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Acrylonitrile

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on Existing Chemicals of Environmental Relevance (BUA)

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Foreword

The German Chemicals Act (Chemikaliengesetz - ChemG) of 1980 stipulates that certain existing chemicals must be reported to the competent authority, if they exhibit properties which indicate that they may be hazardous, either alone or in combination with other substances.
In the summer of 1982, an Advisory Committee on Existing Chemicals of Environmental Relevance (BUA) was set up by the German Chemical Society (Gesellschaft Deutscher Chemiker - GDCh). It brings together representatives from the scientific community, the chemical industry and the governmental authorities. This Advisory Committee is responsible for elaborating appropriate solutions for substances of relevance for health and the environment on the basis of voluntary measures. It selects and examines existing chemicals from the aforementioned angles. The testing and evaluation are based on scientific criteria alone.
It was, therefore, necessary to develop priority setting procedures. In a first phase reports were only prepared for priority chemicals. Within the framework of a first priority setting procedure, chemicals were compiled from several priority lists and 135 chemicals were selected for detailed substance reports.
In a second priority setting procedure the survey of the German Chemical Industry Association (VCI) on all substances with a production volume of more than 10 tons per year was used as a starting list. Since this survey covered 4,600 chemicals, BUA decided to process the corresponding list in several stages. The first stage included approx. 1,050 substances with a production volume of more than 1,000 tons per year.
Detailed reports are drawn up on chemicals suspected of having a hazard potential and abridged reports on those presenting only a minor hazard potential, according to the current state of knowledge.
The detailed BUA reports take in both the published literature and data from industry. If data for the evaluation of the chemicals are not available, additional studies are recommended and the results are published as updates to the reports. The reports serve as a basis for the instigation of administrative measures, when there are indications of risks to health or the environment.

Tübingen, May 1993

Ernst Bayer
Chairman of the Advisory Committee
on Existing Chemicals
of Environmental Relevance

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Occurrence and Distribution among the Compartments

The acrylonitrile production in the Federal Republic of Germany (states of the Federal Republic of Germany before reunification) was estimated in 1990 at about 340,000 t and the total consumption at 310,000 t.

Two other sources specify the import to be 35,000 t and about 66,000 t and the export as 80,000 t and about 73,000 t, respectively.

Acrylonitrile is exclusively processed further by chemical means and is used as a inonomer for producing polymers. Of the total consumption of 310,000 t acrylonitrile in 1990, about 74 % were used for manufacturing polyacrylonitrile fibres, about 12 % for acrylonitrile-butadiene-styrene plastics, about 3% for styrene-acrylonitrile polymers, about 4.5 % for acrylonitrile-butadiene rubber as well as about 7 % for acrylamide and other products.

In the new states of the Federal Republic of Germany after reunification productive capacity was in 1992/93 about 60 000 t/a, about 3 200 t/a have been imported, about 16 000 t/a processed, mainly to polyacrylonitrile fibres and -cable, a minor part to acrylonitrile rubber and polyacrylates.

With the production and further processing of acrylonitrile in the Federal Republic of Germany, one can expect emissions mainly via exhaust gases and to a lesser degree via waste water. Production and processing wastes which contain acrylonitrile are mostly incinerated. Possible emissions into the environment through the acrylonitrile-monomer content of polymers cannot be quantified.

In 1990, the atmospheric emissions during acrylonitrile production and during further processing to polymers and other products (states of the Federal Republic of Germany before Reunification) were estimated respectively at 6.0 t and about 56.2 t.

The acrylonitrile discharge into the hydrosphere of the Federal Republic of Germany (states of the Federal Republic of Germany before reunification) during production was < 520 kg/a in 1990/1991. The acrylonitrile emissions during further processing were estimated at about 5.4 t/a in 1990/l991.

In the new states of the Federal Republic of Germany after reunification 1992/93 the discharge from production and processing was 83 t/a into the atmosphere and 7,1 t/a into the hydrosphere.

In the Federal Republic of Germany, acrylonitrile at concentrations up to 10.4 µg/m^3 was measured in 1977 - 1984 in air of various cities. In measurements performed within the framework of an acrylonitril immissions survey on the measurement network of one acrylonitrile-producing firm and one firm which further processed it (plant area and vicinity), acrylonitrile was not found in 401 of 430 samples at a detection limit of 1.0 µg/m^3. The average value was 0.9 µg acrylonitrile/m^3. In an evaluation according to the Technical Guidelines-Air (TA Luft), the 98th percentile (with 50 % certainty) was calculated at 7 µg acrylonitrile/m^3.

