3.1 Mobility of Environmental Chemicals, Including Abiotic Degradation

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3.1.1 INTRODUCTION

The mobility of chemicals released into the environment governs their bio-availability to organisms and their partitioning between environmental compartments, and thus represents a direct link between environmental pollution and ecotoxicity. The micro- and mesoscale transport processes involved are related to the properties of the chemicals themselves, but also to environmental compartments. Thus, the criteria of mobility, dispersion, and bioavailability are closely related, having partly a common set of influencing variables. A number of these variables depend on climatic factors, especially temperature and water regimes. A knowledge of the relationships would permit prediction of the relevant descriptors for any climatic conditions without performing the respective experiments.

3.1.2 ENVIRONMENTAL VARIABLES AND CHEMICAL PROPERTIES RELEVANT TO MOBILITY OF CHEMICALS

Environmental compartments are multivariate systems, both in space and time. From the point of view of chemical composition it may be stated that in general soil shows the greatest variation, and the air compartment the lowest. The relevant properties for the compartments may be summarized as follows:

For soil the major dispersion-relevant properties reflecting the influence of the matrix on partitioning, diffusion, sorption, and binding processes of a chemical are:

(a) types and amounts of clay materials (variability and three-dimensional structure);
(b) particle size and porosity;
(c) exchangeable ions (including buffering capacity);
(d) pH, conductivity of soil solution;
(e) redox potential;

65

(f) temperature;

(g) air and water regime;

(h) composition and amount of organic matter;

(i) biological activity and biomass.

The significance of these properties differs with the geographical region and with the nature of the chemical involved.

For the freshwater aquatic environment, apart from the water itself as transport medium, further properties of interest are:

(a) sediment and its composition (see soil properties above);

(b) suspended solids and their properties with respect to sorption, solution, and partitioning;

(c) dissolved organic matter with respect to changed water solubility and partitioning behaviour of chemicals (including chelating regime);

(d) temperature;

(e) pH;

(f) buffering capacity;

(g) redox potential;

(h) biota.

For the atmospheric environment, apart from transport (discussed in Section 2.3), relevant variables are particulate matter differentiated for large size and inhalable aerosols, and also differentiated for physical and chemical properties (corresponding to suspended solids in aquatic systems).

The major properties and structural characteristics of chemicals involved in the mobility behaviour are:

(a) physical state;

(b) volatility;

(c) molar mass/molecular size;

(d) dissociation constant;

(e) complexation constant;

(f) vapour pressure;

(g) water solubility;

(h) lipophilicity, water/lipids partitioning;

(i) reactivity;

(j) electronic, geometrical, and topological characteristics.

All variables mentioned above interact in complexity and differently for specific compound-compartment-organism systems.

For the ecotoxicological assessment of the occurrence of chemicals in environmental compartments, the composition of the abiotic and biotic sub-compartments is important and should be taken into consideration with regard to receiving masses and properties e.g. of sediment and suspended solids or of biota in running versus stagnant aquatic systems.

In the soil environment the respective subsystems are organic matter, minerals, soil solution, and soil atmosphere, as well as soil biomass.

Apart from the variables mentioned, processes determining the fate and availability of chemicals have to be considered. These are:
  (a) processes involved in changing mobile portions of chemicals apart from degradation: binding to persistent organic matter, 'irreversible' binding to clay minerals;
  (b) processes involved in the movement into organisms (resorption/transport through membranes): partitioning, diffusion, active transport.

For the retrospective evaluation of the dispersion of chemicals based on monitoring data it should be mentioned that in general the production of analytical data is aimed at maximum recovery from a matrix and does not consider the specific state(s) of the chemical analysed. Therefore, a further analytical characterization would be needed:
  (a) total analysis versus solubilized or naturally solubilizable portions;
  (b) speciation for both inorganic and organic chemicals to be monitored.
To arrive at the required levels of precision the environmental compartment properties as well as the biological processes may be estimated or measured.

Furthermore, several types of interactions need to be considered. They include physico-chemical processes of complexation and changes in solubility and sorption phenomena, but also chemical reactions between chemicals in the environment, including chemical–nutrient interactions.

Water solubility is one of the key properties of a chemical which influences its mobility. Solubility of all chemicals is temperature dependent; for electrolytes involving the solubility product which depends on water hardness. The solubility of electrolytes also depends on ionic species present and thus on geological conditions and climate.

