High concentrations of hexamethoxymethylmelamine (HMMM) in selected surface waters in southern Hesse

Sven Eberhard (svn.eberhard@gmail.com), Sabina Foht (sabina.foht@gmx.de),
Theodoros Potouridis (Potouridis@iau.uni-frankfurt.de),
Wilhelm Püttmann (Puettmann@iau.uni-frankfurt.de)
Working Group „Environmental Analysis“, Goethe University Frankfurt a. M.

Abstract
Hexamethoxymethylmelamine (HMMM) is a monomer of a melamine resin. It is used as a crosslinker in thermoset coatings. High concentrations up to 6.16 µg/L were found in six Hessian river systems, while water samples from storm water retention basins and artificial stagnant waters (StWs), e.g. excavated lakes or old gravel quarries, showed maximal concentrations of 2.29 and 3.49 µg/L, respectively. StWs have to be supplied by a watercourse and not via rain or ground water to contain HMMM. One influent of anartificial stagnant water contained up to 1.6 µg/L of HMMM. The data indicate that contamination of aqueous systems results preferentially from surface run off water and industrial waste water.

Introduction
HMMM is a monomer used as crosslinker in thermoset coatings or as an automotive paint finisher (figure 1)[1]. With its six methoxymethyl side chains, HMMM can create ether bonds with a certain material surface or with itself, leading to irreversible self-condensation. The latter is catalyzed by using acidic conditions with a self-polymerization rate maximum at pH 1.22. However, below pH 1 and above pH 6, the monomer remains stable. The polymerization can be hindered by using methanol as solvent for the monomer, since it is the elimination product of the polymerization [2].

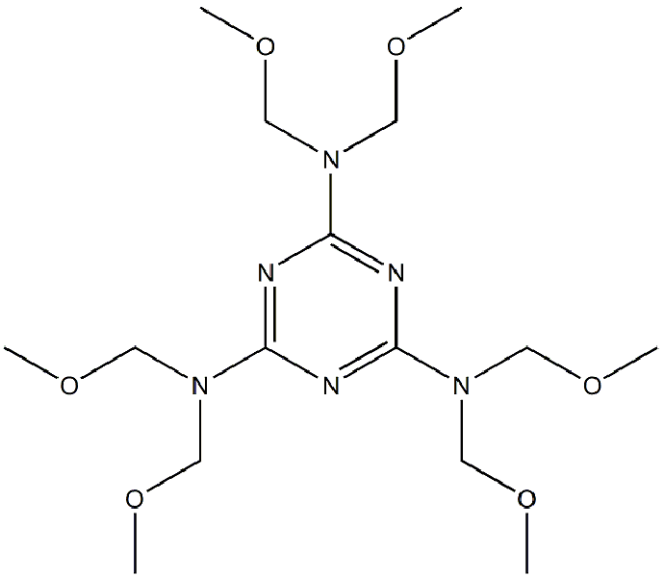

Figure 1: Molecular structure of HMMM

HMMM was firstly detected in natural aquatic systems by Bobeldijk et al. [3]. Ecotoxicological data suggest that HMMM is a rather non-toxic substance with a NOEC of 320 mg/L. In Daphnia magna, no mortality was found after an exposition time of 48 hours [1]. Yet, further tests with D. magna demonstrated that HMMM can enhance the toxicity of 3-cyclohexyl-1,1-dimethylurea [4]. Therefore, ecotoxicological effects in surface waters due to unpredictable combinatory effects of HMMM with other pollutants have to be considered. The half life of HMMM at pH 7 is 67 days and biodegradation of 23 % of the substance takes 28 days [1]. These data suggest a rather stable behavior in the aqueous phase. To the best of our knowledge, there are no data published concerning the behavior or degradation of HMMM in sewage treatment plants (STPs). However, it is possible to remove HMMM from water via active carbon filters [3].