Studies on the occurrence of acrylonitrile in workplace air during production resulted in concentrations below the detection limit of 1.3 µg/m^3 in the period of 1985 to 1991. Measurement values from the data of BG Chemie (Employment

Accident Insurance Fund of the Chemical Industry) during 1981 to 1991 from 26 firms which either produced acrylonitrile or further processed its successive products showed a 90th percentile value of 4.01 mg/m^3. 92.4 % of all the values were below the currently applicable technical guide concentration of 7.0 mg/m^3. In the field “plastic and plastic foam, extruder“, the 90th percentile was determined at 1.0 mg/m^3 All values were below the currently applicable technical guide concentration of 7.0 mg/m^3.

Degradation and Accumulation

The degradation by OH-radicals with an average tropospheric half-life of 3.3 - 5 days represents the main degradation route for acrylonitrile released into the atmosphere. The reactivity of acrylonitrile with ozone is relatively low. The half-life $t_{1/2}$ was calculated to be > 80 days.

Acrylonitrile which reaches the aquatic area is degraded aerobically after adaptation. Anaerobic processes are not inhibited up to a concentration of 20 mg acrylonitrile/l following adaptation.

There are indications of photodegradation of acrylonitrile in water layers dose to the surface. Hydrolytic degradation under environmental conditions is improbable.

Acrylonitrile is degraded aerobically in surface soils (sandy silt, sand, clay). In studies with 14C-labelled acrylonitrile in the concentration range of 10 - 1,000 mg/kg dry soil, at an applied concentration of 100 mg/l, 50 % of the radioactivity were recovered within 6 days as $^{14}CO_2$. The degradation took place clearly slower at concentrations of 500 mg/l and 1,000 mg/l.

The experimentally determined log P_{OW} of ≤ 0.30 infers a low lipophility of acrylonitrile.

Calculations based on the water solubility of acrylonitrile resulted in a bioconcentration factor of 1. In contrast, a bioconcentration factor of 48 was determined for the bluegill sunfish (*Lepomis macrochirus*) (fresh weight of the entire fish). There are no experimental studies on geoaccumulation available. On the basis of the low log P_{OW} value, however, no significant geoaccumulation is expected.

According to the Henry‘s Law constant calculated at 9.013 Pa · m^3 · mol^{-1}, acrylonitrile is moderately volatile from aqueous solutions.

Ecotoxicological Effects

Aquatic Organisms

Microscopic studies on one river microflora showed that acrylonitrile at concentrations ranging from 10 mg/l to 25 mg/l did not affect the culture and that mainly fungi grew at a concentration of 50 mg/l.

An average EC_{50} of 400 mg acrylonitrile/l was found for a microorganism population from communal sewage in a turbidity test after 24 h culturing at 37 °C. Furthermore, an EC_{50} (12 h, oxygen uptake) of 52 mg/l was determined for heterotrophic aerobic bacteria. In one oxygen-consumption test according to Robra (30 min.), a 10 % inhibition of the substrate oxidation of *Pseudomonas fluorescens* strain *Berlin* was measured at an acrylonitrile concentration of 100 mg/l.

Tests showed that a sure operation of laboratory treatment units with adapted activated sludge is possible up to an acrylonitrile concentration of 140 mg/l. Heavy contaminations of 600 mg/l were tolerated at flow-through periods of 4 - 8 hours. All the microorganisms died at a concentration of 2,000 mg acrylonitrile/l.

