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Melamine in the environment: a critical review of available information

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Abstract

Large numbers of chemicals and products thereof are used in our daily routine to ensure a good quality of life. Substances may even serve as raw materials to produce daily life articles including electronic hardware, green houses, cars etc. Melamine is used for a great variety of products, such as wood panels, paints, coatings, foam seating's and mattresses (as flame retardant), automotive brake tubes and hose. Based on the latest discussions, melamine has been concluded in the European Union to be classified as "carcinogenic to humans" (Carc. 2, H351) and "may cause damage to organs (urinary tract) through prolonged or repeated exposure" (STOT RE 2, H737). In addition, there is a self-classification of the European industry as suspect Repr. CAT2. Furthermore, the substance is considered a potential groundwater contaminant, due to a low log octanol carbon coefficient (K_{OC}). However, the underlying data require further evaluation. Therefore, a review of available information related to the presence of melamine (M) and cyromazine (CM, of which M is a transformation product) in surface, ground and drinking water was conducted and the data were critically analysed for plausibility. Available monitoring data are scarce and investigated for the Netherlands and Germany mainly. Measurements in the catchment area of the river Rhine and Maas revealed, that both substances (M, CM) were not ubiquitously found in surface, ground and drinking water in these countries. All in all, it can be concluded that the available monitoring data are considered as conclusive, and thus requiring further investigation before a clear relationship between emission and occurrence of melamine in the environment can be drawn.

Keywords Melamine, Cyromazine, Monitoring data, PMT

Introduction

In our modern world, large numbers of chemical substances are daily used to ensure a good quality of life. Those substances include pharmaceuticals, personal hygiene products, sunscreens, plant protection products, feed and food supplement as well as detergent and cleaning agents. Furthermore, chemicals are used as raw materials to produce daily life articles including electronic hardware, green houses, cars, etc. Melamine has a variety of industrial and domestic uses: it is used in paints and coatings in consumer and commercial products, in foam seating and bedding and it has applications as a plasticiser in concrete and in automobile brake tubes and hose. It is also included in thermally fused melamine paper and shelves, whiteboards and flakeboards, paints, sealants for mechanical, electrical and plumbing applications, and in inkjet ink. It is primarily used in the synthesis of melamine–formaldehyde resins for the manufacture of laminates, coatings, plastics, commercial filters, glues or adhesives, and moulding compounds (dishware and kitchenware) [1]. Furthermore, melamine–formaldehyde resins are used as coatings for seeds, plant protection products and fertilizers [2, 3]. The use of melamine–formaldehyde in shells for fragrance encapsulation such as fabric softeners or laundry detergents represents another application [4].

Melamine can be contained in fertilisers and algaecides but can also trimerize from calcium cyanamide fertilizers [5]; European Food Safety Authority [6]. In addition,

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melamine is the main metabolite/degradation product of cyromazine, which is used as insecticide and biocide [5–7]. Based on conclusions drawn from a misuse of melamine in adulterate milk, dairy products and in powdered infant formula in China and Africa, and the directly linked adverse effects in kidneys and urinary tracts of the exposed children, a re-assessment of the available data was performed in the European Union (EU) by the Member State Competent Authority of Germany (BAuA). Within the re-evaluation, especially the incidences and findings in humans were considered together with all available animal data for other endpoints, such as carcinogenicity. Consequently, a Harmonized Classification and Labeling Dossier (CLH dossier) was announced and submitted. Finally, the ECHA (European Chemicals Agency) Committee for Risk Assessment (RAC) [8] has proposed a harmonized classification and labelling at EU as "carcinogenic to Humans (Carc. 2, H351)" and "may cause damage to organs (urinary tract) through prolonged or repeated exposure (STOT RE 2, H373)". In addition, melamine may be considered as a potential groundwater contaminant following the criteria defined by the German Environmental Protection Agency [8, 9]. Although the substance has been detected in drinking water, the extent and relevance of such detections remains unclear and thus requires further elaboration [9, 10]. Notably, since the conclusions drawn on both persistency and mobility were based on screening information only, not considering eventually available higher tier data and assessments [11]. Therefore, in light of these existing uncertainties, the aim of this work was to review and evaluate available information related to the environmental occurrence and fate of melamine and, furthermore, identify and address potentially relevant data gaps. Based on the results, the question should be answered whether melamine is ubiquitous and widely detectable in the environment, or its occurrence is primarily related to point source emissions. It was decided to start with a focus on data related to Germany and the Netherlands, given the availability of data and the presence of melamine production sites.

