Evaluation Report on Industrial Chemicals

IKSR
CIPR
ICBR

Internationale Kommission zum Schutz des Rheins

Commission Internationale pour la Protection du Rhin

Internationale Commissie ter Bescherming van de Rijn

Report No. 202

Imprint

Publisher:
International Commission for the Protection of the Rhine (ICPR)
Kaiserin-Augusta-Anlagen 15, D 56068 Koblenz
P.O. box 20 02 53, D 56002 Koblenz
Telefone +49-(0)261-94252-0, Fax +49-(0)261-94252-52
E-mail: sekretariat@iksr.de
www.iksr.org

ISBN-Nr 978-3-941994-29-4

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1. Introduction

Industrial chemicals are substances used as components, additives or admixtures in industrial production processes. The industrial chemicals concerned by this report are organic compounds of xenobiotic origin, such as solvants, surfactants, flame retardants, adhesives and pigments. These substances may directly or, when passing through wastewater treatment plants, indirectly flow into surface waters. On the other hand, they may also be contained in products released into waters during their product life, recycling or disposal.

In its list of HPV chemical substances (***h****igh* ***p****roduction* ***v****olume*, substances, of which more than 1,000 tons are put in circulation per year), the OECD lists more than 4,500 substances[1], a major part of which belongs to the category of industrial chemicals.

Considering the high production volumes of these substances and the large number of production and location sites it is not unexpected that individual substances are detected in surface waters. Apart from the characteristics aimed at for their individual uses, may industrial chemicals also have an undesired environmental impact on sensitive water organisms. Therefore, for some chemicals, endocrine disrupting properties already have an effect in low concentrations of less than 1 µg/l. Some substances are also liable to impact the resources for drinking water production. Among the great number of substances, three substances figuring on the list of Rhine substances, diglyme, or bis(2-methoxyethyl), bisphenol A and nonylphenol and the groups of substances of flame retardants (organophosphates) and fluorosurfactants have been chosen as indicator substances. The following information is based on thee separately published substance data sheets on industrial chemicals: phosphorous organic flame retardants, fluorosurfactants (PFT) and diglyme, bisphoenol A and nonylphonol (NP).

2. Problem analysis

Diglyme is a solvant with a broad scope of industrial applications: organic synthesis, entrainer, additive in brake fluids or hydraulic fluids and dispersed dye, production of polyurethane coating, textile dye and as solvant in the semiconductor industry.

In the Rhine basin, the highest concentrations are measured in the lower part of the main river. The rare monitoring results from tributaries of the upper section of the main stream do not indicate any burden. On the other hand, the tributaries in the Rhine delta seem to be impacted by the main river and show higher diglyme concentrations. During the past years, and following emission reduction measures taken with respect to one decisive industrial discharger in 2006, the burden has been reduced in the upper section of the Upper Rhine.

The relevant IAWR target value used by drinking water works for diglyme in surface water bodies used is 1.0 µg/l[2]. Individual events in factories result in temporary peak burdens above this value.

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1 OECD Environment, Health and Safety Publications, Series on Testing and Assessment, No. 112, Paris 2009

2 IAWR, IAWD, RIWA: „Donau-, Maas- und Rhein-Memorandum 2008“, Köln, Wien und Werkendam, 2008

Bisphenol A (BPA) is a chemical base material which is, among others, used for the production of polycarbonate plastics for bottles and the inner coating of tins and beverage cans. Furthermore, bisphenol A is used in epoxy resins and in sealing and packaging materials, as antioxydant in plasticizers and as active agent in thermal paper.

So far, bisphenol A is supposed to have an endocrine disrupting effect on animals and man[3], which, due to recent findings, will be further investigated into[4].

Bisphenol A can adsorb to organic substances and is easily degradable under aerobic conditions. Compared to the tributaries, concentrations in the main stream of the Rhine are thus lower (<0.03 µg/l). Discharges of treated wastewater from industrial and municipal wastewater treatment plants are above all a burden for smaller surface water bodies in the Rhine catchment, where they at times are in excess of the IAWR target value of 0.1 µg/l applicable to xenobiotic organic substances impacting biological systems. The chronic PNEC-value for BPA is 1.6 µg/l[5]. It is underlined that monitoring data were only available for few monitoring stations in the Rhine catchment.

