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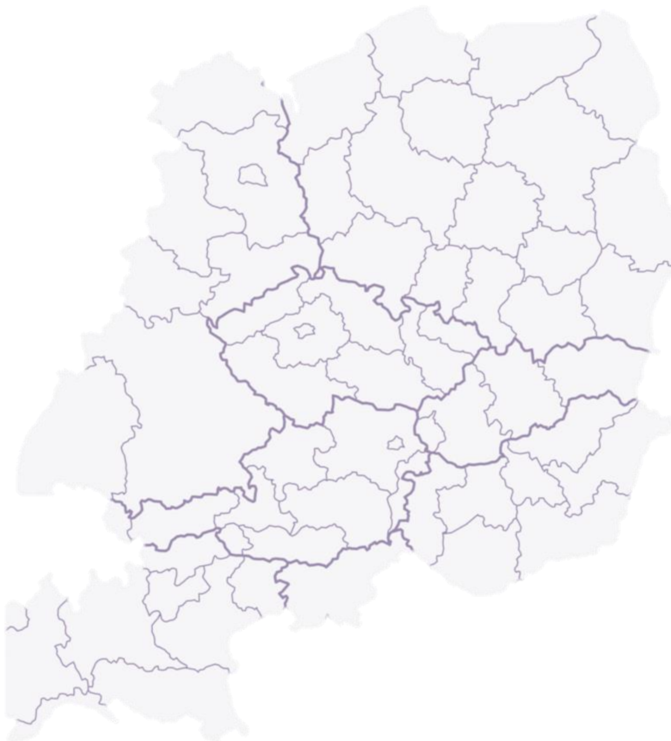

NANOFORCE
EXPOSURE SCENARIO *Draft*

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Introduction

According to the toxicological and ecotoxicological information, as they are reported in the MSDS, ZnO does not pone any concern regarding human exposure, but it can be classified as toxic for environment.

The classification is confirmed on the basis of the reported results from the dissolution test (Table 1)

Table 1 – Dissolution test for ZnO at different sizes. (see MSDS)

Particle diameter (d) nm)	$[Zn^{2+}]$ mg/L
4 ± 2	32 ± 1
7 ± 2	15 ± 1
15 ± 4	14 ± 1
17 ± 3	12 ± 1
24 ± 3	10 ± 1
47 ± 7	9 ± 1
130 ± 21	6 ± 1

Dissolution rate of NPs leads to NP concentrations at 24h that exceeds the LC50 or EC50 calculated for several species (Table 2)

Table 2 – Toxic effects of nano-ZnO in standard ecotoxicological tests

Species	Test material	Test	Toxicity endpoint	Compared to dissolution concentration (mg/L) *
***Pseudokirchneriella subcapitata* (Algae)**	50-70 nm ZnO	Algal growth inhibition test (72h)	EC50 = 0.042 mg/L	9 ± 1
***Daphnia magna* (crustacea)**	nano-ZnO different sizes	Daphnia immobilization test (48h)	EC50 = 1 mg/L	6 ± 1
***Danio rerio* (zebrafish) (fish)**	nano-ZnO	Acute toxicity (96h)	LC50 = 4.92 mg/L	6 ± 1
***Danio rerio* (zebrafish) (fish)**	30 nm ZnO2	Embryo test (96 h post-fertilitation)	LC50 = 50 mg/L	10 ± 1
***Caenorhabditis elegans* (nematode)**	20 nm ZnO	24h	LC50 2.2 mg/L	7.43
***Caenorhabditis elegans* (nematode) larvae**	Bulk ZnO	24h	LC50 2.3 mg/L	5.56

Some considerations should be taken into account when considering the results reported in Table 2.
First of all the dissolution test was performed at 24h when most of tests were performed through a longer period of time. However, results from metazoan can be easily compared, giving evidence of toxic effects from both nano- and bulk ZnO.
Moreover, the embryo fish test, that is considered an in vitro method supporting reproduction toxicity, resulted in EC values higher than the correspondent dissolution concentration.

Based on these results, we confirmed the classification of nano ZnO as toxic for the environment and set the environment ES.