Materials and methods

Data collection

For the purpose of this review, various data sources related to Germany and the Netherlands were evaluated for the presence of measured levels of melamine and cyromazine in the aquatic environment. This report focuses mainly on the catchment area of the rivers Rhine (Germany) and Maas (France, Belgium, the Netherlands). The aim of the data collection was to collect monitoring data of melamine and cyromazine in surface, ground and drinking water and possible associated background information, such as the location of the monitoring sites in Germany and the Netherlands. Furthermore, information on melamine concentration in soil, crops and vegetables and the release from use products into food and beverages are taken into account. The data collection was conducted from 22 February 2021 to 24 June 2021. The databases were checked for the keywords melamine and cyromazine in relation to monitoring data. A second search was conducted on 19 and 20 October for the keyword's melamine and cyanuric acid.

Publicly available data bases

Surface water and wastewater

Publicly available databases (see Additional file 1: Table S1) were searched for relevant information using the keywords "melamine" and "cyromazine" to gain information on the presence and the concentration of these substances in surface and wastewater.

The available measured concentrations from the International Commission for the Protection of the Rhine (ICPR), were subsequently used to calculate an average melamine concentration up- and downstream of industrial production sites at the Rhine. In particular, the monitoring data allow an analysis of the impact of melamine production and formulation sites as point sources on the melamine concentrations in the rivers Rhine and Maas.

Groundwater

Data on melamine concentrations in groundwater were available only to a limited extent. Monitoring data in Germany for melamine were only available from German federal state North Rhine-Westphalia [12] and some data are represented by one publication [13].

According to feedback of German water suppliers, anthropogenic influences on groundwater used for drinking water purposes is unlikely due to the geological structures at two locations. Another water supplier from the Netherlands pointed out that melamine is not monitored at stations, where groundwater is used for drinking water production.

Drinking water

The drinking water supply in Germany is managed by 5845 companies [14]. In the Netherlands only 10 companies are responsible for the water supply [15]. The available data from water suppliers were analyzed according to the scope of the review. In Germany and the Netherlands, 20 and 9 companies, respectively, were selected for this study (Additional file 2: Table S2). On request, some drinking water suppliers kindly provided available monitoring data on surface, ground and/or drinking water as well as the related background information (time and type of the sample, location of the sampling site, etc.).

Soil, crops and vegetables

To obtain monitoring data from soil, crops and vegetables associated with the use of biocides or plant protection products (PPP) containing cyromazine and/or fertilizers containing melamine and calcium cyanamide, relevant publicly accessible literature and databases were evaluated. In addition, websites of the Environmental Ministries of the German Federal States, the German Federal Institutions and relevant Dutch institutions (Additional file 2: Table S2) were screened for relevant data.

Releases of melamine from use of articles

The websites of the German Environmental Ministries were screened for publications and additional information on the migration of melamine from packaging material and tableware into food and beverages.

Emissions from production, formulation and waste

Production, use and waste data of melamine

Data related to production, use and waste of melamine and melamine containing products were kindly provided by the European Melamine Producers Association (EMPA). The melamine manufacturers provided relevant information on the emission of melamine to water and air, which can arise during the manufacturing processes as confidential information (i.e., data not shown). Concerning the production of intermediates and the manufacturing of articles, a worst-case emission scenario was calculated using the data and assuming that all steps including all sources of release take place within one plant. In particular, EMPA was asked for information related to:

1. Information on melamine releases during the production of melamine.
2. Additional information related to the manufacturing sites for melamine applications (also the production of intermediates).
3. Information on melamine releases during the use phase (downstream applications).
4. Information on melamine releases during the waste phase.
5. General monitoring data.

Production and use data of cyromazine

To obtain data of the production and use of products containing the active ingredient (AI) cyromazine, the ECHA website was screened for relevant information and literature. In addition, the reports on domestic sales and exports of crop protection products and their active ingredients published by German Federal institutions were evaluated. For the Netherlands, available information published by the Netherlands Food and Consumer Product Safety Authority under the Ministry of Agriculture, Nature and Food Quality on sales data for plant protection products and as far as available on biocides were screened.

Comparing data on emission and monitoring data on melamine in the environment

The annual freight of melamine present in the waterbodies of the rivers Maas and Rhine was estimated based on the discharge rate of water into the river and the concentration of melamine in the water body and the flow-rate of rivers.

In a next step, different scenarios were used to calculate the releases attributable to the production of melamine, the use as intermediate and the manufacturing of articles including melamine. For this purpose, data on emissions as indicated in the Safety Data Sheet (SDS) of melamine from the OCI Company were used. The release rates indicated are representative for one plant carrying out the respective activity. Since no data are available for the production of melamine in the SDS, the same release rate as for formulating and re-packing activities were used.

For each scenario, a different quantity of melamine producers and downstream users (e.g., manufacturers of melamine-containing articles) was assumed.

Based on these scenarios, the total release of melamine to water associated with the industrial point sources indicated above was calculated.