Nonylphenol was mainly used for the production of non-ionic surfactants, the nonylphenolethoxylates (NPEO). Since 2005, the use of nonylphenol and NPEO containing products has been strongly reduced in the EU and in Switzerland (Directive 2003/53/EC[6], ChemRRV[7]). In commercial dry cleaning business and in metal processing, Nonylphenol and NPEO may, since then, only be used in closed systems under surveillance, in which the cleaning liquids are being recycled or burnt. In textile and leather treatment, these substances may only be used for treatments not generating any NPE flowing into wastewater.

Nonylphenol is formed in wastewater treatment and in the environment due to microbial degradation of nonylphenolethoxylates. Nonylphenol is an endocrine disruptive agent toxic for reproduction[8] and is classified as priority hazardous substance according to the EU Water Framework Directive. The annual average environmental quality standard (EQS) for surface waters is 0.3 µg/l. Monitoring results above the annual average EQS are only regionally observed in surface water bodies in the Rhine catchment.

From the group of organophosphates often used as flame retardants, the substances tris(2-chlorethyl)phosphate (**TCEP**), tris(2-chlorisopropyl)phosphate (**TCPP**), tris(dichlorpropyl)phosphate (**TDCP**), tri-n-butylphosphat (**TnBP**), tri-iso-butylphosphat (**TiBP**) and tris(butoxyethyl)phosphat (**TBEP**) were chosen as indicator substances. These substances are used as softener with flame retardant effect in products containing polyurethane (e.g. in construction, textile, paper, furniture and automobile industry), in

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3 BfR. 2005: www.bfr.bund.de/cm/343/eine_neue_studie_zur_oestrogenen_wirkung_von_bisphenol_a.pdf

4 EFSA 2010 http://www.efsa.europa.eu/en/efsajournal/pub/1829.htm

5 EU RA Bisphenol A (2008). European Union Risk Assessment Report: Bisphenol A, Environment Addendum of April 2008

6 Directive 2003/53/EC of the European Parliament and of the Council of 18 June 2003 amending for the 26th time Council Directive 76/769/EEC relating to restrictions on the marketing and use of certain dangerous substances and preparations (nonylphenol, nonylphenol ethoxylate and cement)

7 Ordinance on the Reduction of Risks relating to the Use of Certain Particularly Dangerous Substances, Preparations and Articles (Chemical Risk Reduction Ordinance, ORRChem) of 18 May 2005 (Status as of 1 August 2011, SR 814.81)

8 Wilfried Bursch, „(Öko)toxikologische Bewertung von Daten zur Festlegung von Umweltqualitätsnormen zur Umsetzung der Richtlinie 76/464/EWG und der Wasserrahmenrichtlinie (WRRL) 2000/60/EG in Österreich“, Gutachten. Teil 1, im Auftrag des Bundesministeriums für Land-, Forstwirtschaft, Umwelt und Wasserwirtschaft, Wien *and*

7 www.oekotoxzentrum.ch/expertenservice/qualitaetskriterien/vorschlaege/index, last consulted 09.08.2012

adhesives, varnish, paint and coatings. Some compounds (e.g. TCEP, TBP) are suspected to give rise to cancer in human beings[9].

In the main stream of the Rhine, TECP and TCPP values in excess of the IAWR target value 0f 0.1 µg/l are monitored. TCPP values in excess of the IAWR value are also detected in some Rhine tributaries. Analysis of bank filtrate in Germany have equally resulted in TCPP and TBEP contents above the IAWR value. However, no contents in excess of the PNEC values have been detected. There does not yet exist any legally binding EQS for this group of substances.

