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SCIENTIFIC COMMITTEE ON TOXICITY, ECOTOXICITY AND THE ENVIRONMENT (CSTEE)

Opinion on the results of the Risk Assessment of:

ALKANES, C_{14-17}, CHLORO
Environmental Part

CAS N° : 8555-85-9
EINECS N° : 287-477-0

Carried out in the framework of Council Regulation (EEC) 793/93 on the evaluation and control of the risks of existing substances[1]

Opinion expressed at the 35th CSTEE plenary meeting

Brussels, 17 December 2002

[1] Regulation 793/93 provides a systematic framework for the evaluation of the risks to human health and the environment of those substances if they are produced or imported into the Community in volumes above 10 tonnes per year. The methods for carrying out an in-depth Risk Assessment at Community level are laid down in Commission Regulation (EC) 1488/94, which is supported by a technical guidance document.

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Terms of reference

In the context of Regulation 793/93 (Existing Substances Regulation), and on the basis of the examination of the Risk Assessment Report the CSTEE is invited to examine the following issues:

1. Does the CSTEE agree with the conclusions of the Risk Assessment Report

2. If the CSTEE disagrees with such conclusions, the CSTEE is invited to elaborate on the reasons for this divergence of opinion.

GENERAL COMMENTS

The medium-chain chlorinated paraffins (MCCPs) are mixtures of a large number of mainly n-alkanes with between 14 and 17 carbons and between 1 to 17 chlorine atoms. The physical properties of these substances vary over wide ranges, and the complexity makes the products difficult to analyse. MCCPs are used in a number of applications, many of which are in consumer products. The risk assessment of such products is very difficult, but the present report is a good example that it is possible to give an estimate also under these circumstances.

The exposure assessment is mainly based on information from industry, but in most cases verified with data from other sources. The emissions from products containing MCCPs and "waste in the environment" are estimated to be of the same magnitude as those from production and primary use together.

CSTEE agrees with most of the exposure assessment, but needs access to the UK report on environmental levels to be able to judge if the detection limits found in that investigation can be accepted as $PEC_{regional}$.

Polychlorinated alkanes can loose hydrogen chloride (dehydrohalogenation) under certain circumstances, such as under heat or in contact with alkaline substances. The products are unsaturated hydrocarbons, and it has been shown that CPs can form also aromatic substances, such as PCB and PCN. This has not been discussed at all in this risk assessment report.

As for all complex mixtures of chemicals, the toxicity of medium-chain chlorinated paraffins cannot be precisely assessed as for individual chemicals. Tests are usually performed on technical mixtures of variable, and often not perfectly defined, composition. Nevertheless, by knowing some properties (density, chlorine % by weight) it is possible to estimate the approximate composition of the mixture. Moreover, the strictly congeneric structure, allows to hypothesise the same toxicological mode of action, presumably narcotic-type, of all components of the mixture.

In spite of a few controversial points, the CSTEE agrees with most conclusions of the effect assessment, as well as with all conclusions of the risk characterisation, but particular care must be addressed to secondary poisoning.

The CSTEE considers that the risk related to secondary poisoning has not been adequately covered in the RAR. Particularly for the aquatic environment, the risk assessment has been conducted using the TGD recommendations but without considering the available data. The assessment of secondary poisoning on birds and mammals on the exclusive basis of the PECsurface water and the fish BCF should be considered an initial step applicable when no additional information is available. The RAR presents, however, valuable information for a proper assessment of secondary poisoning. This information includes the assessment of bioaccumulation in aquatic invertebrates and the bioaccumulation from food. Both aspects are covered in the RAR but not used in the assessment of secondary poisoning. The CSTEE considers that a proper assessment of these factors would lead to potential risk of secondary poisoning from aquatic sources for additional scenarios. These considerations are supported by measured data included in the RAR. The information on the UK report is too briefly described, however, it suggests potential risks of secondary poisoning at several scenarios.