Results

Surface water monitoring sites

Most of the available surface water monitoring data refer to the rivers Rhine and Maas. However, for many other European rivers or even lakes, no such data were publicly available. Due to several monitoring stations installed along the river Rhine, numerous data were available from Switzerland, Germany and the Netherlands. Monitoring data for the Maas are available from several monitoring stations located along the course of the river.

The average measured melamine surface water concentrations for the river Rhine (2017) ranged from 0.30 to 3.23 µg/L at the locations Weil at the Rhein and Worms, respectively [16] (see Table 1). The average concentrations at the Maas (2020) ranged from 1.49 µg/L (Harinqvliet) to 20 µg/L (Roosteren) [17]. Furthermore, even in tributaries of the river Rhine higher melamine concentrations were measured at lowland rivers (i.e., 1.4 µg/L at river Main at Frankfurt, Main, Germany) compared to those rather upstream (i.e., 1.14 µg/L at river Aare,

Table 1 Summary table of the concentrations of melamine and cyromazine in the different water compartments (surface water, wastewater, groundwater and drinking water)

Substance	Water compartment	Location	Concentration [µg/L]	Years	Source
Melamine	Surface water	Weil am Rhein, Germany (Rhine)	0.30	2017	[16]
		Worms, Germany (Rhine)	3.23	2017	[16]
		Haringvliet, Netherlands (Maas)	1.49	2020	[17]
		Roosteren, Netherlands (Maas)	20.0	2020	[17]
		Frankfurt, Germany (Main)	1.4	2016	[16]
		Felseneau, Swiss (Aare)	0.14	2016	[16]
		Dinslaken, Germany (Emscher)	21.0	2019	[16]
	Wastewater	Augsburg, Germany	< 0.001	2017	[18]
	Groundwater	NWR, Germany	1.2	n.a.	[12]
		Near the river Thur, Swiss	0.06	2018	[26]
	Drinking water	Netherlands	> 1.0	n.a.	[10]
Cyromazine	Surface water	Netherlands	0.05	2019	[19]
		Germany	0.8	2019	[20]
	Wastewater	n.a.			
	Groundwater	Netherlands	0.05	2017	[27]
		Nord-Brabant and Limburg, Netherlands	< 0.03	n.a.	[27]
	Drinking water	n.a.			

Felsenau, Switzerland). In the river Emscher (Germany) maximum melamine concentrations of 21 µg/L were detected. However, it has to be mentioned that this river is characterised by a high proportion of municipal wastewater [17].

Publicly available databases

Surface and wastewater

The search for "melamine" in the publicly available Norman Empodat Database from 2017 to 2020 for measurements in surface and wastewater resulted in 1,004 hits (673 in Germany and 331 in the Netherlands), whereas only 1 hit was in fact related to wastewater in Germany (Augsburg, 2017), respectively. For wastewater, measured concentrations were below the limit of detection (LOD) of 0.001 µg/L [18]. 61 of the 673 measurements of surface water in Germany were below the LOQ of 0.025 µg/L. From 331 measurements in Dutch surface waters, 8 measurements were below the LOQ (ranging from $\leq$ 0.0005 µg/L). The detectable median concentrations were 0.31 and 1.14 µg/L for Germany and the Netherlands, respectively [18].

In an upstream/downstream comparison by the International Commission for the Protection of the Rhine (ICPR) [16] average melamine concentrations ranged from 0.30 to 0.55 µg/L (upstream) and from 0.86 to 3.23 µg/L (downstream), respectively. Melamine was frequently detected in German and Dutch surface waters, although it was not a ubiquitous substance.

Surface water monitoring data from the Netherlands on cyromazine indicated that the concentrations were below the maximum permissible risk (MTR) of 1.9 µg/L. In general, a decreasing trend for cyromazine concentrations in surface waters from 0.25 to 0.05 mg/L was observed in this country between the years 2006 and 2019 [19]. The surface water concentrations of melamine in Germany was constant during the observation period from 2015 to 2020, but increased from 0.5 µg/L to more than 0.8 µg/L during the period of 2017 to 2020 [20]. In the Netherlands, an overall decreasing trend can be observed. The average concentration of all available measurements in Dutch surface water decreased from above 1.8 µg/L in 2017 to less than 1.1 µg/L in 2020 [20].

Groundwater

The review revealed that the number of freely available ground water monitoring data on melamine is very limited. However, these data demonstrated that compared to 1,4-dioxane and perfluorinated substances [21–25] melamine is not ubiquitous in groundwater rather than being detected more locally. In fact, it was detected in some of the samples, whereas in others, it was not. The data from German federal state North Rhine-Westphalia [12] showed average melamine concentrations in some ground water bodies of 1.2 µg/L. On the other hand, more recent investigations did not detect any melamine above the LOD/LOQ (no specific value indicated) in the groundwater [10]. In Switzerland, melamine was detected in groundwater at individual monitoring sites in 2017 and

2018 as part of a pilot study on the screening of micropollutants ICPR [26]. Melamine was detected in groundwater near the river Thur in concentrations of 0.06 µg/L and downstream of Lake Thun in concentrations of 0.03 µg/L. At these sites, the proportion of river water infiltrate to groundwater is more than 60%. As the concentrations of melamine upstream of the estuary of the Rhine into Lake Constance and at the confluence of the Emme and Reuss rivers were below 0.015 µg/L, the ICPR [26] concludes, that melamine is likely to have entered the groundwater through the infiltration of river water at the locations mentioned above.