To evaluate the distribution of HMMM in natural watercourses, its content in water samples of six river systems in the south of Hesse [Weschnitz (We), Modau (Mo) & Sandbach (Sa), Schwarzbach (Sw) & Landgraben (La), Main (Mn), Nidda (Ni), and Kinzig (Ki)] was determined. Additionally, quantification in samples of nine storm water retention basins (SRB), eight stagnant waters (StW), and one of the stagnant water influents (IN) was performed.

Materials and Methods
Sampling
Forty-four river water samples were collected. Sample spots were numbered in a downstream manner along the river course. The rivers and river systems Schwarzbach & Landgraben, Modau & Sandbach, and Weschnitz are located in a geographic region with an agricultural imprint, called Hessian Ried, while the Main passes three larger cities on its sampled course (Hanau, Offenbach, and Frankfurt am Main), including two industrial parks (Fechenheim between Mn2 and Mn3 and Höchst between Mn5 and Mn6).

Landgraben and Schwarzbach confluence prior to Sw3. One sample was taken at the Apfelbach (Sw1), which is a contributing stream to the Schwarzbach, previous to Sw2. The Modau splits up into Modau and Sandbach subsequent to Mo1. The site Sa2 belongs to the Lohrreingraben, which connects Modau and Sandbach. The Weschnitz splits up into the old and the new Weschnitz between We1 and We4; separate samples were collected from these two streams (We2 and We3, respectively). The only difference of these two streams is a sewage treatment plant, discharging sewage

water into the new Weschnitz. Throughout its sampled course, the two major contributing streams of the Main are the Kinzig between Mn1 and Mn2 and the Nidda between Mn5 and Mn6. Ki4 represents water of a dammed lake being part of river's course.

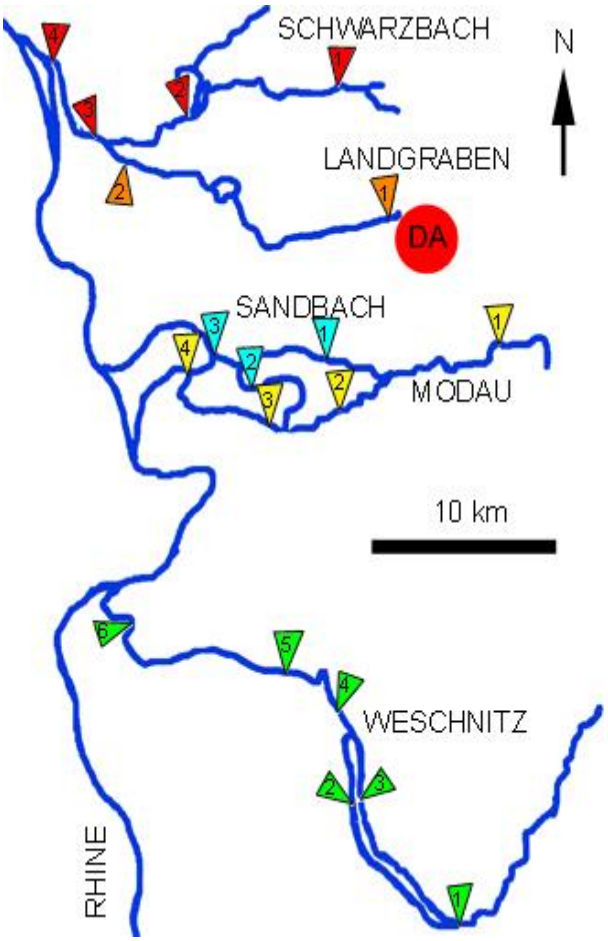

Figure 2: Geographical overview of the river systems in the Hessian Ried
Triangles Schwarzbach: red; Landgraben: orange; Sandbach: turquois; Modau: yellow; Weschnitz: green;
Circle The city of Darmstadt

In Frankfurt am Main, 48 samples were collected from selected SRBs, StWs, and one IN. Samples were taken over a time period of seven and nine months from IN1 and StW1, respectively. StW1 is an artificial pond that is further used as a storm water retention basin. It is fed by IN1, which solely contains surface runoff water of a new housing area. Besides StW1, only StW2 has an inflow, while StW3 to StW8 contain ground- and rainwater.