Fluorosurfactants (PFT) are chemicals used in many applications, e.g. in non-stick coatings for frying pans, weather protection in garments, fire fighting foam or for paper refinement[10] In the EU, the use of perfluorooctanesulfonic acid (PFOS) has been restricted[11] [12]. However, the use of other compounds belonging to the group of fluorosurfactants and polyfluorinated surfactants is increasing. These restrictions do today not apply to certain applications, e.g. applications in photography, photo-lithography, paper production or galvanic processes. Furthermore, due to the Stockholm Convention[13], PFOS is today subject to worldwide restrictions.

At EU level, as at an international levelm efforts are made to replace PFOA and PFOS in production[14][15].

The proposal submitted by the EU Commission (see PFOS EQS dossier 2011) for a general environmental quality standard (P-AA-EQS) for PFOS is based on the environmental quality standard for fish consumption and for the protection of human health and has been set to 0.00065 µg/l [16]for the water phase. In many cases, the average concentrations measured in the Rhine and its tributaries are many times over these P-AA-EQS. For PFOA and PFOS the IAWR value has been set to 0.1 µg/l for each individual substance. In most cases, values in the Rhine and its tributaries are not in excess. Some maximum values monitored for individual PFOS are an exception. PFOS is also observed in groundwater or in groundwater recharged with river water and certain values are equal to or in excess of the IAWR value.

3. Analysis of pathways

Diglyme mainly originates from industrial production and cleaning processes and gets into water bodies together with wastewater. Presumably, the observed values in excess of the IAWR target value in the Rhine are due to insufficient industrial wastewater treatment in production or processing plants. So far, there is no ban on the use of diglyme in industrial applications and thus emissions into the wastewater pathway remain

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9 Umweltbundesamt Wien: Fact Sheet Trisphosphate; http://www.umweltbundesamt.at/fileadmin/site/umweltthemen/gesundheit/fact_sheets/Fact_Sheet_Trisphosphate.pdf

10 Umweltbundesamt Deutschland: Per- und Polyfluorierte Chemikalien. http://reach-info.de/kritische_eigenschaften.htm#PFCs

11 Official Journal of the European Communities (2010): COMMISSION REGULATION (EU) No 757/2010 of 24 August 2010.

12 Official Journal of the European Communities (2010): COMMISSION REGULATION (EU) No 757/2010 of 24 August 2010.

13 The Stockholm Convention (Stockholm Convention on Persistent Organic Pollutants) is a legally binding convention on interdiction and restriction measures for certain persistent organic pollutants (POPs). The convention entered into force 17 May 2004 and has so far been signed by 152 states. Convention website: www.pops.int

14 EPA 2010: http://www.epa.gov/opptintr/pfoa/pubs/stewardship/index.html

15 3M: http://www.3m-pressnet.de/3m/opencms/newsdata/industrie/Dyneon_ADONA_Emulgatorx.html

16 PFOS EQS Dossier 17.01.2011; WG-E (03/2011, drafted)

possible. In the EU, the use of this substance as emulsifying agent in cosmetics has however been restricted since 2004[17].

There are no data available on emissions originating from the use of diglyme containing products and resulting diglyme concentrations.

According to EU risk assessment[18], **bisphenol A** largely reaches surface waters via discharges of industrial and municipal wastewater treatment plants. This is above all due to the use of bisphenol A containing products. Additionally, bisphenol A is also directly discharged into surface waters via the wastewater arising from production, production works producing epoxy resins and thermal paper as well as from further plastic material processing.

In this connection, the uses of bisphenol A without polymerization are important. This particularly applies to the use of thermal paper and the disposal of thermal paper for paper recycling. Bisphenol A containing recycling paper is e.g. used for toilet paper and is thus discharged into wastewater.[19] [20]

Further sources are landfill leachate and ducts coated with epoxy and sealants. During monitoring campaigns carried out in Germany and Switzerland, bisphenol A concentrations above 0,1 µg/l were found in direct industrial discharges and in municipal wastewater.

After national legal restrictions concerning the handling of nonylphenol and nonylphenolethoxylates (NPEO) were introduced in the Rhine catchment, emissions into the water pathway considerably fell. Discharges into surface waters were mainly due to wastewater discharges and predominantly originated from washing water of imported textile goods treated with nonylphenolethoxylates.[21][22]

Diffuse inputs into surface water bodies may also originate from sewage sludge containing nonylphenol and from seepage water from landfill sites.