Measured groundwater concentrations for cyromazine were only available for the Netherlands (provinces of Nord-Brabant and Limburg) and the overall amount of data was very limited. These monitoring data revealed concentrations below 0.03 µg/L [27]. In another study, groundwater concentrations up to 0.05 µg/L were detected [27].

Drinking water

The amount of available monitoring data for melamine in drinking water is limited and only available for the Netherlands. In Germany melamine is not among the substances monitored regularly during drinking water production. According to monitoring data from Flanders (Belgium) and the Netherlands melamine was detected in 2 out of 12 drinking water samples indicating that this substance might be present in drinking water samples in concentrations > 1 µg/L (in 1 out of the 12 drinking water samples) [10].

For cyromazine, no data related to measured drinking water concentrations were identified for Germany and the Netherlands.

Soil, crops and vegetables monitoring data

The EFSA (European Food Safety Authority) [28] collected and summarized data on food and feed samples from different EU Member States including Germany. Melamine was detected in 96% of the 136 food samples but only in 5% of the 52 feed samples. The agency concluded that consumers might be exposed to melamine via food due to the use of cyromazine as pesticide and as veterinary drug [29].

Furthermore, due to use of calcium cyanamide fertilizer in conventional agriculture may result in the formation of the degradation products melamine and cyanuric acid [5]. Consequently, the analysis of melamine in fertilizers showed concentrations up to 7.3 mg/kg and high concentrations of cyanuric acid [5]. The same author concluded that the high concentrations of both transformation products were due to the high persistency in soil.

Based on the website of the German Federal Institution, more than 3100 German plant-based food products were analyzed for residues of cyromazine and melamine from 2013 to 2017. In none of the samples was cyromazine detected. Melamine residues were detected in 21% of the samples, with levels above 0.01 mg/kg [5]. Products from organic farming in particular showed high concentrations of 17.0 mg/kg in potatoes (2015). In addition, a study from China, cereals were tested for melamine. Melamine concentrations above 0.1 mg/kg were measured in less than 20% of the samples. Only 3 out of 557 crop samples contaminated more than 1 mg/kg melamine, with the highest level of 2.05 mg/kg in a wheat sample [30].

Melamine migration through the use of melamine-based products

The review of articles published by the Landeslabor Schleswig–Holstein [31] and the VerbraucherFenster Hessen [32] revealed that no significant migration of melamine from melamine formaldehyde resin (MFR) tableware occurs, when the equipment is used at temperatures below 70 °C. In another study, however, the amount of leached melamine ranged from < 0.03 to 49.0 ng/cm^2 and from 0.37 to 70.2 ng/cm^2 at water temperatures of 25 and 90–100 °C, respectively [33]. The authors also found out that acidic or methanolic water at 25 °C did not enhance extraction of melamine from the product. The study by Hanhi et al. tested a new method to measure the level of melamine migration in melamine-tableware products by HPLC method and the effect of the food-type on migration [34]. The study showed that although melamine migration occurred in all samples and acidic conditions had a significant influence, the levels were not higher than the European standard (125 µg/L).

Investigations from the German Federal Institute for Risk Assessment (Bundesinstitut für Risikobewertung, BfR) in 2020 showed an increase in melamine concentrations in food and drinks after repeated contact, which suggests that materials degrade by contact with hot liquids [35]. Furthermore, the median release for conventional MFR was 0.69 mg/L ranging from < LOQ to 8.37 mg/L and for bambooware the median release was 1.55 mg/L ranging from < LOQ to 20.7 mg/L [35]. The tolerable daily intake (TDI) for melamine was 0.2 mg/kg body weight per day [28]. Taking this TDI into account, it was concluded that the average melamine concentrations released from the products did not pose a human health risk to adults. Especially, since the specific migration limit of melamine from those products has been lowered from 30 to 2.5 mg/kg food [36].

Degradation/Formation processes of cyromazine and melamine

In both Germany and the Netherlands, cyromazine is authorized as an AI in biocidal products (BPs). The use in plant protection products (PPPs) is not approved in Germany. The substance likely enters the environment through these pesticide applications via soil, food and feed and surface run-offs [7, 37]. Several studies have indicated that melamine is the primary metabolite and degradation product of cyromazine [5, 7, 29] (Fig. 1).