Analysis

Previous to the extraction via solid phase extraction (SPE), the water samples were filtered using cellulose Rotilabo®-folded filters, type 113P (Carl Roth GmbH + Co KG, Germany), which were extracted with dichloromethane before use. Samples were then extracted using Bond Elut PPL cartridges (1 ml, Agilent Technologies, USA) that were conditioned using 1 ml methanol and 1 ml of a 1:1 mixture of methanol and acetone, consecutively. The SPE was performed with a mean extraction rate of 2.08 – 2.38 ml/min. For the elution of the substances, the cartridges were filled once again with the solution of methanol and acetone (1:1). After removing the solvent by evaporation, the residue was resolved in methanol and analyzed by gas chromatography-quadrupole mass spectrometry using a Trace GC Ultra coupled with a DSQ II system (ThermoFisher Scientific, Germany). Sample injections were carried out in splitless mode. Mass fragmentation was performed using electron impact ionization (EI) at 70 eV and an ion source temperature of 220 °C. HMMM can analytically be identified by its primary ion 207 and the qualifier ions 163, 177, 267, 343, and 390. The analytes were quantified by using an external standard of HMMM (purity: >98 %, TCI Europe N.V., Belgium). The limit of detection (LOD) was determined at 0.07 µg/L, the limit of quantification (LOQ) was estimated at 0.21 µg/L.

Table 1: Concentrations of HMMM in river water
Mn = Main, Ni = Nidda, Ki = Kinzig, We = Weschnitz, Mo = Modau, Sa = Sandbach, Sw = Schwarzbach, La = Landgraben;
Sample spots are numbered downstream the respective river; Sa2 depicts a connection between Mo and Sa

Sample spot	Number of samples	c [µg/L]	Sample spot	Number of samples	c [µg/L]
Mn1	1	<LOQ	We 1	1	<LOD
Mn2	1	<LOQ	We 2	1	<LOD
Mn3	1	5.83	We 3	1	<LOQ
Mn4	1	4.07	We 4	1	<LOQ
Mn5	1	4.06	We 5	1	<LOQ
Mn6	1	0.72	We 6	1	0.30
Mn7	1	1.91	Mo 1	1	<LOD
Ni1	1	<LOD	Mo 2	1	0.26
Ni2	1	<LOD	Mo 3	1	0.26
Ni3	1	<LOD	Mo 4	1	0.24
Ni4	1	<LOD	Sa 1	1	<LOQ
Ni5	1	<LOD	Sa 2	1	0.55
Ni6	1	<LOQ	Sa 3	1	<LOQ
Ni7	1	<LOQ	Sw 1	1	<LOD
Ni8	1	<LOQ	Sw 2	1	0.26
Ki1	1	<LOD	Sw 3	1	0.29
Ki2	1	1.78	Sw 4	1	0.37
Ki3	2	0.91 / 1.50	La 1	1	0.69
Ki4	1	1.01	La 2	1	0.47
Ki5	1	0.75			
Ki6	1	2.48			
Ki7	1	1.58			
Ki8	1	6.16			
Ki9	1	2.09			
Ki10	1	1.66			