As a general descriptor for the partitioning behaviour (hydrophilicity) of a chemical, the octanol/water partitioning coefficient is used, which is only slightly temperature dependent (Mackay, 1980). The effect of temperature on K_{ow} is in the range of 0.001–0.01 log K_{ow} units and may be positive or negative (Lyman *et al.*, 1982). It is inversely related to water solubility.

In considering the importance of soil organic matter in immobilization of chemicals in soils it would be interesting to know whether there are specific climatic zone differences in their sorption-binding characteristics.

Various humic acids isolated from cool-temperate acidic soils, subtropical neutral, and temperate neutral soils and one fulvic acid from a Canadian spodosol were analysed by NMR. Neither in aromaticity (varying between 35 and 92%) nor in total acidity (varying between 6.3 and 8.9 meg/g; fulvic acid 12.4) or carboxyl and phenolic strength were there differences which could be related to a climate zone. Only the carbonyl equivalents were higher in the cool-temperate than in the subtropical samples investigated (Hatcher *et al.*, 1981).

Turnover times for soil organic matter, which are important in the kinetics of behaviour of chemicals, vary from days to months in the case of plant residues, and are in the range of hundreds of years for fulvic acids, and of

thousands of years for humic acids and humins. Being related to microbial activity turnover they depend significantly on temperature and humidity (Paul and Huang, 1980).

Sorption processes in soils play a major role in the availability of pollutants to flora and soil inhabitants, as well as in their movement as compared to the bulk movement of water. The most important soil (and sediment) property in this respect is the organic carbon content, but clay minerals and amorphous oxides (surface area and cation exchange capacity) may also play a role, especially with increasing polarity of the chemicals and decreasing soil organic carbon content. For nonpolar compounds K_{oc} is a frequently used normalized characteristic, and empirical relationships have been developed between organic carbon and lipophilicity (solubility, octanol/water partition coefficient) and also including the conditions for mineral sorption to become significant (Karickhoff, 1981; 1984). For rather lipophilic chemicals, such as o-chlorotoluene at a clay : total organic carbon ratio of 60, mineral contribution to sorption was indicated (Banerjee *et al.*, 1985). In view of the frequently low carbon content of soils in hot climates, e.g. for sandy soils in arid regions, either due to low long-term biomass production or to its rapid turnover, it must be assumed that at least the capacity of these soils for immobilizing less polar chemicals is largely reduced. Thus, the hazard for movement into groundwater is increased. It should be mentioned that sorption of chemicals to colloidal organic macromolecules and clay particles plays an important role in transport in surface waters (*see* Section 3.1.5).

Diffusion of chemicals is of interest with respect to bioavailability and volatilization. The apparent total diffusion coefficient in soil is composed of vapour and non-vapour diffusion (theory from Ehlers *et al.*, 1969a). It is influenced by water content of the soil, bulk density, and temperature. Depending on soil sorption characteristics, water content modifies soil diffusion only to a maximum of about 10%. For lindane and a silt loam it was constant above 5%, going via a maximum to zero at lower water content. Changing bulk density from 1 to 1.5 g/cm^3 reduces the total diffusion coefficient of lindane by about a factor of two. Increasing temperature from 20 to 30°C increases the total diffusion coefficient of lindane in soil by a factor of 2.5 at water saturation, which is explained by a temperature effect on water viscosity and on the interaction between chemical and soil (Ehlers *et al.*, 1969b). Since the total diffusion coefficient increases exponentially with temperature at constant humidity, increased micromobility of chemicals in hot-humid climates, and marked seasonal variations between rainy and dry, winter and summer seasons have to be considered. A more detailed description of partitioning processes in soil has been given by Huang (1980).

The influence of temperature on diffusion in a water-sediment system has been reported for bromacil (Corwin and Farmer, 1984). There is a direct and positive influence of temperature via the viscosity coefficient. Additionally, adsorption is reduced at elevated temperatures at constant humidity.

Chemicals present in soil may be subject to transport into other media by erosion/surface runoff. This depends on topography, and wind and water regimes, but also to a large extent on agricultural practice and soil properties. As an example, surface runoff from ferralite soils in a humid tropical region of the Ivory Coast was found to be 62–70% of the rain from bare soil, 26–39% under pineapple with residues burnt, and 0–2% under pineapple with residues mulched (Roose and Fauck, 1981).