Cyromazine is stable to hydrolysis and photolysis in aqueous solutions [29]. In soil, it has a low to moderate persistence under aerobic conditions. A geometric mean half-life in the soil through aerobic solid degradation of 37.89 days at 20 °C was calculated by the European Commission [39]. After 190 days a maximum melamine concentration of 36% was found in anaerobic soils, whereas under aerobic conditions, between 60% and 74.5% melamine were formed [39]. This indicates that the presence of oxygen favored the formation of melamine during the degradation of cyromazine.

Based on its Freundlich distribution coefficient (kfoc), which ranges from 40.2 to 1.784 mL/g, the adsorption potential of cyromazine varies depending on the soil type [29].

In soil, melamine may be considered as non-persistent or very persistent with half-life ranging from 46 to 211 days at 20 °C depending on the soil type [1, 29]. The European Commission (calculated a geometric mean half-life of melamine in aerobic soil ranging from 37.89 to 307.6 days, respectively, based on the literature used for the assessment [37, 39, 40].

Based on its kfoc which was reported to be between 54 and 423 mL/g it was assumed that melamine is mostly bound to the soil matrix [29]. Out of 100% cyromazine application < 12% melamine was found to be distributed to the receiving water.

However, in a worst-case scenario considering the application in the case of rainfall, a cyromazine loss of 23.7% due to run-off was concluded [7]. In water, cyromazine was considered as being persistent, while it was slowly partitioning from water to sediment compartment [29]. Accordingly, a half-life for rivers and ponds of 401 and 464 days, respectively, were reported [39]. However, ECHA [41] reported no unacceptable risk to the aquatic compartment (including surface water and sediment) due to cyromazine use in PPPs.

Emissions from production, formulation and waste

As this information was provided by the various stakeholders as confidential information, no details were provided within this manuscript.

Comparing data on emission and monitoring data on melamine in the environment

The calculated annual freight of melamine in waterbodies of the Rivers Maas and the Rhine ranges between 3.0 and 22.6 and 82,6 tons/year, respectively, depending on the calculation parameters (water discharge and melamine concentration) (see Additional file 3: Table S3).

For checking the plausibility of this result, an additional calculation was performed. The annual freight of melamine was calculated based on the average freight of melamine of 1.93 g/s [17] (at the location of Lobith). This resulted in an annual melamine freight of approximately 60.9 tons/year in the waterbody of the Rhine. Thus, the annual freight of melamine calculated on the basis of the average flow rate and melamine concentration was about 26% lower compared to the value calculated based on the average melamine freight.

Discussion

The analysis of surface water monitoring data of both the river Rhine and Maas revealed that melamine indeed is present in both rivers. Considering additional monitoring

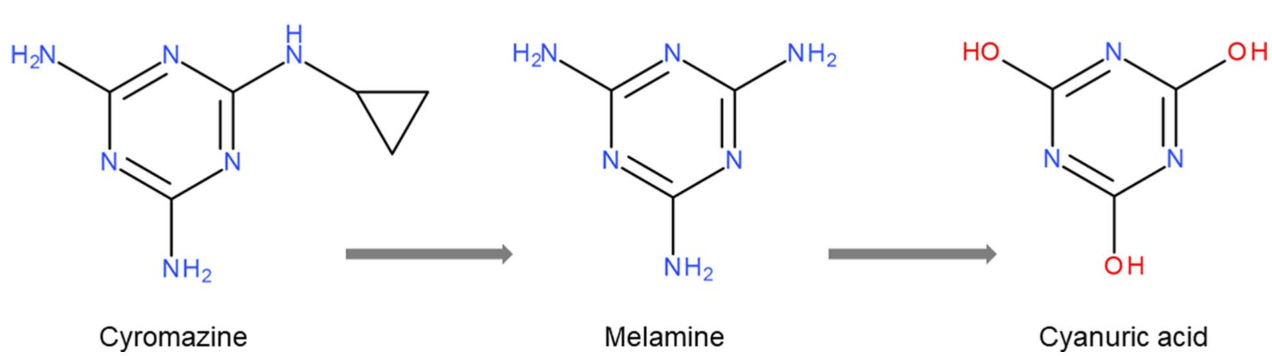

Fig. 1 Degradation pathway of cyromazine via melamine and cyanuric acid (according to [38])

data from the Norman Empodat database, it can be concluded that the entry path via wastewater seems to be rather low (i.e., below the LOD). However, it has to be acknowledged that the number of measurements is also rather low. In surface waters, melamine was not detected in all samples, but in approximately 90% of the samples above the LOQ, indicating its presence in the aquatic freshwater environment, although the concentrations were in the Rhine between 0.30 and 3.23 µg/L and in the Maas 1.49–20 µg/L.