Results and Discussion

River water

In the water samples from rivers of the Hessian Ried, concentrations of HMMM ranged between 0.24 and 0.69 µg/L with a median of 0.30 µg/L (10 positive values). For the Modau, concentrations rise significantly between sampling locations Mo1 and Mo2 (Table 1, Figure 4). Between these sites, three STPs with a mixed sewer system discharge their waste water into the river. The concentration remains further downstream on a stable level. In the Sandbach, HMMM was not detected above the LOQ. Interestingly, the connection between Sandbach and Modau, represented by sampling spot Sa2, showed the highest concentration measured in the river system of Modau and Sandbach. However, it might be influenced by the low water level of this trench. The highest value in the Hessian Ried was found in La1 (0.69 µg/L). Nevertheless, the HMMM concentration decreased during the course of the Landgraben. In the Schwarzbach, concentrations increased from <LOD in Sw1 to 0.26 µg/L in Sw2. Hereafter, the concentrations keep rising downstream with a moderate gradient to a concentration of 0.37 µg/L (Sw4). A similar trend on a by far lower level has been detected in the Weschnitz. The HMMM concentrations in water samples of Main, Nidda, and Kinzig (Table 1, Figure 3) varied between 0.72 µg/L (Mn6) and 6.16 µg/L (Ki6) with a median of 1.78 µg/L (15 positive values). In the Main, a strong concentration increase between Mn2 and Mn3 has been detected. In this section, the effluent of the STP of the industrial park Fechenheim is discharged into the river Main. Amongst others, one melamine resin producer is situated in this industrial park. Subsequent to the influx of the Nidda into the Main, the concentrations found in the Main samples decreased. The Nidda was found to contain only small amounts of HMMM below the LOQ subsequent to Ni5. Thus, the decrease of the concentration in Main can be explained as a result of dilution. In the Kinzig, most values ranged between one and two micrograms per liter. Only at Ki6 a very high concentration of 6.16 µg/L was found. However, no contamination source could be identified as origin for this high level of pollution. However, taking the results of all river water samples into account, not all STP-effluent are sources of HMMM in the surface water.

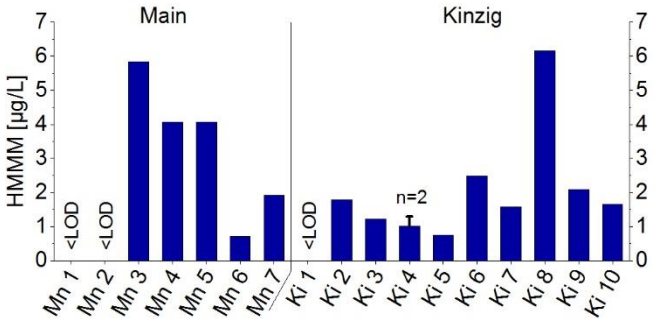

Figure 3: Concentrations of HMMM in Main and Kinzig

Storm water retention basins and stagnant waters

IN1 and StW1 contained HMMM in six and eight samples, respectively. Concentrations in the samples of IN1 varied from <LOD to 1.60 µg/L with a median of 1.47 µg/L (5 positive values). In StW1, concentrations ranged between <LOD and 3.49 µg/L with a median of 2.34 µg/L (8 positive values). However, in the remaining StWs, HMMM was only found in one of ten samples (Table 2, Figure 5). Interestingly, the substance was only detected in StWs that have an inflow HMMM was also detected up to 2.3 µg/L in four of nine SRBs. The large geographic distribution of the SRBs and the sampling during different rain events could be the reason for the high variety of the HMMM concentrations in the SRBs.

