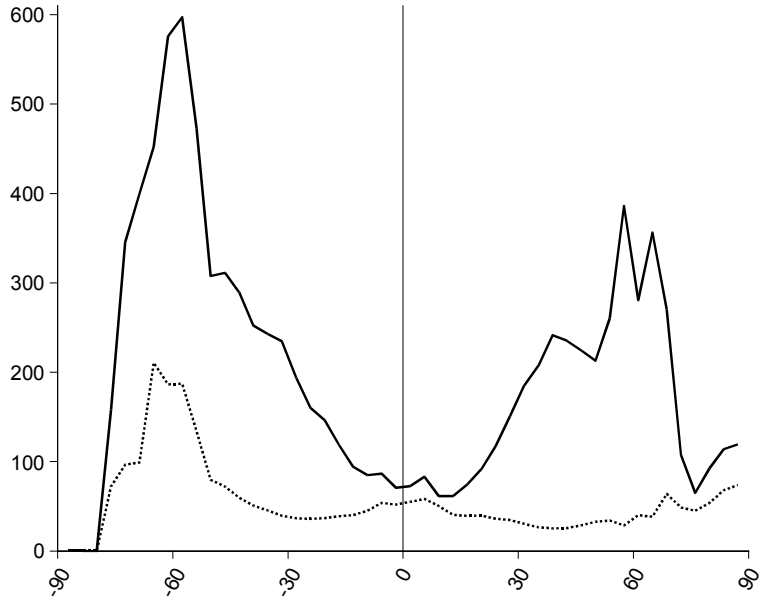
0.0E+00
OH concentration (1/cm³)
latitudes 90°S-90°N

Fig 3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400
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200
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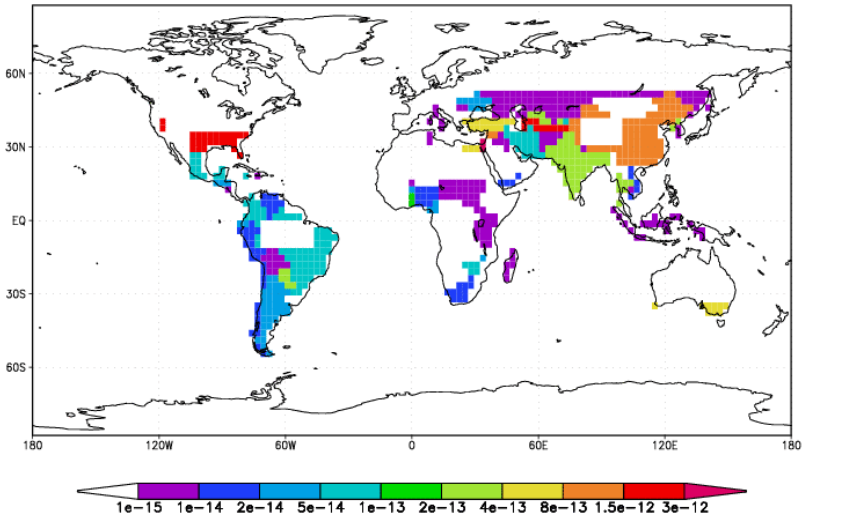
0
-90
-60
-30
0
30
60
90

Fig. 4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1e−15 1e−14 2e−14 5e−14 1e−13 2e−13 4e−13 8e−13 1.5e−12 3e−12