Models have been developed to assess the evaporation rate of chemicals from water surfaces. The rate of evaporation may be calculated as a function of diffusion coefficients in air and water, the Henry constant, water temperature, and water depth, and further as a function of wind speed, and resulting turbulence with qualitative changes depending on water turbulence. Feasible pragmatic models developed by Wolff and van der Heijde (1982) and by Mackay and Yeun (1983) may be used to calculate volatilization from water, especially for temperature and wind regime changes.

Models for environmental compartmentalization, movement and estimation methods, including the relevant mobility parameters, volatility, and partitioning behaviour have been compiled in various handbooks (Baughman and Burns, 1980; Mackay, 1980; Paterson and Mackay, 1985; Lyman *et al.*, 1982).

For temperature-dependent physico-chemical properties the models generally use constant values, most frequently for 25°C. If temperature dependencies are known it is easy to make adjustments for non-temperate conditions. According to presently known relationships it would be difficult to estimate the influence of non-temperate conditions on bioaccumulation, which is an important descriptor in environmental compartmentalization models. If measured values are not available, bioconcentration factors are frequently estimated from log K_{ow}, which has little temperature dependence. However, there is a greater effect of temperature on bioaccumulation via effects on passing biological barriers and on metabolism, so that modified constants should be used in the empirical correlation equations. This influence, however, has to be weighed against species differences and lipid content variations to judge the significance. Examples are known of slight temperature differences measurably changing toxicity. The few data available show a high influence of temperature on bioaccumulation in fish, but with no general direction (Bude, 1981).

3.1.3 MOBILITY IN SOILS: EXAMPLES OF INTERACTIONS WITH CLIMATE-RELATED FACTORS

The mobility of chemicals in soils is of interest with respect to leaching, volatilization, and bioavailability to flora and soil inhabitants.

There is a marked spatial variation in soil properties relevant to the dispersion of chemicals even for small areas, e.g. 1 ha. The water-soluble carbon was determined in a 200 point grid on a 1.4 ha cropped field. The concentration

ranged from 24 to 274 mg/kg, with over 90% of the values around the mean of 40 ppm. Spatial dependence could not be demonstrated in a transect with sampling points every 1.37 m (Liss and Rolston, 1983).

There is additionally a seasonal variation, with maxima of the mean in spring and fall (up to 25% higher than in summer).

Mobility of chemicals in soils is largely dominated by sorption processes following various mechanisms. These processes depend on the polarity (lipophilicity, ionic/non-ionic) of the chemical, soil mineralogy and organic matter content, and especially soil humidity between zero and monolayer of water. Adsorption being generally an exothermic process (decrease at higher temperatures), competitive adsorption, distribution, and ion-exchange processes in the multivariate soil systems result in complex relationships. There are some general tendencies, which, however, need to be confirmed for specific cases:

(a) decreasing water content increases adsorption and decreases mobility;
(b) increasing temperature decreases adsorption and increases mobility;
(c) increasing clay mineral content and organic matter increase adsorption and decrease mobility;
(d) plant cover increases metabolism, and decreases leaching.

Water regime and temperature change the mobility of nutrient and other ions directly, and also that of non-ionic organic compounds via varying soil properties, such as carbon content and microbial biomass. The availability of Zn in different soils increased by 46% when elevating the temperature at field capacity moisture from 10°C to 45°C, while submerging increased the available portion by 20% (Budhewar and Omanwar, 1980).

Changes of climatic factors in one direction may have opposite effects on the movement of different chemicals, e.g. the leaching from soil of the highly mobile cations Na^+ and K^+ may be augmented for both with increasing rainfall, but increasing temperature (4°C to 15°C) may augment the leaching of K^+ and decrease that of Na^+. Low temperatures reduce nitrate losses (Buldgen, 1982).

As an example, for ionic organic compounds, much work has been performed on paraquat and diquat. High humidity and high temperature and low light intensity increase foliar uptake. In soil, diquat and paraquat cations are tightly adsorbed to clay minerals and organic matter, and thus are immobile at levels below the strong adsorption capacity of soil. The ion-exchange process is independent of pH, temperature, and exposure time (Ackhavein and Linscott, 1968).