In tests on the inhibitory effect of acrylonitrile on methanogenic, unadapted anaerobic sludge, the so-called “problematic“ concentration was determined at 150 - 500 mg/l under substrate-limiting conditions and at 100 mg/l under non-substrate-limiting conditions. In a further test, an EC_{50} (48 h, methane formation) of 90 mg/l was found for methanogenic bacteria. Based on methanogenesis, an EC_{50} (5 h) of 412.5 mg/l was found within the development of an ATP-TOX test founded on the sensitivity of growth and luciferase activity of *E. coli* and *Ps. fluorescens.*

The data on the inhibition of nitrification of micro organisms are inconsistent. Whereas in one test an acrylonitrile concentration of 100 mg/l did not inhibit nitrification by *Nitrosomonas sp.* and *Nitrobacter sp.,* in another test by a different laboratory an inhibition of the nitrification of saprophytic microorganisms was observed at an acrylonitrile concentration of 50 mg/l. An EC_{50} (24 h, ammonium consumption) of 6 mg/l was determined for *Nitrosomonas sp.* enriched from mixed liquor of a waste treatment plant.

Acrylonitrile at concentrations above 100 mg/l completely inhibit photosynthesis and respiration of cultivated sea grass (*Ruppia maritima*). A reduction of sprout growth was observed with all tested concentrations (no data). Apparently, the growth rate of the roots was stimulated at acrylonitrile concentrations below 1 mg/l.

Studies on the acute toxicity of acrylonitrile in water fleas (*Daphnia magna*) resulted in LC_{50} values (48 h) of 7.6 mg/l and 22 mg/l. The NOEL (48 h) was determined at 0.78 mg/l. A NOEL of 3.6 mg/l was measured in a daphnia life-cycle test. LC_{50} values of > 10,000 mg/l were ascertained for the shrimp *Crangon crangon* in static short-term tests of a few minutes. These values clearly decreased after a 24 h recuperation phase. A LC_{50} (24 h) of 25 mg/l and a LC_{50} (96 h) of 6 mg/l were found in flow-through tests. Static tests yielded LC_{50} values (24 h) ranging frost 8 mg/l to 26.7 mg/l.

A LC_{50} (40 h) in the range of 33 - 100 mg/l was determined for the setaceous worm *Ophryotrocha diadema*. In a study, which - due to a low number of animals - has to be evaluated critically, fish-nourishing aninials of the *Gammarus* species (fresh-water shrimps) survived longer than 72 hours at an acrylonitrile concentration of 25 mg/l and less than 22 hours at a concentration of 50 mg/l. In contrast, in a research paper, which is in hand of BUA only as abstract and therefore could not be validated, a LC_{100} of 0.024 m/l is reported. The same source cites a LC_{100} (24 h) of 0.04 mg/l for *Asellus aquaticus* and accordingly values (48 h) of 0.24 mg/l and 0.16 mg/l for the snails *Lymnea stagnalis* and *Radix peregra*.

The acute toxicity of acrylonitrile in fish was studied on several freshwater and saltwater species. A LC_0 (96 h) of 3.0 mg acrylonitrile/l (closed container) was measured in fresh water for the zebra fish (*Brachydanio rerio*) and LC_0 values (48 h) of 5 - 16 mg acrylonitrile/l (open container) were measured for the golden orfe (*Leuciscus idus*). The TLm (median Tolerance limit) and LC_{50} values (96 h) ranged from 10 mg/l (bluegill sunfish, *Lepomis macrochirus*) to 33.5 mg/l (guppy, *Lebistes reticulatus*). The studies in salt water showed a LC_0 (24 h) of 20 mg/l and a LC_{50} (24 h) of 24.5 mg/l for the sea-bream (*Lagodon rhomboides*). Depending on the time, LC_{50} values (24 - 96 h) between 20 mg/l and 14 mg/l were found for the sand goby (*Gobius minutus*).

Flow-through studies on the chronic toxicity of acrylonitrile showed a TLm after 30 days of 2.6 mg acrylonitrile/l for the fathead minnow (*Pimephales promelas*) and a LC_{50} (100 days) of 2.2 mg/l for the rainbow trout (*Oncorhynchus mykiss*). A NOEC (NO Observed Effect Concentration) of 0.34 mg acrylonitrile/l was estimated for the fathead minnow in an “early life stage“ test.

Terrestrial Organisms

Acrylonitrile concentrations of 1,000 mg/l inhibited the growth of *E. coli* by about 50 % without affecting the cell size. The same concentration caused a 48 % inhibition of the growth of yeast (*Saccharomyces cerevisiae*) with a simultaneous 170 % increase of the cell size in comparison with the controls.