Flame retardants are mainly discharged into surface waters together with treated wastewater from municipal wastewater treatment plants. On the other hand, the inputs of TnBP are mainly due to direct discharges from industrial wastewater treatment plants and those of landfill sites. Since some of the substances concerned are volatile, they also spread via the air and rainwater.

Considerable **PFT** discharges originate from municipal wastewater treatment plants and are mainly due to indirect inputs of industrial and commercial origin. Additionally, there

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17 Annex 2 to the Commission Directive 2004/93/EC of 21 September 2004 amending Council Directive 76/768/EEC for the purpose of adapting its Annexes II and III to technical progress

18 EUR 20843 EN, European Union Risk Assessment Report, Volume 37: „4,4'-isopropylidenediphenol (bisphenol-A)“, Luxemburg, 2003 und EUR 24588 EN, European Union Risk Assessment Report, Environment Addendum of April 2008, “4,4'-isopropylidenediphenol (Bisphenol-A)”, Luxemburg, 2010

19 Gehring, M.J.; Vogel, D.; Bilitewski, B., 2009 „ Belastung von Recycling-Toilettenpapier aus verschiedenen Ländern mit 2,4,7,9-Tetramethyl-5-decin-4,7-diol (TMDD) und den endokrin aktiven Stoffen Bisphenol A, 4-*tert*-Octylphenol,technischem 4-Nonylphenol und Pentachlorphenol“ 4. Dresdner Tagung Endokrin aktive Stoffe in Abwasser, Klärschlamm und Abfällen. Beiträge zu Abfallwirtschaft und Altlasten, Schriftenreihe des Institutes für Abfallwirtschaft und Altlasten der TU Dresden, Bd. 61, Pirna: Forum für Abfallwirtschaft und Altlasten, 91-106.

20 EUR 20843 EN, European Union Risk Assessment Report, Volume 37: „4,4'-isopropylidenediphenol (bisphenol-A)“, Luxemburg, 2003 and EUR 24588 EN, European Union Risk Assessement Report, Environment Addendum of April 2008, “4,4'-isopropylidenediphenol (Bisphenol-A)”, Luxemburg, 2010

21 Hillenbrand, T.; Marscheider-Weidemann, F.; Strauch, M.; Heitmann, K.; Schaffrin, D., 2007, „Emissionsminderung für prioritäre und prioritäre gefährliche Stoffe der Wasserrahmenrichtlinie. Datenblatt Nonylphenol.“ Umweltbundesamt, Dessau

22 The Swedish Society for Nature Conservation (Naturskyddsföreningen) 2008, T-Shirts with a murky past, Stockholm

are direct discharges from industrial sites and landfill sites[23]. Further shares of less importance get into the water bodies via groundwater, surface runoff and combined sewer overflows. Due to poor biodegradability and sorption, spreading may also be caused by spreading and stocking of contaminated sewage sludge.

4. Possible measures

According to the substance, different measures may be taken in order to reduce the discharge of industrial chemicals into surface waters. Among others:

- Measures at the source (interdiction of substances, reduction of use, avoid emissions e.g. by using substitutes)
- Information of the public
- Decentralized measures (treatment of split wastewater streams)
- Centralized measures in wastewater treatment plants
- Adapt monitoring programmes
- Adapt assessment systems

Measures at the source

For persistent substances it must be examined in each individual case whether the dosage of these substances in processes relevant for water and wastewater (cleaning, rinsing) can be considerably reduced or whether these substances can be substituted by less problematic ones. Also, production and manufacturing processes could be adapted in order for less problematic substances to reach the wastewater.

The following measures at the source deserve to be indicated:

- Analysis and reduction of the use of diglyme, particularly in consumer products (varnish, pain, etc.) for which it cannot be excluded that they get into the wastewater.
- Based on the most recent findings, regular checking and limiting the use of bisphenol A in packaging material (polycarbonates, epoxy resins, PVC) and in thermal paper.
- Checking and limiting the use of the flame retardants considered in consumer products (products made of polyurethane, such as textiles, furniture, varnish, paint).