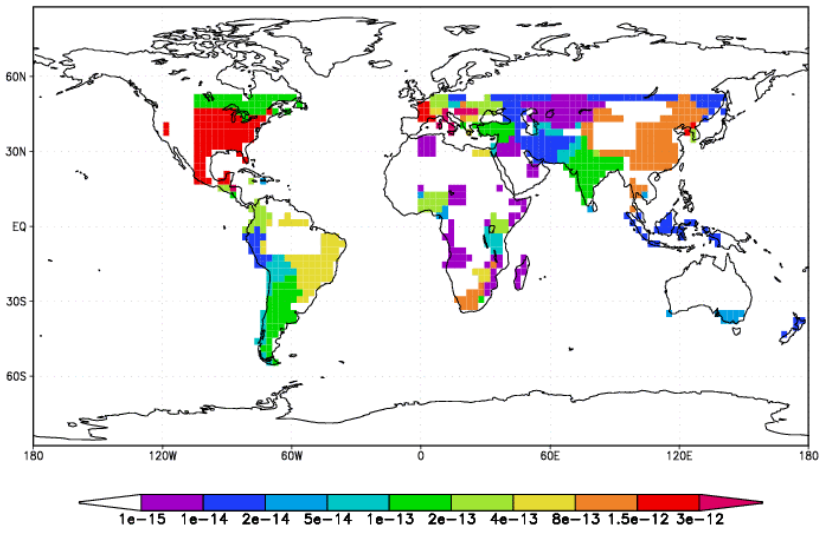
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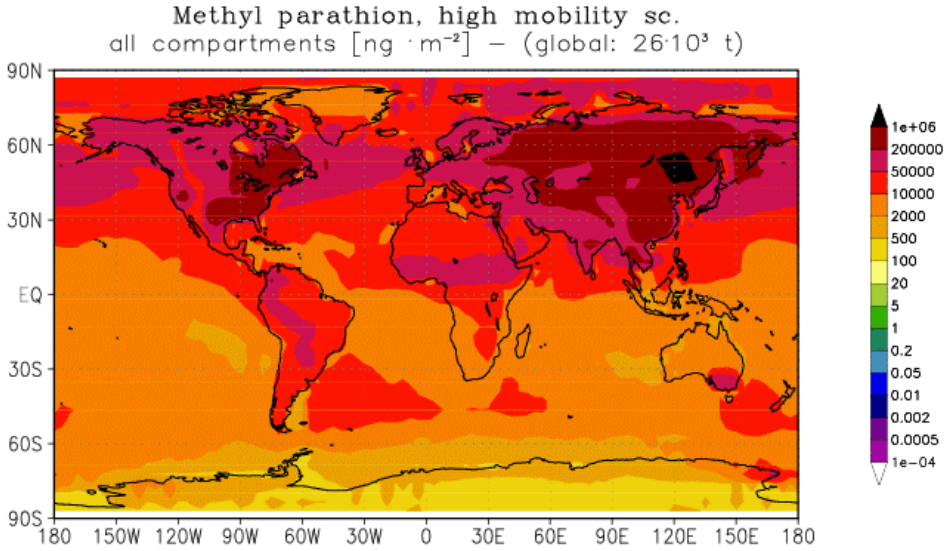
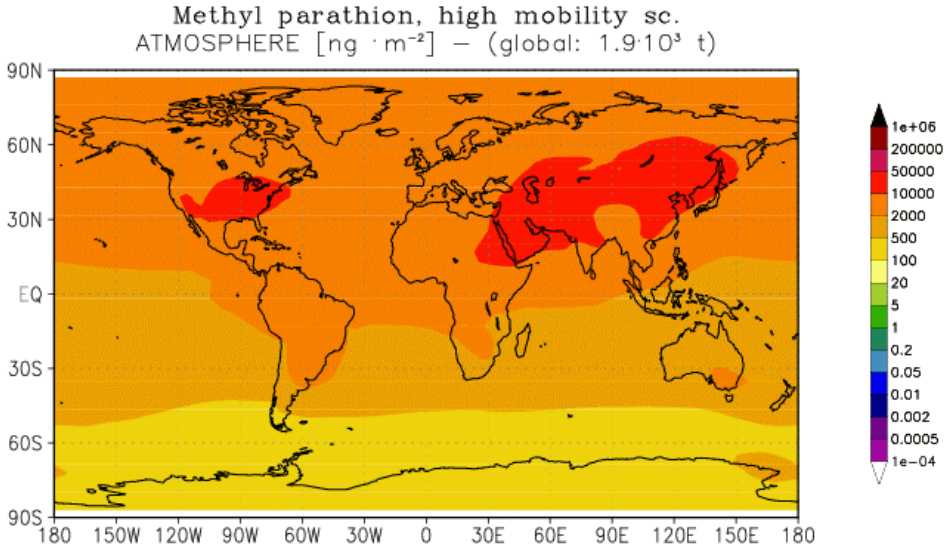
Fig. 5

a.


Methyl parathion, high mobility sc.
all compartments [ng · m⁻²] – (global: 26·10³ t)
90N
60N
30N
EQ
30S
60S
90S
180 150W 120W 90W 60W 30W 0 30E 60E 90E 120E 150E 180
1e+06
200000
50000
10000
2000
500
100
20
5
1
0.2
0.05
0.01
0.002
0.0005
1e−04

b.