For dry desert soils with prolonged periods of high temperature and intensive sunlight, although volatilization is lower than in humid conditions, it may be assumed that disappearance of chemicals is nevertheless effective. The loss of DDT and methyl parathion was studied in three dry soils at 30°C and 50°C with low-energy UV irradiation (300–400 nm) and in the dark. About 50% of initial 5 ppm methyl parathion was lost within 50 days at 30°C, 65% at 50°C

in the dark, and irradiation added 10 to 17% to the loss. Whereas the same change in temperature doubled the loss of DDT from 25% to about 50%, the effect of light was only about 8% (Baker and Applegate, 1970).

In three Israeli soils with highly differing clay (6–56%), cation exchange capacity (CEC 4–63 m/100 g), surface area (39–410 m^2/g), and organic matter (0.3–1.9%), the influence of water and temperature on parathion adsorption was measured (Yaron and Saltzmann, 1972). In agreement with other findings (Mills and Biggar, 1969) it may be concluded from the results that for slightly polar compounds the effect of temperature on adsorption isotherms under saturated conditions increases with a lowering of temperature and also with soil quality. Using a three-phase solid-hexane-parathion system, varying humidity between 0 and 98% RH, and temperatures of 10, 30, and 50°C, an increase of adsorption with increasing humidity was found, dominated by water desorption. The initial water content had much less influence at the higher than at the lower temperatures. For the clay, the effect of soil humidity at the highest temperature is several times greater than for the soils poorer in nutrients.

Foliar absorption of chemicals is of interest for several reasons: elimination from the atmosphere, uptake into crops, and phytotoxicity of airborne substances. Increasing temperatures increase uptake of foliar deposits, but higher volatility may lead to an opposite overall temperature effect. High humidity in general facilitates leaf uptake into plants. With significant quantities of rainfall and depending on its components both leaching and runoff may occur, influenced by preceding leaf water loss.

Although light intensity does influence foliar uptake, no general tendency can be given (Hull, 1970). At higher light intensities, which result in increased photosynthetic activity, carbohydrate transport from the leaves is increased, moving away other chemicals in the assimilate stream (Morrison and Cohen, 1980).

A study was made of soil-applied phorate uptake by plants in relation to light intensity and temperature. By increasing light intensity (500 or 3000 foot candles) and/or temperature (13°C and 28°C) separately and in combination, translocation into plants was increased (Anderegg and Lichtenstein, 1984).

Complex interactions of physical, chemical, and biological environmental variables may eliminate the influence of temperature on the fate of the chemicals. The large number of investigations with 'classical' pesticides like aldrin/dieldrin may be used for demonstration (Weisgerber *et al.*, 1974). In temperate climates aldrin residues, including dieldrin, were found to persist for periods of 6 months to more than 15 years (using the detection systems available at the time) in different soils and under different environmental conditions. Under the agroclimatic conditions of the soils of northern India persistence is normally about 6 months. By changing the water regime, under flooded sandy loam soil,

it is increased to 9 months. This has been explained by higher movement into soil and increased sorption, less volatilization, decrease of soil temperature due to stagnant water, and reduced biodegradation (*see* Section 3.2; Lichtenstein *et al.*, 1971; Singh *et al.*, 1985).

In a comparative long-term outdoor lysimeter experiment using local soils, which was performed concurrently in the south of England, south of Spain, California, and West Germany, the disappearance of residues from soil, including transformation products, was greatest in Spain, a little less in California, and lowest in England. Residues in the dosed 0–10 cm soil layer were least in Germany and highest in England. Leaching into deeper soil layers was highest in Germany, low in Spain, and insignificant in England and California (Klein, 1975; Scheunert *et al.*, 1977).

In order to arrive at a better understanding of these interactions and for improvement or validation of environmental fate models, a detailed description of all relevant variables in field and environmental simulation experiments would be needed.

In an early review of insecticide residues in soil (Edwards, 1966), empirical conclusions were drawn on the importance of chemical and soil/environmental characteristics, which—as far as movement of the classes of chemicals under consideration is concerned—are still valid, despite relatively poor analytical techniques compared with current ones. The direct influence of climatic factors on mobility is in general the acceleration of volatilization and desorption with increasing temperature. Volatilization is markedly retarded when soil becomes dry. This is less pronounced for poor sandy soils (low content of organic carbon and clay minerals).