Calculation of Predicted No Effect Concentration
Predicted No Effect Concentrations (PNECs) were calculated on the basis of available ecotoxicological tests from scientific literature (Table 3). PNEC for freshwater is 5 times higher than that that calculated on the basis of the NOEC (0.042 mg/L) from the growth inhibition test in the most sensitive species (*Pseudokirchneriella subcapitata).*

Table 3

PNEC/endpoint	Literature data	MSDS
PNEC freshwater	20.5 µg/L	4.2 µg/L
PNEC marine	6.1 µg/L	
PNEC STP	100 µg/L	
PNEC Sediment freshwater	117,5 µg/L	
PNEC Sediment marine	56.0 µg/L	
PNEC Soil	35.6 mg/kg soil die	2.2 µg/L

For the purpose of this ES we set PNEC for freshwater at 20 µg/L

The results provided for terrestrial toxicity (*Caenorhabditis elegans)* give evidence for a level of toxicity much higher than that from other literature reports.
The calculation of PNEC on the data provided in MSDS would lead to a value of 2.2 µg/L.

According to guidelines, when PNEC for soil is calculated on only one terrestrial test result (either earthworms or plants), the risk assessment should be performed both on this test result and on the basis of the outcome of the aquatic toxicity data.
It should be also considered that both $PNEC_{freshwater}$ and $PNEC_{soil}$ were calculated on short-term acute toxicity tests reported in MSDS while PNECs from literature data were calculated on longer time of exposure.
In conclusion, we considered two PNEC values for freshwater and soil from the tests considered in the MSDS. This approach was related to the worst scenario. We compared the results with PNECs obtained from literature data.

Exposure Scenario
Zinc is an essential element naturally present in the environment. Thus, the total concentration of zinc in the environment is due to natural processes, which result in a natural background concentration in all compartments and organisms, to the chemical processes that affect the speciation of zinc, and, finally, to the industry production and personal uses of zinc-containing products.

For this reason, it should be taken into account that the exposure to zinc from industrial emission and disposal of zinc-contaning products should be regarded in terms of added risk approach calculated on the basis of an added Predicted Environmental Concentration (PEC_{add}) and an added Predicted No Effect Concentration ($PNEC_{add}$).

The contribution of PEC_{add} to the background environmental concentration (BC) is calculated on the production volumes provided by the industry. Since in the present case, the amount of annual production has not been set, we adopted a parameter derived by the European production average reduced by 10 to derive a regional emission, from which a local emission can be derived by considering the local production and uses. For the purpose of this exposure scenario we only considered the uses specified in the MSDS.

In Table 4 the sources of ZnO emissions are reported.

Table 4 – Environmental exposure to ZnO

	Life cycle stages (category)
1	Production of zinc oxide
2	Processing in automobile tyres
3	Processing in general rubber
4	Processing in glass
5	Processing in ceramics
6	Processing in ferrites
7	Processing in varistors
8	Processing in catalysts

9	Formulation as feedstuff additive
10	Formulation and processing in zinc chemicals
11	Formulation and processing in lubricant additives
12	Formulation and processing (spraying) in paints
13	Formulation in cosmetics and pharmaceuticals

Sources #12 and #13 have been considered in the MSDS

The European average production for ZnO, including all the industrial categories reported in Table 4, ranges around 10,600 t/y that means a regional production of 1060 t/y, accounting for about 2100 kg/y of Zn emission in air. However, the level of production is different according to the category (Table 5)

Table 5 – Level of exposure according to categories of emission

	Category	Production (exposure) (%)
1 2 3	Production of zinc oxide Processing in automobile tyres Processing in general rubber	36%
4 5	Processing in glass Processing in ceramics	27%
6 7 8	Processing in ferrites Processing in varistors Processing in catalysts	12%
9	Formulation as feedstuff additive	9%
10	Formulation and processing in zinc chemicals	4.5%
11	Formulation and processing in lubricant additives	4.5%
12	Formulation and processing (spraying) in paints	4.5%
13	Formulation in cosmetics and pharmaceuticals	2%

According to Table 5 and uses considered in MSDS, we can set the annual level of emission at a maximum of 11% of the total annual production, that at the regional scale would be around 1570 t/y for both bulk and nano ZnO. This would be the worst scenario.
On this bases we calculated the $C_{add,}$ considering the calculated local C_{add} values in air, based on European emission values, ranging from 0.05 to 7.60 μg/m^3. The highest C_{add} value in air calculated with the realistic worst case scenario is 13.1 μg/m^3.
Using the same approach, we calculated the emission in water. Looking at the European emissions in water, it is clear that the zinc emissions to effluent water are

reduced when industrial waste water is treated in a local (industrial) waste water treatment plant (WWTP) or in a municipal sewage
treatment plant (STP). Adsorption is the most important removal process. The treatment result in most cases in zero emission to surface water. In a possible worst scenario, we found that the Cadd can be set at 1.26 µg/l, based on literature reports for those few cases when emissions impact on the surface water.