Methyl parathion, high mobility sc.
ATMOSPHERE [ng · m⁻²] – (global: 1.9·10³ t)
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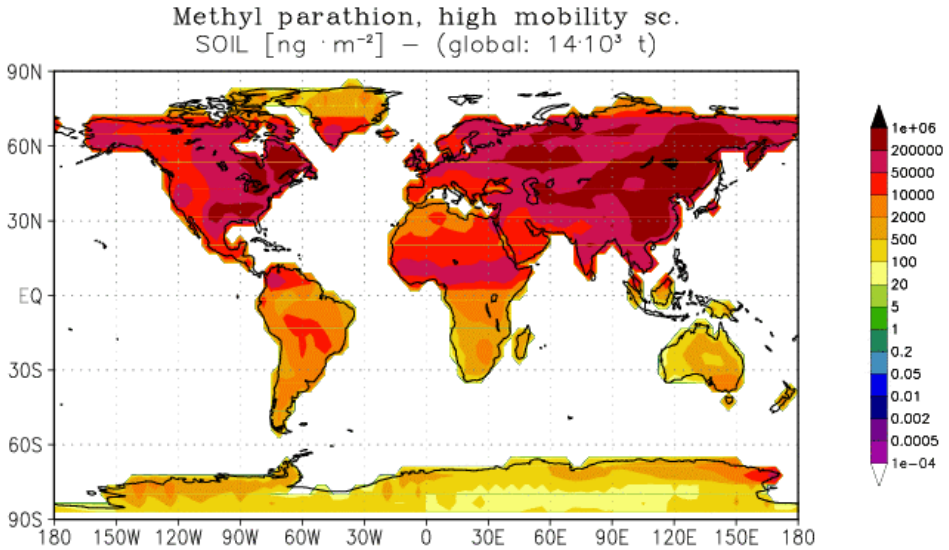
60N
30N
EQ
30S
60S
90S
180 150W 120W 90W 60W 30W 0 30E 60E 90E 120E 150E 180
1e+06
200000
50000
10000
2000
500
100
20
5
1
0.2
0.05
0.01
0.002
0.0005
1e−04

c.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SOIL [ng · m⁻²] – (global: 14·10³ t)
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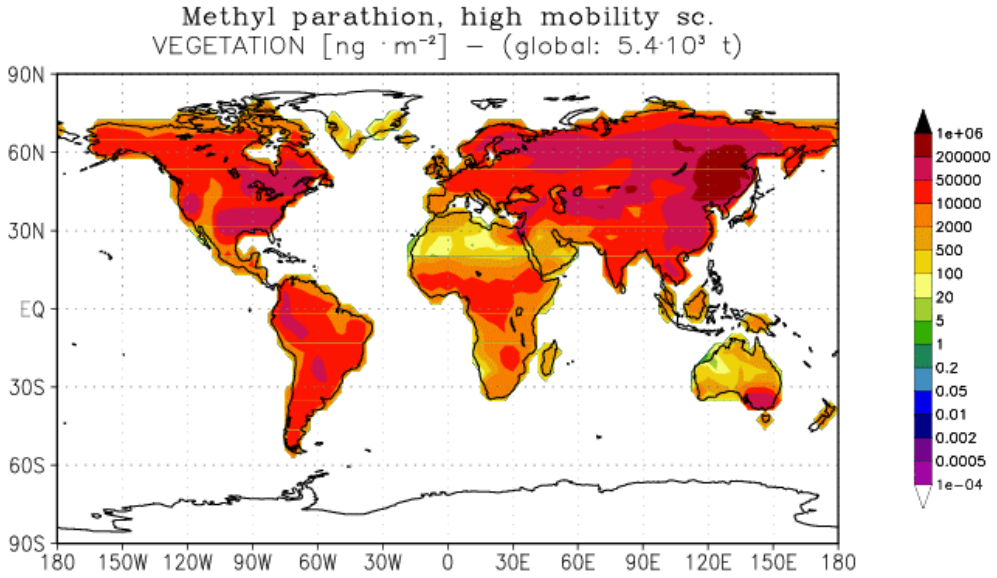
60N
30N
EQ
30S
60S
90S
180 150W 120W 90W 60W 30W 0 30E 60E 90E 120E 150E 180
1e+06
200000
50000
10000
2000
500
100
20
5
1
0.2
0.05
0.01
0.002
0.0005
1e−04

(Fig. 5)
d.


Methyl parathion, high mobility sc.
VEGETATION [ng ·m⁻²] – (global: 5.4·10³ t)
90N
60N
30N
EQ
30S
60S
90S
180 150W 120W 90W 60W 30W 0 30E 60E 90E 120E 150E 180
1e+06
200000
50000
10000
2000
500
100
20
5
1
0.2
0.05
0.01
0.002
0.0005
1e-04

e.