As a replacement for PFT/PFOS in galvanic processes, in fire fighting foam and other PFT/PFOS applications, the use of products without fluorine should be strived for, developed or further developed in order to increase the consumption of other perfluorinated or polyfluorinated compounds with similar characteristics. As an alternative to substitutes not containing fluorine, standards aimed at avoiding input at source might be considered (e.g. closed systems, closed loop circulation, wastewater split flow treatment, thermal disposal, etc.).

Instead of regulating individual substances (as is the case for PFOS), the marketing authorisation, use and application of the entire group of PFT substances or of per- or polyfluorinated chemicals should be considered as a whole.

The example of restricted handling of nonylphenolethoxylates in Europe proves that, if technologically comparable alternative products exist, environmental pollution due to a problematic substance can be considerably reduced.

However, nonylphenol is still detected at the outlet of wastewater treatment plants and is to a large extent due to NPEO-treated textiles. The restriction of or ban on importing NPEO-treated textiles could further reduce this emission source. Preferably, such an

[23] Indications are based on LANUV data concerning the North Rhine Westphalian Rhine catchment during 2007-2010.

interdiction should be introduced at EU level. A further restriction of use and compulsory labelling for products containing NP/NPEO could further reduce substance inputs into water bodies.

The input of these substances into the environment could be reduced, if sewage sludge in particular originating from sewage treatment plants with a considerable share of industrial wastewater was not spread in the environment but burnt.

Information of the public

Handling products containing the industrial chemicals mentioned or liable to release them during disposal is an important measure of good professional practice. Easily readable product labelling such as "keep away from wastewater" and indications concerning correct disposal could represent a positive contribution. Information of the public on the environmental impact of products may ideally achieve a change in consumer behaviour. Information, e.g. on NPEO containing textiles might increase the sale of textiles with eco-label. That would contribute to reducing the nonylphenol input into wastewater and water bodies.

Decentralized measures (treatment of split wastewater streams)

For industrial uses it is easier to treat specific pollutions in the individual wastewater split streams than to treat the combined wastewater in a municipal wastewater treatment plant. Emissions of persistent substances originating from industrial plants and flowing into on-site wastewater treatment plants or municipal wastewater plants and further into surface waters should normally be reduced on-site.

- For production sites this would mean that existing wastewater treatment plants should be optimized with a view to the specific pollutions (e.g. to eliminate PFT: Application of sorptive procedures or ion exchanger resins).
- In application plants (e.g. galvanic plants), decentralised installations for wastewater or wastewater split treatment or a separate disposal constitute effective measures, if emissions of the problematic substances cannot be avoided (at the source) by taking measures in the production process. This could be controlled by means of specific requirements concerning the discharge of wastewater from production and processing procedures.

Available measures should be defined as BAT (best available techniques) and be prescribed as obligatory standards. Before discharging process wastewater, bisphenol A contained should be reduced by means of appropriate measures. For diglyme, such measures should not only concern process water flows but also wastewater from exhaust air scrubbers. In plants using, producing, processing or disposing of products containing PFT, measures aimed at reducing input into wastewater in galvanic plants, such as regulated dosage, closed loop circulation, evaporators and activated carbon or ionic exchangers as a measure for treating (residual or partial) wastewater flows must be considered.

Centralized measures in wastewater treatment plants

In municipal wastewater treatment plants with an important share of industrial wastewater (from several plants) the cleaning capacity for industrial chemicals can be increased. This might be achieved by an additional treatment stage. According to the state of the art and depending on the group of substances, treatment procedures such as ozone treatment, activated carbon treatment or partial membrane processes applied to [24] [25] [26] may be applied.

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[24] Abegglen C., Siegrist H. 2012: Mikroverunreinigungen aus kommunalem Abwasser. Verfahren zur weitergehenden Elimination auf Kläranlagen. Bundesamt für Umwelt, Bern, Umwelt-Wissen Nr. 1214: 210S.