A concentration of 1,000 mg acrylonitrile/kg dry soil inhibited the carbon dioxide formation (respiration) of soil microorganisms from silty or sandy loam soil by 50 % (4th day) down to 30 % (6th day) and by 70 % (2nd day) down to 20 % (6th day). The reduction was greater for the soil with a higher content of organic carbon.

Studies on the effect of acrylonitrile on morphological alterations of the pea seedling (*Pisum sativum*) showed that a concentration of 9.0 mg/l acts toxic (without more precise information) and that no effects could be observed below this concentration.

LC_{50} values (8 h) of 0.7 - 2.8 mg/l air were found in fumigation tests on the detrimental effect of acrylonitrile on the weevil, cockroach and cadelle (*Sitophilus sp.*, *Stegobiuim paniceum*, *Tenebrioides mauretanicus*). In tests with *Callosobruchus chinensis,* LC_{50} values (24 h) of 0.11, 0.13, 1.26 and 0.15 mg/l air were determined respectively for eggs (1 d), larvae (3rd stage), pupae (2 - 3 d) and adult animals (1 d).

Toxicological Aspect

Acrylonitrile is absorbed via the respiratory tract, the gastrointestinal tract and the skin. Following glutathione conjugation, it is excreted within 24 hours mostly with the urine primarily as mercapturic acid derivatives, thioglycolic acid and thiocyanate. Moreover, acrylonitrile or its epoxide can react with cell proteins and nucleic acids.

The LD_{50} values for oral uptake range from 25 mg/kg body weight to 186 mg/kg body weight. The LD_{50} values for invasive application (s.c., i.v., i.p.) lie in the same dosage range. LD_{50} values of 148 - 693 mg/kg body weight were determined after dermal application. LC_{50} values in the range of 300 - 900 mg/m^3 are specified for 4 hours inhalation. Acute intoxication is characterized by agitation, convulsions, paresis and paralysis, respiratory embarrassment until apnoea. Independent of the uptake route but depending on the dosage, acrylonitrile leads to glutathione depletion in the blood, liver, kidney, lung, brain and stomach, whereby it causes cell damage manifested in various degrees of organ alterations depending on the singly administered dose.

Acrylonitrile irritates the skin and mucous membranes. In the maximization test, acrylonitrile showed a sensitizing potential in guinea pigs.

Repeated uptake of acrylonitrile results in damage to the kidney, liver, gastrointestinal tract, central nervous system and adrenal gland. The respiratory tract is also affected from inhalation. With the application with drinking water, the NOEL for rats and dogs in the subchronic test lies at 8 mg/kg body weight. A NOEC cannot be derived for any species from the inhalation experiments (concentrations ≤ 234 mg/m^3). The LOEC is 58 mg/m^3 (6 hours daily, 57 exposures within 90 days).

A carcinogenic effect of acrylonitrile in the rat was detected in long-term studies with oral (drinking water and by gavage) and inhalative uptake. Increased incidences of tumors of the central nervous system, zymbal gland, the mamma and the forestomach are characteristic. The results of short-term carcinogenicity tests are inconsistent.

Acrylonitrile often shows a mutagenic potential in *in vitro* test systems. However, no mutagenic effect was observed in most *in vivo* genotoxicity tests. The more likely negative *in vivo* findings can be explained by the detoxification of the epoxide via a glutathione conjugation which is effective *in vivo*.

For the rat, a fetotoxic and teratogenic effect was determined in the maternally toxic dosage range. The oral acrylonitrile uptake of 10 mg/kg body weight for 60 days led to damage of the testis.

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Experiences at the workplace have shown that acrylonitrile first irritates the mucous membranes of the eyes and nose. Furthermore reported are nausea, vomiting, lower abdominal pain, diarrhea, jaundice, dizziness, dyspnea, coughing irritation, bronchitis and obstructive ventilation disturbances. More recent epidemiological studies do not indicate an increased risk of cancer from acrylonitrile exposure. In addition, no correlation could be found between the degree and length of exposure and the increased occurrence of prostatic cancer illnesses in workers exposed to acrylonitrile/dimethylformamide.

Recommendations

Ecotoxicology

The ecotoxicological effect profile of acrylonitrile can be estimated on the basis of the available studies.

Toxicology

Acrylonitrile has been comprehensively investigated. Because the present results allow a description of the toxicological effect profile, further studies are not considered to be a priority.