Increasing soil temperature from 10°C to 30°C increased aldrin volatilization by a factor of about 4 at constant humidity, and dieldrin volatilization by a factor of 2 to 4, depending additionally on initial concentrations (Harris and Lichtenstein, 1961; Farmer *et al.*, 1972). Increasing the air flow-rate over soil by a factor of 4 roughly doubled dieldrin volatilization, which, however, approached zero for the soil investigated when its water content was below 3% (Igue *et al.*, 1972). Wind speed increases volatilization depending on upward movement of soil solution, codistillation, and diffusion. Volatility as influenced by vapour pressure and water regime also determines whether and to what extent movement in soil occurs within the soil solution or soil atmosphere. Apart from surface runoff, rain may cause leaching into deeper soil layers of the chemicals dissolved in water, or it may move particle-bound material through cavities. In an experiment with Indian loam soils aldrin volatilization was highest at 25°C as compared to 35°C and 45°C due to drying of soils during incubation (Kushwara *et al.*, 1978). Volatilization is reduced by cover crops due to reducing air movement on the soil surface, although increased release into the atmosphere by covering plants has also been reported (Klein *et al.*, 1968; 1973).

3.1.4 ABIOTIC DEGRADATION

The significance of abiotic degradation with respect to the exposure assessment component of ecotoxicology as well as experimental methods and their predictability have been discussed in SCOPE 12 and 25; therefore only those aspects which are related to climate factors are summarized here.

Photochemical processes relevant to the degradation of xenobiotics have been reviewed in SCOPE 25 (1985) and in the *Handbook of Environmental Chemistry*, Vol. 2 (Hutzinger, 1982).

For the present purpose, it should be mentioned that light energy and intensity and sunshine (direct or indirect) duration enhance the rates of degradation, either directly or indirectly via the formation of active species. Radiation and energy transport and their global distribution have been reviewed by Bolle (1982). In the northern temperate zones with higher concentrations of pollutants providing reactive species upon photochemical reactions, these rates may be enhanced. Although chemistry in the lower atmosphere differs over the various types of world ecosystems (Graedel, 1980) no conclusions on degradation of xenobiotics can be drawn from this.

For oxidations in water mainly reactions with RO_2 and singlet oxygen are of importance resulting from photolysis of e.g. humic materials. Thus, apart from the effect of temperature on reaction kinetics it is mainly the climatic influences on the occurrence of donors for the reactive species which are important. In specific cases the respective rate constants will show whether the process is significant ($k > 10^{-3}$ Mol sec^{-1}) (Mill, 1984).

The hydrolysis rate of chemicals usually following first-order kinetics depends directly on temperature and is of importance both in water and also in soils with interstitial soil solution. Apart from temperature, the pH of the medium plays a major role, reflecting acid- and base-catalysed and non-catalysed reactions. The finding that the non-persistent pesticide aldicarb may penetrate groundwater at low pH and sandy soil conditions (Bull *et al.*, 1970) has drawn attention to the importance of ambient pH changes resulting in half-lives from days to months for several pesticides. Many measurements exist on the influence of these variables, including structure-reactivity correlations, the latter being generally validated for temperatures between 5°C and 30°C and a pH range of 5–9 (Mill, 1980; Mabey and Mill, 1978).

For quantitatively relating hydrolysis rate with temperature the Arrhenius approximation ($k = A_e(-E_A/RT)$, where $E_A =$ activation energy and other equations are in use which all fit rather well with experimental data, although they neglect second-order temperature dependencies. As a rough approximation of the influence of temperature on hydrolysis rate in the range 0–50°C, a difference of 10 °C results in a change in *k* by a factor of 2.5, a 25 °C difference by a factor of 10 (Lyman *et al.*, 1982). This shows that the significance of hydrolytic transformation of chemicals, leading to derivatives with unpredicted

environmentally relevant physico-chemical and toxicological properties, drastically differs between cold and hot climates. In hot climates hydrolysis thus may become a significant parameter for assessing the fate of chemicals, whereas it is less significant compared to other loss processes in temperate zones, and negligible in cold zones. For persistent chemicals, e.g. bis-chloro ethers and chlorinated aliphatics, hydrolysis seems to be the major loss process in hot (humid) climates (Suffet and Harris, 1984), although it is very slow in temperate climates.