In a study from the USA, melamine and cyanuric acid were measured in a river and a lake in New York State. Melamine was the most abundant compound in river water with concentrations between 0.017 and 3.650 µg/L [42]. It can be seen that the concentrations are in a similar range compared to the Rhine and the Maas. Unfortunately, it is not clear from the paper by Zhu et al. what the flow rate of the river was and at what time the measurements were carried out. However, the data suggest that the rivers in large American cities have similar melamine concentrations as in Europe. The presence of cyanuric acid in American surface waters (river 0.147 µg/L, lakes 1.068 µg/L und seawater 0.157 µg/L) can be explained by the direct discharge of wastewater. In the USA, cyanuric acid is used in dishwashing detergents, sanitizer and drinking water treatment products [42].

In summary, it can be concluded that there is a good database concerning monitoring data in surface water along the rivers Rhine and Maas. Based on these measurements, it was concluded that there is a correlation between industrial production sites and melamine concentration in surface water [43–45]. Nevertheless, no clear trend in the annual melamine surface water concentrations during the entire observation period (from 2015 to 2020) was identified. Overall, it should be noted that the analysis of trends based on annual averages does not provide a complete picture of the melamine concentrations in surface water. Melamine concentrations are subject to strong fluctuations throughout the year. There might be a correlation between the melamine concentrations and the flow-rate of the river indicating low melamine concentrations a high flow-rates.

The number of available melamine groundwater detections are scarce, and the results are not consistent across various water bodies, as it was present in some areas, whereas it was not in others (i.e., below LOQ/LOD). This indicates that the occurrence of melamine in some groundwater areas is likely to be more dependent on local conditions and possible point sources than on a general soil leachability issue. Due to the lack of sufficient groundwater monitoring data and relevant additional information, however, no reliable conclusions can be drawn regarding the correlation between monitored surface and groundwater concentrations of melamine.

Considering the presence of melamine in drinking water, it has to be emphasized that there are currently no freely available monitoring data available as this substance is not part of measurements campaigns carried out on regular base. Despite this fact, some authors already stated that based on its substance properties melamine belongs to PM (persistent and mobile) substances, which cannot be removed by conventional or advanced treatment processes, such as activated carbon [46]. Due to this assumption, it was concluded that melamine may reach drinking water and associated resources. However, as mentioned previously this assumption lacks a causality check and/or a proof of concept as the few monitoring data available are not conclusive at this stage. Furthermore, it has to be emphasized that melamine may be considered as persistent in water using a standardized OECD 309 lab test but was shown to be non-persistent under realistic field conditions with half-life of 39 days [47].

In a study from the USA, melamine and cyanuric acid were detected in tap water and bottled water. Melamine was found with a mean concentration of 0.033 µg/L in tap water and 0.075 µg/L in bottled water. Cyanuric acid was detected at a mean concentration of 0.515 µg/L in tap water and 0.075 µg/L in bottled water [42]. According to the authors, the occurrence of melamine in tap water could be due to the presence of indoor dust [48]. Since it is not clear from the article what material the drinking bottles are made of, it cannot be ruled out that melamine or cyanuric acid has dissolved from the bottles. Drinking water in the USA is usually purified with chlorine [49]. Cyanuric acid is commonly used as a drinking water treatment product to stabilize the chlorine [42]. It has been also reported that drinking water can contain up to 1.6–3.2 mg/L cyanuric acid form the use of disinfectants (sodium dichloroisocyanurate) [50]. This use can explain the high concentrations in drinking water from the tap and the bottle.

Cyromazine, was not measured in drinking water at all. In summary, there is a lack of data regarding melamine and cyromazine measured concentrations in drinking water.

The presence of melamine in agricultural soil is due to use of the plant protection product active ingredient (AI) cyromazine and the use of fertilizers. Whereas, melamine is a relevant transformation product of the AI, it is also freely available within the fertilizer. Based on the results from a soil leachability study, a horizontal transfer of both cyromazine and melamine through the soil column was considered negligible [7]. If degradation to melamine already took place within the soil, melamine is primarily bound to the soil and hence, does not present a dominant entry path for melamine into waterways. Thus, it can be assumed that the presence of melamine in crops and vegetables is linked to the agricultural use of cyromazine and the use of fertilizers rather than by an uptake of melamine leached from surface water to the agricultural area [30]. A study from Korea shows that melamine and cyanuric acid were measured in high concentrations in the sediment of a lake near Seoul. The mean concentration was 0.182 µg/g dw for melamine and 0.0262 µg/g dw for cyanuric acid [51]. In a study from Japan, melamine concentrations between 10 and 400 ng/g dw were measured in river sediment (OECD, 1998, Primary source no longer available) [51]. The high concentrations can be explained by the fact that melamine and cyanuric acid were added to fish feed to increase the protein content [52, 53].