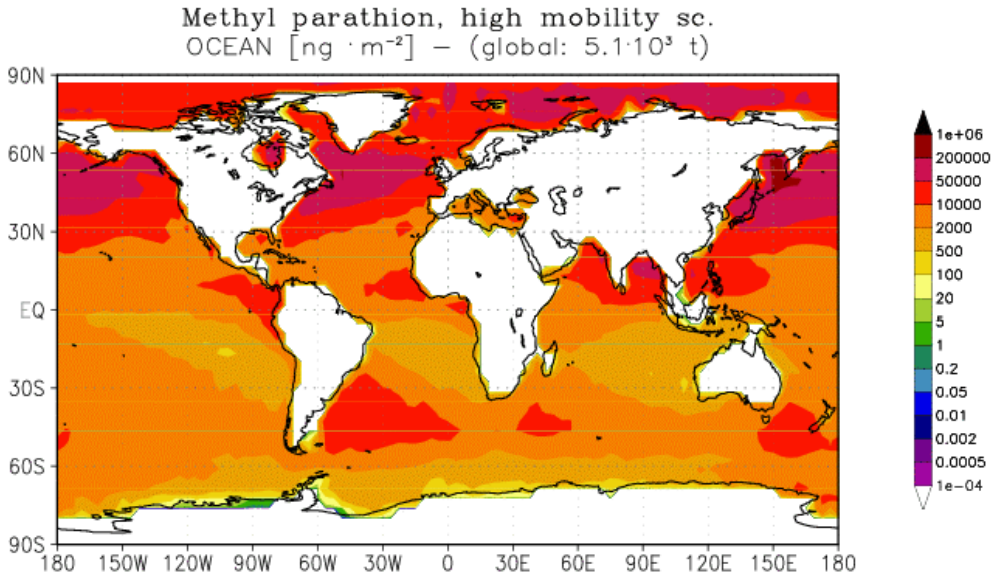
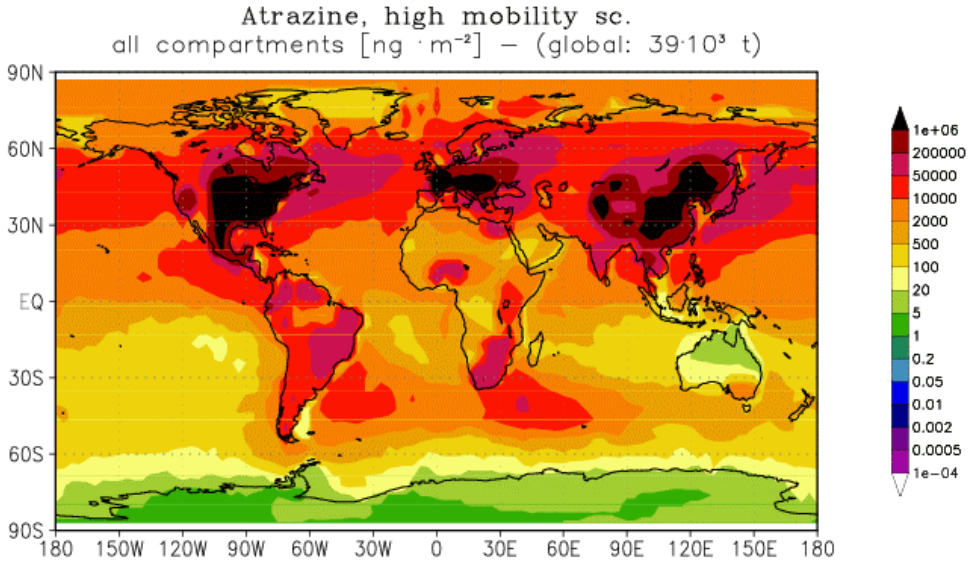
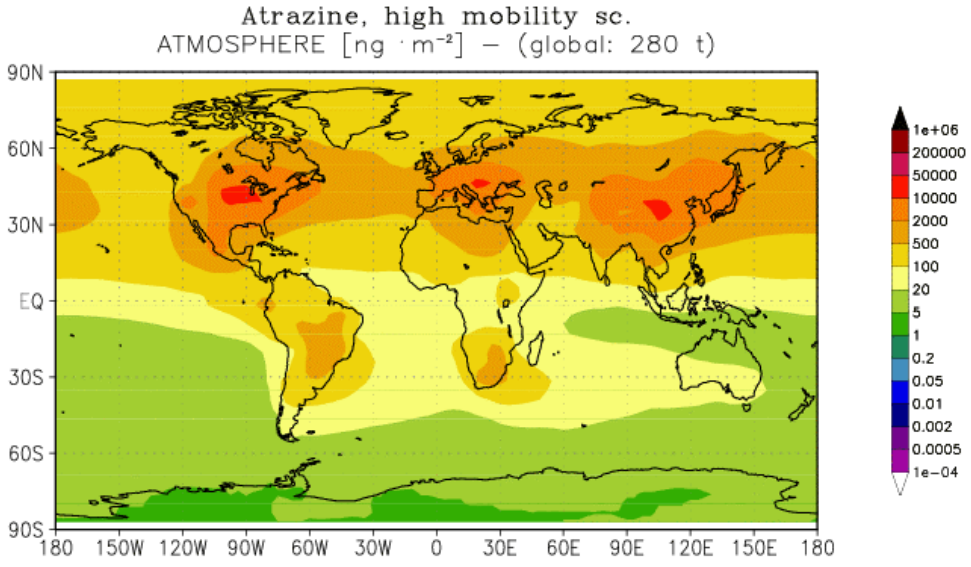