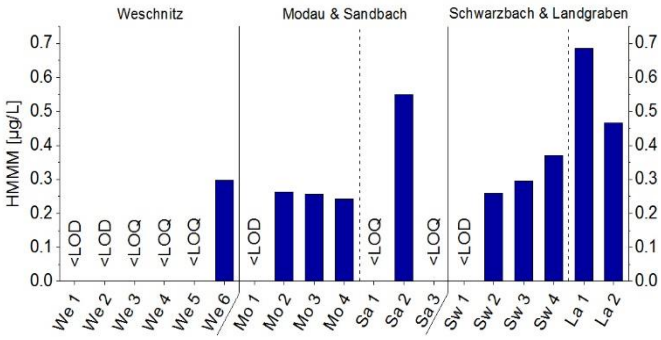

Figure 4: Measured concentrations in the rivers of the rural region Hessian Ried

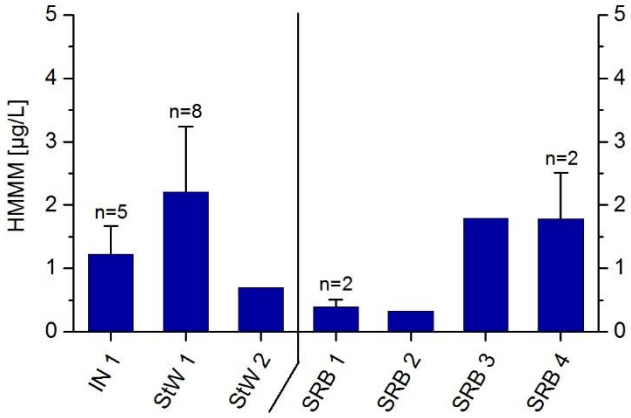

Figure 5: (Mean) concentrations and standard deviations of HMMM in the influent of StW1 (IN), stagnant waters (StW), and storm water retention basins (SRB)

Table 2: Min, max, and mean values of HMMM in one influent (IN), stagnant waters (StW), and storm water retention basins (SRB). IN1 belongs to StW1.

Sample	Number of samples	>LOD	>LOQ	min	max	mean
IN 1	7	6	5	0.68	1.60	1.23
StW 1	9	8	8	0.91	3.49	2.20
StW 2	1	1	1	0.70	0.70	0.70
StW 3	1	0	0	-	-	-
StW 4	1	0	0	-	-	-
StW 5	1	0	0	-	-	-
StW 6	2	0	0	-	-	-
StW 7	2	0	0	-	-	-
StW 8	2	0	0	-	-	-
SRB 1	5	2	2	0.40	0.33	0.33
SRB 2	1	1	1	0.33	0.95	0.80
SRB 3	1	1	1	1.79	0.35	0.35
SRB 4	2	2	2	1.78	0.15	0.15
SRB 5	4	1	0	-	-	-
SRB 6	5	1	0	-	-	-
SRB 7	2	1	0	-	-	-
SRB 8	1	1	0	-	-	-
SRB 9	1	0	0	-	-	-
total	48	21	20	0.33	3.49	0.82

Conclusion

HMMM has been detected at high concentrations in surface water of the Lower Main and the Hessian Ried. The data obtained from the river water samples indicate that the compound reaches the aquatic systems preferentially through the effluents of STPs. In the City of Frankfurt am Main surface runoff water represents an additional source. Until now it could not be clarified whether HMMM reaches the sewage system by municipal waste water or industrial wastewater from indirect dischargers. Further research on combinatory ecotoxicological effects of HMMM together with other compounds should be conducted considering the results obtained from a previous study of De Hoogh et al. [4].

Literature

[1] HMMM Coalition (2004). Final Submission for Hexamethoxymethylmelamine (pp. 1–11).

[2] Snyder & Vuk (1992). Self-condensation of aqueous hexa (methoxymethyl) melamine: Effects of concentration, pH, and alcohol content. J. Appl. Polym. Sci. 46, 1301–1306.

[3] Bobeldijk, Stoks, Vissers, Emke, van Leerdam, Muilwijk, Berbee, & Noij (2002). Surface and wastewater quality monitoring: combination of liquid chromatography with (geno)toxicity detection, diode array detection and tandem mass spectrometry for identification of pollutants. J. Chromatogr. A 970(1-2), 167–181.

[4] De Hoogh, Wagenvoort, Jonker, Van Leerdam, & Hogenboom (2006). HPLC-DAD and Q-TOF MS techniques identify cause of Daphnia biomonitor alarms in the River Meuse. Environ. Sci. Technol. 40(8), 2678–2685.

Korrespondenzadresse

Sven Eberhard
J.W. Goethe Universität Frankfurt am Main
Institut für Atmosphäre und Umwelt
AG Umweltanalytik (Prof. Wilhelm Püttmann)
Altenhöferallee 1
60438 Frankfurt/ Main