Releases to the soil from production have not been reported and is considered as negligible. If releases occur, melamine would primarily be bound to the soil reducing the risk of introduction into waterways. However, a run-off from the agricultural field straight into nearby surface waters after heavy rain falls could not be excluded. This was also demonstrated in another study, where 23.7% cyromazine was observed in the run-off water [7]. It can be assumed that the soil does not present a dominant entry path for melamine into waterways including groundwater taking into account that melamine release from the degradation of cyromazine is negligible.

A comparison with the potential impact of agriculture is limited due to the lack of available monitoring data. In this context, another author refers to the decreasing and low concentrations of cyromazine in surface waters, indicating that agricultural use of cyromazine most likely does not significantly contribute to the observed melamine concentrations in Dutch surface waters [1]. Another major gap is the lack of data for surface water in remote areas.

The available data on the occurrence of melamine due to the use of cyromazine as PPP suggest that the presence of melamine in plant food can rather be attributed to environmental contamination or residues from fertilizers and disinfectants than to the use of cyromazine as PPP [5, 54]. Cyromazine is commonly added to animal feed in concentrations up to 0.5 mg/kg to control the hatching from flies in the manure [55, 56]. However, data indicate that agricultural activities (manure/slurry treatment and veterinary purposes) might contribute to the occurrence of melamine in food and feed and hence, to melamine background exposure. Studies on consumer exposure to melamine indicate that consumers are exposed to low levels of melamine (migration from food contact materials and from feed ingredients). Data evaluated suggest that melamine can leach from melamine resin products, such as tableware. The rate increases with water temperature but seems to be not affected by acidity. This suggests that melamine resin products can contribute to releases into the environment, but only at a low emission rate. However, the available data did not allow for an assessment of specific quantities or shares.

Waste from melamine production is mainly incinerated, which leads to the thermic destruction of melamine. However, no detailed information on releases regarding waste from the manufacturing of intermediates, mixtures and articles was available but it is suggested to be also incinerated. Concerning professional and consumer use, the contribution to waste is considered negligible as products should typically be incinerated and not disposed of in landfills. However, releases from existing landfills may be relevant as they may even be connected to ground water resources [57–59].

In conclusion, quantified figures regarding releases of melamine into the environment can only be established for releases from the production of melamine, its use in the manufacturing of articles.

Although a correlation between releases from industrial point sources and the concentrations of melamine in surface water has been identified, the presence of melamine in surface water cannot exclusively be ascribed to a specific segment of the production and manufacturing chain. Further research should, therefore, also focus on other possible emission pathways of melamine to the environment.

However, when interpreting these shares, it must be kept in mind that no full picture including all emissions of melamine into the environment rather than a proportionate allocation of melamine emissions based on known (and assumed) emissions, i.e., a relative comparison of known sources and their (assumed) emissions is possible. Furthermore, it should be noted that the releases from the production of intermediates and manufacturing of articles using melamine might be overestimated as these are solely based on worst-case releases presented within the SDS for melamine and data submitted by EMPA members within the questionnaires.

Other contributions to melamine in the environment cannot be calculated or estimated due to the data gaps identified above (contributions resulting from the use of cyromazine) or as they were not the focus of this assessment (contribution from cyanamide containing fertilizers).

Based on the data presented in this report, the main contributions to surface water resulted from the production of melamine, intermediates and from the manufacture of melamine-containing products, while the significance of contributions from other sources (e.g., waste, landfill) to the release of melamine to water remains unclear.

This is further substantiated by the available monitoring data, which shows elevated melamine concentrations downstream of industrial point sources. In a study from China, wastewater from 37 production plants was analysed for its melamine content. Melamine was measured in only 9 samples with a content of 22–100 µg/L [30]. Therefore, a correlation between discharges of industrial point sources and the concentrations of melamine in surface water may be plausible. However, significant concentrations are already detected upstream of such point sources, indicating the presence of other sources.

Hence, while a connection between releases from industrial point sources and the concentrations of melamine in surface water has been identified, the presence of melamine in surface water and the environment as a whole may not exclusively be allocated to the production of melamine, the production of intermediates and the manufacturing of articles using melamine. Further research on sources and pathways of melamine to the environment should, therefore, also focus on other possible sources, such as:

i) The degradation/metabolization of melamine from cyromazine resulting from its use as PPP and biocide and the emission to surface water via the feed and food chain and organic slurry.
ii) Potential releases of melamine from the use of cyanamide-containing fertilizers.
iii) Emissions from consumer uses such as tableware made from melamine–formaldehyde–resin.
iv) Emissions from the degradation of incapsulated fragrances or.
v) Emissions from waste.

Regarding the question whether melamine in the environment is ubiquitous and widely dispersive detectable or primarily occurs in direct relation to point sources, the following can be concluded.