In addition, a potential for biomagnification through the food chain has been identified, and it should be considered in the risk assessment of secondary poisoning. Therefore, the CSTEE does not agree with the conclusion (ii) for secondary poisoning from aquatic sources presented in the RAR for most of the scenarios.

SPECIFIC COMMENTS

Exposure assessment

(As CSTEE is aware of that this version is not the final draft, these specific comments may be a bit more detailed than usual.)

The exposure part of the assessment is extensive and very well performed. There is very limited data on emissions and many estimates have to be done both for direct emissions from production/use and for diffusive emissions during use and disposal of articles containing the MCCPs. The amount of data on environmental levels is also very scarce, and the analytical techniques available are only able to give estimates of the concentrations. The release estimates are mainly based on information from industry, complemented with default values from the TGD where appropriate.

The C_{14} – C_{17} alkanes range looks narrow, but taking into account also the different chlorine amount and substitution patterns, a huge number of structures are possible, and many of these are probably present in the technical products. A consequence of this is that the physical and chemical properties for the compounds can vary over wide ranges. The sensitivity for such variations has been tested in Appendix H, and the strongest influence found was the value for biodegradation in soil, which had a marked influence on $PEC_{regional}$. The other parameters influenced the outcome of the predictions to a much lower degree. The CSTEE would, however, have liked to see data for the extremes (C_{14} with a low chlorine content and a highly chlorinated C_{17}) included in this analysis with realistic data. The $C_{14}H_{24}Cl_6$ presently in the table H1 contains 52 % chlorine and has an unrealistic vapour pressure.

In section 1.2.1 it is said that the commercial products are complex mixtures of isomers, which should be congeners. It is also concluded that there is < 1 % of substances outside the C_{14-17} range based on information from industry saying that there is < 1 % with less than 14 carbons and < 1 % with more than 17 carbons. In section 1.3.7, paragraph starting Fisk et al., compounds should be exchanged by mixtures.

The site-specific release information obtained from industry (section 3.1.0.1.2) for site A seems to be in water to WWTP, but is used as a release to the environment in the report. It is also interesting to see how one plant seems to be four order of magnitude better than the others, but as the background material is not available to the CSTEE it is not possible to give a more detailed analysis of these data.

The second most important use of MCCPs is in metalworking fluids, and the major loss from this process is on the swarf. This is mainly re-used by the metallurgic industry. A potential problem in this process is the formation of more toxic compounds (such as chlorinated aromatic substances, including dioxins) from the MCCPs during the heating of the swarf before it is introduced into the melting process. This possibility of formation of more toxic substances may also be present in other processes where the substances are heated, such as metalworking. There may also be other processes that may give rise new, more toxic, compounds, such as the alkaline washing of cutting fluids from work pieces. In this case there is a risk for dehydrohalogenation of the MCCPs, thus producing unsaturated compounds.

A considerable amount of MCCPs are used in leather fat liquors and the major part of that is retained in the leather. There is presently insufficient information available on the emission from these articles, which may be important for the estimation of human exposure, and here is an obvious need for further investigations if MCCPs are going to be used for this purpose in the future.

The leaching of phthalate plasticisers from roofing material is used for the estimation of MCCP emissions from this application. The figure used (0.7 %) is said to represent the loss over four years, but the document referenced (UCD, 1998) is giving it as an annual loss. Thus the estimated leaching of MCCP in Table 3.4 should be four times higher.

It is remarkable that there are no results available from standard biodegradation test on a chemical used in the EU at almost 100,000-ton level. The low water solubility makes experiments in this medium difficult, and higher accumulation can often be seen at low concentrations than at high.

It is very difficult to measure MCCP concentrations in environmental samples, and in the RAR there is an Appendix where the used methods are reviewed. Several of these report total CPs and the results are thus not very useful in the assessment of MCCPs. Generally, however, the measured data seems to support the predicted reasonably well. A recent study in UK was not able to detect MCCPs in water and the detection limit (0.1 microg/L) is used to override the predicted $PEC_{regional}$ (0.389 microg/L). The CSTEE has not access to the UK report to check the appropriateness of this change.