Methyl parathion, high mobility sc.
OCEAN [ng ·m⁻²] – (global: 5.1·10³ t)
90N
60N
30N
EQ
30S
60S
90S
180 150W 120W 90W 60W 30W 0 30E 60E 90E 120E 150E 180
1e+06
200000
50000
10000
2000
500
100
20
5
1
0.2
0.05
0.01
0.002
0.0005
1e-04

Fig. 6

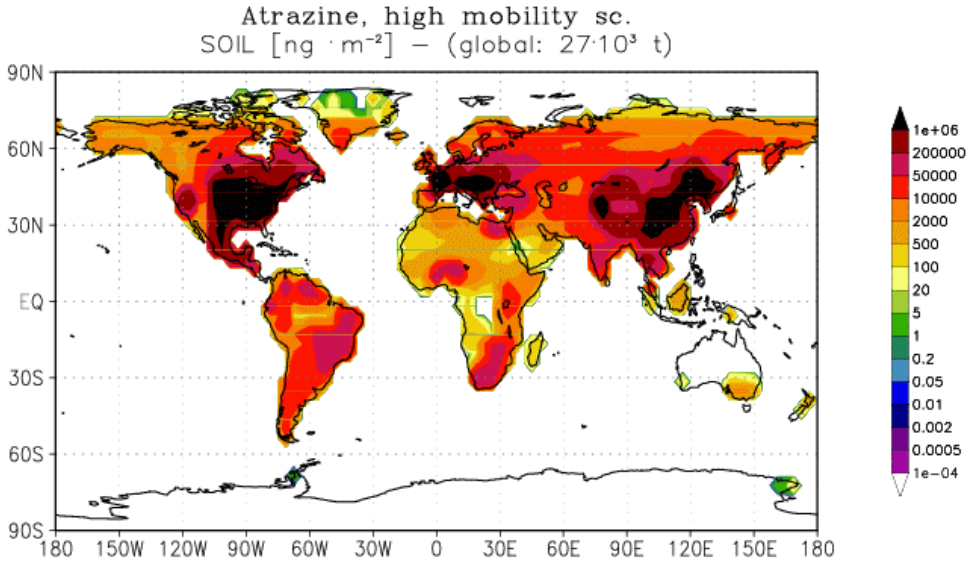
a.


Atrazine, high mobility sc.
all compartments [ng · m⁻²] – (global: 39·10³ t)
90N
60N
30N
EQ
30S
60S
90S
180 150W 120W 90W 60W 30W 0 30E 60E 90E 120E 150E 180
1e+06
200000
50000
10000
2000
500
100
20
5
1
0.2
0.05
0.01
0.002
0.0005
1e−04