[25] TU Dortmund, 2008: Abschlussbericht an das MUNLV NRW. Untersuchungen zum Eintrag und zur Elimination von gefährlichen Stoffen in kommunalen Kläranlagen – Phase 3.

Centralized measures in municipal wastewater treatment plants reduce the loads of substances remaining in the wastewater together with the load of municipal origin after targeted decentralized measures in industrial and commercial plants They are particularly relevant for the flame retardants, bisphenol A and nonylphenol concerned by this report, as these substances resulting from consumer products are mainly found in domestic wastewater.

Expanding wastewater treatment plants could improve the protection of drinking water production and the ecological/chemical state of water bodies. The extension of wastewater treatment plants could be controlled if the Rhine bordering states formulated minimum emission requirements.

Adapt monitoring programmes

So far, no monitoring data were available for the sources and emission pathways of diglyme passing by wastewater treatment plants. This indicator substance or the group of persistent glycolethers should be added to the monitoring programmes.

There is no basic interdiction in all Rhine bordering countries to fertilize agricultural surfaces with sewage sludge from wastewater treatment plants. In countries where wastewater treatment sludge is spread in agriculture it should be recommended to monitor the contents of easily adsorbable substances (e.g. nonylphenol, bisphenol A, PFT) in sewage sludge.

Adapt assessment systems

If this is not yet the case, the endocrine disrupting properties of certain industrial chemicals (e.g. bisphenol A, nonylphenol) should be taken into account when deriving environmental quality standards (according to the rules of the Water Framework Directive).

5. Conclusion

Summary of the most efficient measures to be further elaborated and examined:

Measures at the source: in order to reduce the emissions of industrial chemicals, e.g. by a ban on the import of products with problematic constituents (e.g. NPOE containing textiles), by restricting use or substitution by more environmentally friendly substances.

Information of the public: An indication of the substances contained on the product itself, in particular with respect to its relevance for water bodies, may lead to reduced use and water pollution.

Decentralized measures: Reducing substance inputs to a minimum by optimizing processes relevant for wastewater and use of more advanced wastewater treatment procedures. Definition, publication and implementation of BAT (best available techniques) and their binding introduction into national or EU law[27].

[26] TU Dortmund, 2005: Abschlussbericht an das MUNLV NRW. Einsatz und Wirkungsweise oxidativer Verfahren zur Nachbehandlung von Abwasser aus kommunalen Kläranlagen, Teil 2a. Versuche zur Elimination relevanter Spurenschadstoffe.

[27] Within the framework of the European "Directive on industrial emissions" with its trans-media indications concerning the approval and surveillance of industrial plants, emission limit values corresponding to the best available technology (BAT) are to be determined within the environmental protection integrated into production. The BAT are materialized in extensive so-called BREF-documents (Best Available Technique Reference Documents) according to individual industrial sectors and published by the Joint Research Centre (http://eippcb.jrc.es/reference/). Emission scopes determined in the BAT conclusions are binding and must be respected.

Centralized measures

Centralized measures in municipal wastewater treatment plants can neither replace measures at the source in production processes nor decentralized measures in industrial and commercial plants. However, they may reduce the remnant industrial chemicals in pre-treated wastewater from industry and trade together with the load originating from households and other micro-pollutants of municipal origin. The experience made in wastewater treatment plants, in which further treatment procedures are used to remove micro-pollutions (e.g. ozonisation, activated carbon) must be collected and interpreted in order to be exploitable for future decisions.

Adapt monitoring programmes: Regular analysis of industrial chemicals at the outlet of wastewater treatment plants and in surface waters and of well adsorbed industrial chemicals in sewage sludge.

Adapt assessment systems: Consider the endocrine disrupting effects of certain industrial chemicals when establishing environmental quality standards.

Environmental quality standards must be defined according to specifications of the European Commission[28]. Take into account possible cumulative effects of substances / groups of substances with similar bandwidth of effects (e.g. endocrine disrupting effect) in addition to regulations, surveillance and assessment of individual substances.

[28] Common Implementation Strategy for the Water Framework Directive (2000/60/EC); Guidance Document No. 27 "Technical Guidance For Deriving Environmental Quality Standards"