In parallel to the RAR on DEHP, the assessors have tried to estimate the importance of "waste remaining in the environment" for the exposure to MCCPs. As the chlorinated paraffins are used as a secondary plasticiser, most often together with a phthalate, parallels can be drawn if the differences in physical properties are taken into account. This is done in Appendix F, and in the flooring section there is an error, as 5.4 - 8.2 m^2 should be 5.4 - 8.2 x 10^8 m^2. The emissions of this type are believed to be comparable to the releases predicted from the production and use.

In table G3 the figure for "Revised release estimates for 52 % Cl for air"/ "Polymers – service life" should be 55035.

Both, bioconcentration from water and bioaccumulation from food have been identified as relevant properties. Absorption on algae/organic suspended matter is suggested as a potential explanation for the higher BCF found in mussels when compared to fish. Both processes indicate that aquatic organisms including fish will be simultaneously exposed to bioaccumulation from water and food. As kinetic data are available and reported in the RAR, these data could be used to perform a quantitative estimation of the contribution of waterborne and food in the overall bioaccumulation. Unfortunately, these aspects have not been included in the RAR.

An additional possible explanation of the higher BCF in mussels may be a lower metabolic rate. Again, this issue is not discussed.

The relevance of these factors can be appreciated in the comparisons of predicted versus measured data. The RAR suggests that predicted and measured data (basically from the UK report) are within the same order of magnitude. This is obviously true, however, the RAR does not consider the large difference in the predicted versus measured concentrations in water. If water concentrations in water are much lower than predicted, but biota concentration is within the same order, it should be concluded that additional mechanisms, other than bioconcentration from water, should be considered.

Effects assessment

Aquatic organisms

Short-term acute toxicity of three different mixtures was studied on *Alburnus alburnus.* No effect was observed at the maximum concentrations tested (5000 to 10000 mg/L), many orders of magnitude above the water solubility, estimated around 27 μg/L. Tests were performed in static conditions and concentrations are nominal.

Other short-term tests were performed on *Leuciscus idus,* showing no effects at 500 mg/L, but tests conditions are poorly described and the reliability of data is unknown.

In a 14-day semi-static test on *Alburnus alburnus*, no effects were observed at 0.125 mg/L (single, nominal, concentration tested).

Long term experiments (60 days) with flow trough conditions and measured concentrations were performed on rainbow trout (*Oncorhyncus mykiss*). No effects were observed at the maximum concentration tested (4.5 mg/L).

Finally, 20-day toxicity tests were performed on embryos of *Orizias latipes*, in static conditions, with measured concentrations. No effects were observed at the maximum concentration tested (3.4 mg/L), but some questionable methodological aspects (low hatching rate in the controls, no oxygen control in test vials, etc.) allow classifying as low reliable these data.

It follows that the most reliable fish data are those on rainbow trout, indicating a NOEL=4.5 mg/L.

All described tests were performed using co-solvents (mainly acetone).

Toxicity data on *Daphnia* are highly controversial. Thompson *et al*. (1996) found a 48h EC50 of 5.9 µg/L. Surprisingly, the same authors (Thompson *et al*., 1997) found a 21-day NOEC of 10 µg/L, higher than the short term EC50. Other authors (Frank, 1993; Frank and Steinhauser, 1994) found a 48h EC25 of 339 µg/L, a 48 h NOEC of 140 µg/L and a 21-day NOEC of 12.6 µg/L. In these assays there are some doubts about the form of the chemical (really dissolved or undissolved droplets). A 21-day NOEC of about 4-8 µg/L was found in a third assay, again with some doubt about the real concentration. In all these tests, several methods were used to solubilise the chemicals (co-solvents, sonication).

Toxicity tests on other crustaceans showed 96h LC50 ranging from 1 up to 10000 mg/L.

A test on mussels showed a 60-day NOEL of 220 µg/L.