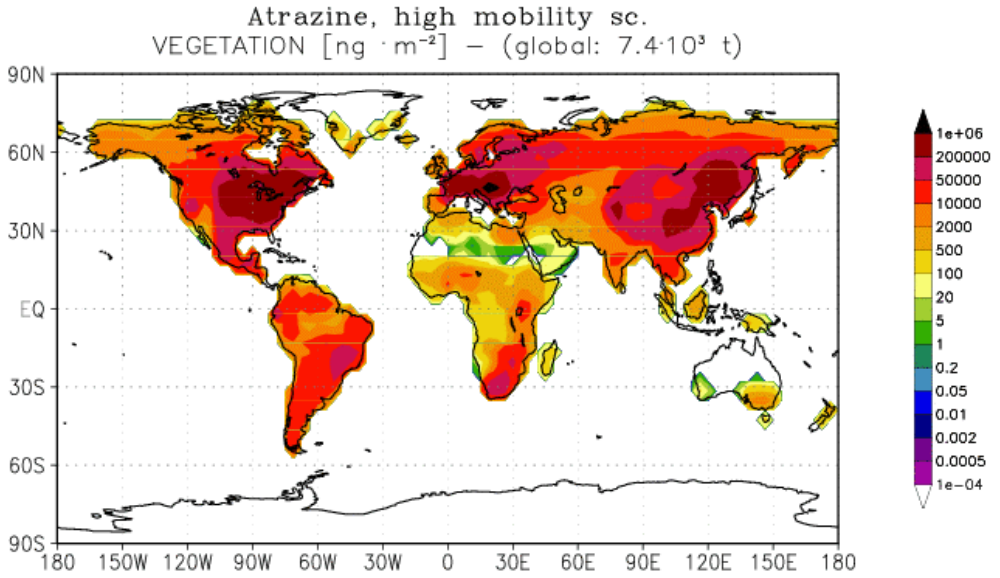
b.


Atrazine, high mobility sc.
ATMOSPHERE [ng · m⁻²] – (global: 280 t)
90N
60N
30N
EQ
30S
60S
90S
180 150W 120W 90W 60W 30W 0 30E 60E 90E 120E 150E 180
1e+06
200000
50000
10000
2000
500
100
20
5
1
0.2
0.05
0.01
0.002
0.0005
1e−04

c.


Atrazine, high mobility sc.
SOIL [ng · m⁻²] – (global: 27·10³ t)
90N
60N
30N
EQ
30S
60S
90S
180 150W 120W 90W 60W 30W 0 30E 60E 90E 120E 150E 180
1e+06
200000
50000
10000
2000
500
100
20
5
1
0.2
0.05
0.01
0.002
0.0005
1e−04

(Fig. 6)
d.


Atrazine, high mobility sc.
VEGETATION [ng ·m⁻²] – (global: 7.4·10³ t)
90N
60N
30N
EQ
30S
60S
90S
180 150W 120W 90W 60W 30W 0 30E 60E 90E 120E 150E 180
1e+06
200000
50000
10000
2000
500
100
20
5
1
0.2
0.05
0.01
0.002
0.0005
1e-04

e.

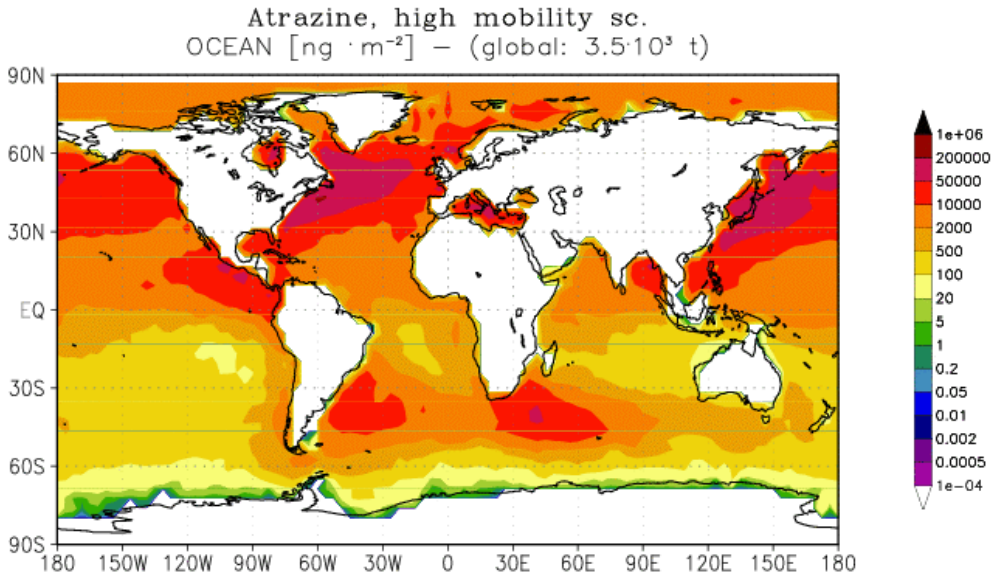

Atrazine, high mobility sc.
OCEAN [ng ·m⁻²] – (global: 3.5·10³ t)
90N
60N
30N
EQ
30S
60S
90S
180 150W 120W 90W 60W 30W 0 30E 60E 90E 120E 150E 180
1e+06
200000
50000
10000
2000
500
100
20
5
1
0.2
0.05
0.01
0.002
0.0005
1e-04