The influence of other environmental variables catalysing or retarding hydrolysis is poorly understood. There are reports that humic materials catalyse the hydrolysis of pesticides, although retarding of the rate has also been reported. Ion strength, heavy metals content, and suspended solids also may change the rate of hydrolysis (Wolfe, 1980). For chloropyrifos a change of the hydrolysis rate by a factor of 15 has been reported. Apart from retardation by sorption and binding to humic materials and solids, the mechanisms are unknown (Suffet and Harris, 1984; Lyman *et al.*, 1982). Given the wide variation of these environmental factors in the world's ecosystems the range of their effects should be investigated and integrated into environment fate models.

Although hydrolysis is in general a transformation process only, for a number of pesticides it presents a potent detoxification mechanism and reduces their bioaccumulation potential. This has been demonstrated, e.g. for fenitrothion in an aquatic microcosm (Fisher, 1985).

Since pH values vary locally or regionally within the range of concern, pH does not appear to be an important variable within the scope of this report.

3.1.5 EXPERIMENTAL METHODS

The general methodology for studying the fate of chemicals in the environment includes investigations on their bioavailability. This methodology also includes experiments giving fragmentary information, such as transfer rates, total uptake by a species, resorption, binding to macromolecules, leaching in soil and partitioning between the environmental media.

The most comprehensive methodology has been developed for studying the environmental behaviour of radionuclides, pesticides, and heavy metals, and has been adopted for a few further persistent or hazardous groups of chemicals. Most experiments with organic chemicals are performed with labelled test chemicals to facilitate quantification and to allow for assessment of conversion products (Korte, 1980). This methodology covers a wide range of sophistication according to the specificity of problems investigated: single factor testing, multiple factor testing, and experimental models; outdoor investigations, field studies, and environmental monitoring. The respective methods have been broadly reviewed and appraised elsewhere (SCOPE 25, 1985; SCOPE 12, 1978; Nürnberg, 1985).

Given the complexity of interacting chemical and environmental factors, experiments with appropriate model ecosystems would be most helpful. A great number of terrestrial, aquatic, and mixed systems — both of laboratory and outdoor type — have been developed for studying mobility, transformation, and degradation, all three being important criteria within the area of study. A critical evaluation of feasibility and predictability of model ecosystems revealed — despite the use of labelled chemicals — common limitations with respect to number of species and environmental factors, lack of representativity of food chain organisms, and lack of equilibrium of trophic levels (lower trophic organisms are frequently consumed in too short a period, physiological conditions for component organisms are not optimal). Larger open and outdoor models may overcome these limitations but their costs are very high, and they do not provide reproducible results (SCOPE 25, 1985; IUPAC, 1985).

Soil- and plant-bound residues — a phenomenon which is not restricted to pesticides (Führ, 1984) — are of great importance and due to respective variations of the relevant environmental properties are to some extent climate-zone dependent. Published data on pesticide-bound residues reveal that their bioavailability cannot be excluded a priori (Review IUPAC, 1984), and a sequential approach for studying these residues based on their bioavailability has been proposed (Huber and Otto, 1983).

3.1.6 CONCLUSION

Standardized and internationally harmonized test methods for investigating the properties of chemicals relevant to their mobility mostly use temperate climate conditions as the standard. Partial exceptions are hydrolysis for which different temperatures are considered, and direct and indirect photolysis, which is investigated at various light intensities and duration (OECD, 1981).

To permit the extrapolation of test data to real field conditions and to generalize specific data from simulation and outdoor experiments, the real influence of the discussed environmental variables on the fate of chemicals should be known on the basis of systematic or comparative experiments. This would involve the understanding of the respective prevailing processes and thus provide the basis to improve considerably the environmental fate models and consequently the prediction of exposure to chemicals under the environmental conditions under study. A tremendous research effort for the advancement of the understanding of the behaviour of chemicals in the environment is lost worldwide by repetition of experiments, finding differences without elaborating the causes. It should be, therefore, a task for research planners to emphasize and support:

(a) systematic investigations on the influence of single climate or climate-related factors;

(b) systematic investigations on the interactions of these factors as they modify their influence;

(c) improved predictions by data interpretation and modelling, on the basis of reliable and quantified inclusion of the variations of the relevant processes.

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