Test on algae growth rate showed a 72h EC50>3.2 mg/L and a NOEC of 0.049 mg/L.

Data are also available for micro-organisms from waste water treatment plants. Different tests showed a 24 hours harmful threshold of 800 and 2500 mg/L and a 3 hours NOEC for respiration of 2000 mg/L. For all these tests, methodological details are not reported and the reliability of results cannot be checked.

Finally, some data are available for sediment organisms. A 28-day NOEC of 3800 and 130 mg/kg dw was found for *Chironomus riparius* and *Lumbriculus variegatus* respectively. Assuming the default value for water content for sediment proposed by the TGD, these figures correspond to 1460 and 50 mg/kg ww, respectively.

In conclusion, a relatively large amount of data is available, but their reliability is questionable. For short-chain chlorinated paraffins, the narcotic mode of action was documented. It seems reasonable to hypothesise for medium chain paraffins the same mode of action. Nevertheless, the large differences observed among toxicity data for different aquatic organisms (e.g. fish and *Daphnia*) seem to suggest a non-narcotic mode of action.

Moreover, the low solubility of the chemicals makes sometime doubtful the concentration of the test solutions. Even if various methods were used to increase solubilisation, values are often controversial.

Taking into account that long term data are available for two different organisms, in the RAR, a $PNEC_{water}$ = 0.2 µg/L is calculated by applying a factor of 50 to the NOEC of 10 µg/L taken from the long term *Daphnia* study. For a preliminary approach, this figure could be accepted; nevertheless, a refinement of toxicity data is recommended by the CSTEE.

A PNEC of 80 mg/L is calculated by applying a factor of 10 to the lowest threshold concentration on bacteria.

For sediment, according to the equilibrium partitioning method, a $PNEC_{sed}$ of 0.26 mg/kg can be calculated. By applying a factor of 50 to the NOEC on *Lumbriculus variegatus,* a PNECsed of 1 mg/kg has been calculated and used for risk characterisation.

These figures are considered appropriate by the CSTEE.

Terrestrial organisms

The toxicity of medium-chain chlorinated paraffins (52% wt Cl) was tested on three terrestrial plants (wheat, oilseed rape, mung bean). The end-points determined were seed germination and emergence, vegetative growth and visual conditions of the seedlings. The methodological procedures are adequate and the data can be assumed as reliable. No effects were observed in any of the species studied, at the maximum concentration tested (5000 mg/kg dw).

A comparable mixture was used to test the toxicity on earthworm (*Eisenia foetida*) in a 56-day assay. The end-points determined were survival, growth and reproduction. The methodological procedures are adequate and the data can be assumed as reliable. A NOEC= 280 mg/kg dw was observed. By assuming the default value of water content in soil proposed by the TGD, this corresponds to 248 mg/kg ww.

No data are available on soil micro-organisms.

According to the equilibrium partitioning method, a $PNEC_{soil}$ 0.21 mg/kg ww can be calculated. In the RAR a $PNEC_{soil}$ = 2.12 mg/kg ww is calculated by applying a factor of 50 to the NOEC on earthworm and by normalising to the organic carbon content. It is the opinion of the CSTEE that this figure can be accepted since long-term NOECs on two trophic levels (plants and earthworms) are available. Nevertheless, data on micro-organisms are strongly recommended.

Secondary poisoning

Due to the high Kow, medium-chain chlorinated paraffins have a high potential for bioaccumulation. Tests on terrestrial vertebrates showed a NOAEL>24,000 mg/kg feed in a 5 day study on birds and NOAEL=5 mg/kg feed in a 90 day feeding study with rat. By applying a factor of 10 to the rat NOAEL, a PNEC=0.5 mg/kg feed can be calculated. The PNEC = 5 mg/kg suggested by the RAR, but not used for risk assessment, is not enough justified.