Fig. 7

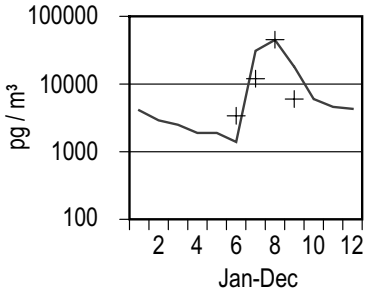


Fig. 8

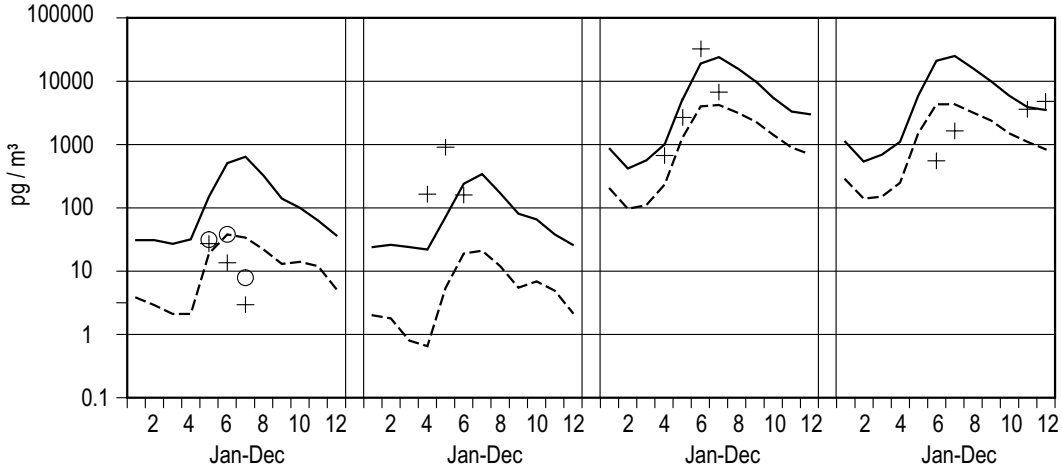


Fig. 9

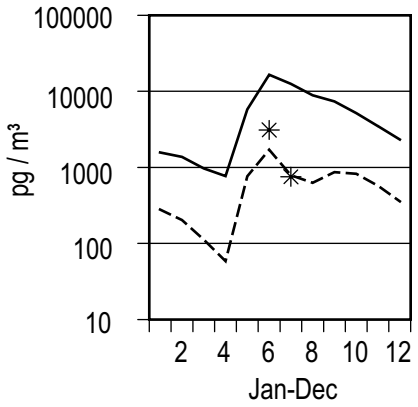
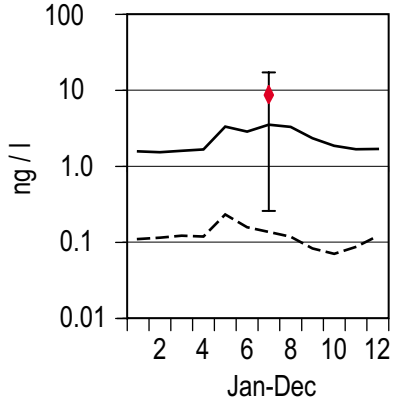
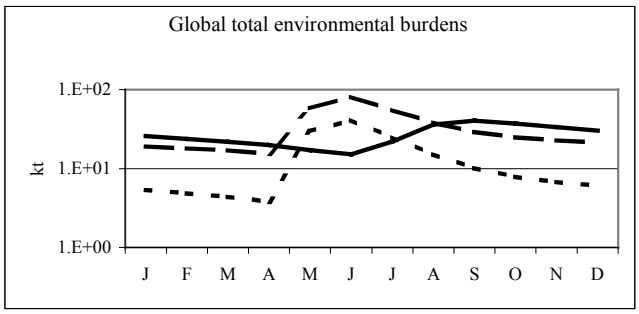