Exposure scenario related to life cycle for formulation and processing in paints (generic scenario)

Zinc oxide is mainly used in the fabrication of marine paints and in decorative paints. The European average usage of ZnO in paint producing plants (formulation stage) is about 100 t/y and the largest zinc oxide usage is 1,500 t/y, based on literature report. Also in this case, there is no release in water. Also when ZnO is used in anti-corrosion marine coatings, there is no emission into water. Some literature reports claim for emission during the application of the paint to the ships due to overspraying, that may result in emission at the point of application (docks). However, no measurements are reported that can be used in the calculation of the exposure scenario. We accepted a worst scenario proposed in some literature report that considered a 2% release directly to water and, again, we applied the 10% reduction to EU average production and usage in order to model the exposure scenario. With these entries, we obtained a $C_{add.water}$ = 12.3 µg/L that exceed the $PNEC_{add}$ calculated on the basis of data proposed in MSDS, but not the $PNEC_{add.freshwater}$ calculated on the basis of literature data.
For soil we obtained a $C_{add.soil}$ = 51.2 mg/kg that exceed both the $PNEC_{add\cdot soil}$ calculated on the basis of data proposed in MSDS and the $PNEC_{add.soil}$ calculated on the basis of literature data.
In Table 6 we reported the results from the exposure scenario analysis and included a local exposure scenario for 1 plant producing 100 t/y of ZnO, assuming that 70% of its production is used in formulations for paints.

Table 6 – Results from exposure scenario model for paints

$C_{add -}$	Generic scenario	Local Plant
$C_{add.water}$	12.3 µg/L	8.6 µg/L
$PNEC_{add.freshwater}$ from literature data	4.2 µg/L	
$PNEC_{add.freshwater}$ from literature data	20.5 µg/L	
PNEC marine from literature data	6.1 µg/L	
$C_{add.soil}$	51.2 mg/kg	35.8 mg/kg

$PNEC_{add.soil}$ from literature data	35.6 mg/kg soil die
$PNEC_{add.soil}$ from MSDS	2.2 mg/kg

Exposure scenario related to life cycle for formulation in cosmetics and pharmaceutical (generic scenario)

Zinc oxide is used for a variety of applications. It is used as an UV absorber in sunscreen creams, healing aid in ointments, astringent and skin conditioning in creams, preparation of dental cements, fungistatic properties in deodorants and soaps..

The European average zinc oxide usage per cosmetics or pharmaceutical producing plant is about 60 t/y and the largest zinc oxide usage is 500 t/y (information from industry). By applying the 10% reduction we calculated the C_{add} based on the average 6 t/y and obtatined a value for $C_{add.water}$ = 2.1 µg/L, that is lower than both $PNEC_{add.water}$ from MSDS data and PNEC water from literature data and $C_{add.soil}$ = 6.55 mg/kg that is much lower than $PNEC_{add.soil.}$ calculated on literature reports but exceeds $PNEC_{add.soil}$ from MSDS data.

In Table 7 we reported the results from the exposure scenario analysis and included a local exposure scenario for 1 plant producing 100 t/y of ZnO, assuming that 30% of its production is used in formulations for cosmetics and pharmaceuticals.

Table 7 – Results from exposure scenario model for cosmetics and pharmaceuticals

C_{add} -	Generic scenario	Local Plant
$C_{add.water}$	2.1 µg/L	10.5 µg/L
$PNEC_{add.freshwater}$ from literature data	4.2 µg/L	
$PNEC_{add.freshwater}$ from literature data	20.5 µg/L	
PNEC marine from literature data	6.1 µg/L	
$C_{add.soil}$	6.55 mg/kg	32.75 mg/kg
$PNEC_{add.soil}$ from literature data	35.6 mg/kg soil die	
$PNEC_{add.soil}$ from MSDS	2.2 mg/kg	

Conclusions

The results from modeling the exposure scenario related to the production of ZnO in formulations for paints, cosmetics and pharmaceuticals lead to concentration values that exceeds the PNEC values calculated on the basis of standard tests.
However, the model was based on the worst scenario and taking into account the experimental data reported in MSDS and related to acute toxicity. Looking at results for prolonged exposure in standard tests the only risk is related to the contamination of agricultural soil only when procedures for industrial waste water treatment plant or in municipal sewage treatment are not properly carried out.

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