Risk characterisation

Aquatic compartment

Using the PNECwater=0.2 µg/L, most of the local scenarios for surface water give a PEC/PNEC>1. Therefore, the CSTEE agrees with conclusion i) and with the proposal expressed in the RAR of more reliable long-term tests on fish to refine the PNEC assessment. Moreover, it is opinion of the CSTEE that there are some doubts related to the reliability of long-term data on *Daphnia*.

Besides the need for PNEC refinement, the CSTEE also agrees on the need for risk reduction measures for particular industrial processes, were the likelihood of a risk is higher, in particular:

- some processes in the production of PVC;
- formulation and use of metal cutting fluids;
- use in leather fat liquors.

For sediments, almost all local PEC/PNEC values were higher than 1 indicating a potential risk. Only at the regional level a risk trigger is not overcome. The CSTEE agrees with the need for additional long-term data on sediment-dwelling organisms. Nevertheless, the maximum result achievable with this additional information could be the application of a factor of 10 instead of 50 and a reduction of PEC/PNEC by a factor not higher than 5. With this reduction, about one half of site-specific scenarios would maintain a PEC/PNEC >1. Therefore the CSTEE agrees with the need for risk reduction measures for many industrial processes.

Alternatively, higher tier approaches, such as field or microcosm/mesocosm studies, could be used for the risk refinement. These studies are particularly suitable for these chemicals as all exposure routes (waterborne, food) and compartments (water column, sediment) can be evaluated simultaneously, and under more realistic conditions than those provided by standard ecotoxicity tests.

The CSTEE also agrees with conclusion ii) for wastewater treatment plants. In all site-specific scenarios PEC/PNEC ratio is far below a risk trigger.

Terrestrial compartment

For most site-specific local scenarios a PEC/PNEC ratio higher than 1 has been calculated. Only in production sites and in a few use typologies there is no need for more information or reduction measures. Therefore, the CSTEE agrees with conclusion i). In particular, as previously mentioned, a test on soil microorganisms is strongly recommended for a better assessment of the PNEC.

Nevertheless, as in the case of sediments, this new information will reduce PEC/PNEC for a maximum factor of 5 and this will not give values lower than 1 for many industrial sites. Therefore, the CSTEE agrees with the need for limiting the risk for some industrial uses, in particular:

- uses in PVC in open systems;
- uses in metal cutting/working fluids;
- uses in leather fat liquors.

In the case of the terrestrial environment, some problems may also arise at the regional level. Due to the large uncertainties in the predictive approaches and to the scarcity of experimental data, the need for a refinement of the assessment is underlined.

Atmosphere

Even if information on the effects of medium-chain chlorinated paraffins through air exposure is lacking, and a precise risk characterisation is not possible, the CSTEE agrees with the conclusion ii) due to the low volatility of the chemicals and the unlikelihood of an atmospheric contamination.

Nevertheless, due to the persistency and the bioaccumulation potential, the CSTEE also agrees with the suggestion for investigating the potential for long-range atmospheric transport and transfer in the food chain at global level.

Secondary poisoning

Different conclusions have been drawn in the RAR for the aquatic and terrestrial environment.
In the first case, a few local scenarios shows a PEC/PNEC>1. Nevertheless, the biota monitoring data indicate concentrations over the PNEC in aquatic organisms associated to uses for which PEC/PNEC ratios are below 1. This information is considered critical for the assessment, suggesting risks of secondary poisoning at additional scenarios than those identified in the RAR.

In the second case, all scenarios (with the only exception of production sites and uses in sealant formulation and paints for domestic application) give PEC/PNEC values substantially higher than 1.

The CSTEE agrees with the position expressed in the RAR that there are not realistic possibilities for a substantial change of the opinion by refining the assessment. Therefore, the CSTEE agrees with conclusion iii). The need for limiting the risk should be applied to almost all industrial scenarios for the terrestrial environment and to many scenarios for the aquatic environment, with particular care to:

- uses in PVC in open systems;
- uses in metal cutting/working fluids;
- uses in leather fat liquors.

The biomagnification risk should be considered at the local, regional and continental level.