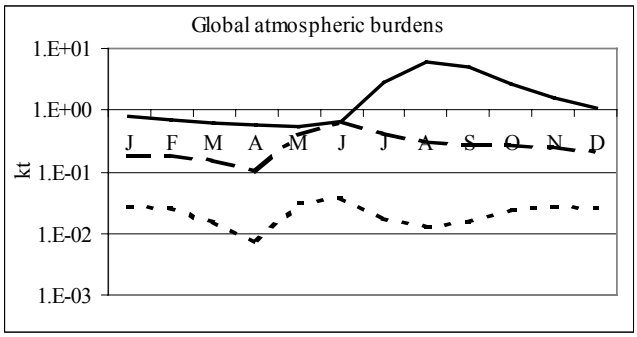
Fig. 10



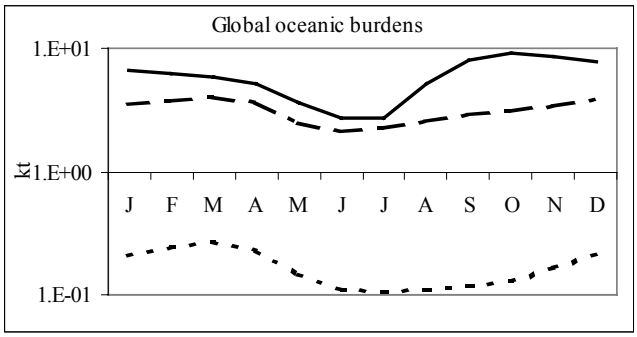
a.


Global total environmental burdens
1.E+02
1.E+01
1.E+00
kt
J F M A M J J A S O N D

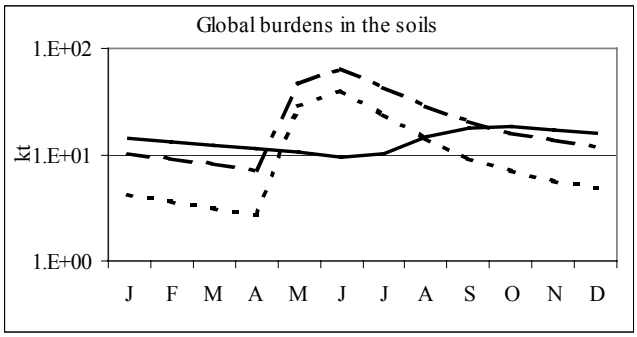
b.


Global atmospheric burdens
1.E+01
1.E+00
1.E-01
1.E-02
1.E-03
kt
J F M A M J J A S O N D

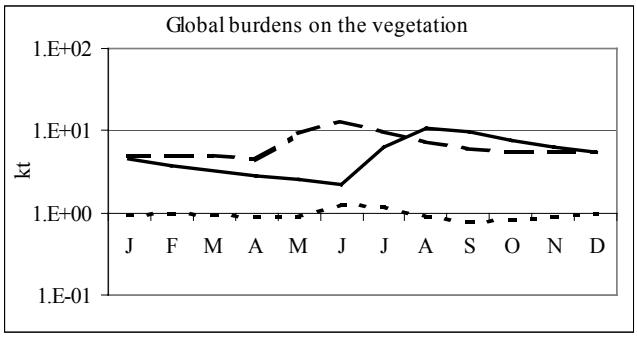
c.

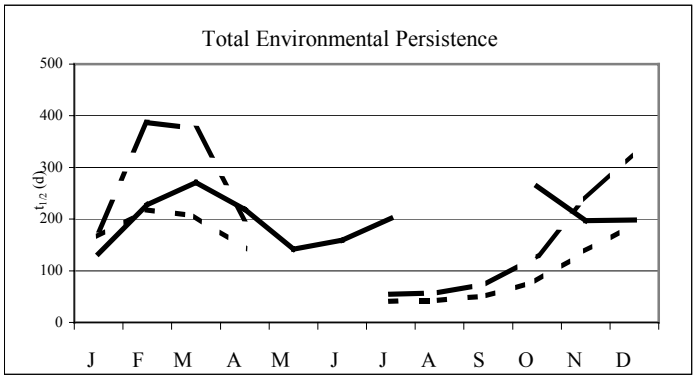

Global oceanic burdens
1.E+01
1.E+00
1.E-01
kt
J F M A M J J A S O N D

d


Global burdens in the soils
1.E+02
1.E+01
1.E+00
kt
J F M A M J J A S O N D

e


Global burdens on the vegetation
1.E+02
1.E+01
1.E+00
1.E-01
kt
J F M A M J J A S O N D


Total Environmental Persistence
500
400
300
200
100
0
$t_{1/2}$ (d)
J F M A M J J A S O N D

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