As regards surface water, data are mainly available for monitoring stations related to the rivers Rhine and Maas. The data indicate that melamine concentrations at these locations frequently exceed the ERM target value of 1 µg/L and that higher melamine concentrations can be observed downstream of industrial point sources. Thus, the available data suggest a relationship between releases from industrial point sources and the measured concentrations of melamine in surface water. However, high melamine concentrations can also be observed in surface water, where no discharge of melamine is known. In the river Emscher (Germany) are high concentrations of melamine (max. value of 21 µg/L) detected. The river is characterised by a high proportion of wastewater, but there is no known industrial discharger of melamine into the Emscher [17, 21].

The available data also show that melamine is not detected in all surface water samples in the rivers Rhine and Maas above the corresponding LODs. It can, therefore, be concluded that melamine is not a ubiquitous substance in surface waters in Germany and the Netherlands.

Monitoring data for melamine in groundwater are scarce. The available data demonstrate that the presence of melamine in groundwater depends on local conditions (such as infiltration rates or the presence of point sources). Therefore, it is concluded that melamine is not ubiquitously found in ground water. Due to existing data gaps, no reliable conclusion can be drawn regarding the correlation between monitored surface and groundwater concentrations of melamine.

The rather large number of melamine detections in surface water did not comply with the low detection rate in groundwater (GW) and drinking water (DW), although it has to be acknowledged that the data from latter two are rather rare (i.e., 1 out of 12 for DW). In areas with high river water infiltration rates, detection of melamine in such filtrates (RWF) occur, but more on a local rather than on a general basis. The local occurrence in RWFs depends also on the melamine concentrations present in the surface water and as the concentrations may increase during the course of the river, it may result in exceedance of any threshold at the lower end of larger rivers (i.e., river Rhine: the Netherlands), rather than at the upper or middle region (i.e., Switzerland, Germany). However, river water infiltrations often lead to rather constant water flow from the river to the well. The associated soil, therefore, may be considered as fully saturated, which means that both physical and chemical absorption of substances may be limited. Furthermore, in case of high flow rates in combination with short distances (i.e., 1–10 m), the biodegradation does not play a relevant role. This result in the detection of substances such as caffeine typically not being considered as persistent or a substance of low absorption [8, 9, 11, 60, 61]. On the other hand, substances such as long-chain perfluoroalkyl carboxylic acids (PFOAs) considered as highly absorptive (log Koc of > 4) [21–23], may end up in groundwater, river filtrates and associated drinking water resources if they (a) are particle bound and/or (b) are highly persistent (i.e., half-life of several decades) so that they may travel through the horizontal and/or the vertical soil layer, respectively [21–23, 62].

Taking the available information into account, it remains questionable whether melamine is an abundant potential groundwater contaminant or whether the individual detections are due to high local emission rates in combination with high local river-water infiltrations, thus requiring further elaboration and research. If the additional data indicate that local sources are the main driver for melamine detections in groundwater further site-specific emission reduction are considered necessary.

Abbreviations

AI	Active ingredient
BAuA	Member State Competent Authority of Germany (Bundesanstalt für Arbeitsschutz und Arbeitsmedizin)
BfR	German Federal Institute for Risk Assessment (Bundesinstitut für Risikobewertung)
BPs	Biocidal products
CLH	Classification and labeling
CM	Cyromazine
DW	Drinking water
ECHA	European chemicals agency
EFSA	European Food Safety Authority
EMPA	European Melamine Producers Association
EU	European Union
GW	Groundwater
ICPR	International Commission for the Protection of the Rhine
Kfoc	Freundlich distribution coefficient
Koc	Octanol carbon coefficient
LOD	Limit of detection
LOQ	Limit of quantification
M	Melamine
MFR	Melamine formaldehyde resin
OECD	Organization for Economic Co-operation and Development
PFOA	Perfluoroalkyl carboxylic acids
PM	Persistent and mobile
PPP	Plant protection products
RAC	Risk assessment committee
RWF	River water filtration
SDS	Safety data sheet
TDI	Tolerable daily intake

Supplementary Information

The online version contains supplementary material available at https://doi.org/10.1186/s12302-022-00707-y.

Additional file 1: Table S1. List of used databases and additional sources.

Additional file 2: Table S2. Identified and contacted water suppliers in Germany and the Netherlands.

Additional file 3: Table S3. Calculated annual freight of melamine present in the Maas and in the Rhine based on the discharge and melamine concentration in the rivers.

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Author contributions

LHL and SP were involved in the conceptual framework and the writing of the manuscript. All other authors reviewed and provided comments on the manuscript. IR was the project lead. All authors read and approved the final manuscript.

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Availability of data and materials

All data used are either publicly available through published articles or available through the Ramboll report entitled "Melamine in the environment", issued on 02.02.2022 on behalf of EMPA.

Declarations

Ethics approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

Competing interests

All authors are employed by BASF SE, a producer of melamine.

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