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Nitrosamines released from rubber crumb

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Rapport in het kort

Nitrosaminen in rubbergranulaat

Het RIVM heeft op verzoek van en in samenwerking met de Hulpverleningsdienst Gelderland Midden (HGM) luchtmetingen gedaan boven vier kunstgrasvoetbalvelden in Arnhem. Deze kunstgrasvelden zijn ingestrooid met rubbergranulaat. Het doel van de metingen was om na te gaan of uit de rubberkorrels kankerverwekkende nitrosaminen kunnen vrijkomen, die een gezondheidsrisico zouden kunnen zijn voor sporters. Het RIVM heeft op twee hoogten boven verschillende sportvelden luchtmetingen verricht. In geen van deze metingen konden nitrosaminen in de lucht boven het veld worden aangetoond. Uit aanvullend materiaalonderzoek onder laboratoriumomstandigheden bleek dat nitrosaminen slechts in geringe mate uit rubbergranulaat zijn vrij te maken. Op basis van deze bevindingen concludeert het RIVM dat nitrosaminen geen gezondheidsrisico's vormen voor de gebruikers van de sportvelden.

Abstract

Nitrosamines released from rubber crumb

At the request of Hulpverleningsdienst Gelderland Midden (HGM, the Gelderland regional fire, rescue and health service), RIVM (National Institute for Public Health and the Environment) worked with this service to sample the air above four artificial football pitches in Arnhem containing rubber crumb. The objective of the measurements was to determine if the rubber crumb could release carcinogenic nitrosamines which could pose a health hazard to the users of these pitches.

RIVM undertook a number of measurements above several pitches, at two different levels above the surface. None of these measurements showed the presence of nitrosamines in the atmosphere above the pitch. Supplementary laboratory tests on the materials showed that nitrosamines can only be released from rubber crumb to a very limited extent.

Further to these findings, RIVM concluded that nitrosamines do not pose a health hazard to the users of these artificial pitches.

CONTENTS

1 INTRODUCTION

In August 2006, Hulpverleningsdienst Gelderland Midden (HGM, the Gelderland regional fire, rescue and health service) commissioned a study on the presence of toxic compounds in the atmosphere above artificial sports pitches containing SBR (styrene butadiene rubber) crumb. This crumb is produced by shredding used car and truck tyres. The measurements were undertaken during and after a football training session. HGM used the results to assess the risks of the use of artificial pitches containing SBR crumb. This study was described in the report published by HGM[1] on 31 August 2006. At the request of HGM, RIVM (National Institute for Publich Health and the Environment) determined standards for nitrosamines but did not have any involvement in the air measurements.

One of the conclusions of the HGM report was that the measured nitrosamine concentrations might pose a health hazard to anyone exposed to them long term. Consequently, HGM recommended to the municipality of Arnhem that SBR crumb should not be used in new artificial pitches until further investigation. This recommendation was based on a single measurement. The measured concentration of NDEA[2] (93 ng/m^3) was significantly higher than the limit set for this substance for health reasons (0.3 ng/m^3). Hence, HGM decided that further investigations were needed.

As RIVM has significant expertise in the field of nitrosamine investigations, HGM requested RIVM to participate in a joint follow-up investigation. This investigation was to provide reliable information about the extent to which significant quantities of nitrosamines may be released during sports activities on artificial pitches containing rubber crumb.

The objective of the investigations was firstly to determine if nitrosamines are indeed released from rubber crumb used in the investigated artificial pitches, and if so, secondly to determine if the measured nitrosamine concentration in the atmosphere above the pitches is high enough to pose a health hazard to the users of these pitches. For this purpose RIVM took air samples over a number of artificial pitches in Arnhem. These air samples were then analysed for nitrosamines. Additionally, several types of rubber crumb were tested in the laboratory for the release of nitrosamines.

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1 HGM: Onderzoek gezondheidsrisico's SBR-granulaat in een kunstgrasveld van sportcentrum Rijkerswoerd (2006)

2 N-nitrosodimethylamine

This report includes a brief explanation of the measurement methods and the results, followed by a discussion of the results and conclusions. The appendices to this report include details of the analyses.

2 METHOD

2.1 AIR SAMPLES

For this investigation, RIVM took air samples over the artificial pitch of the Rijkerswoerd sports park (the subject of the earlier investigation) and three other pitches in Arnhem. The four pitches contain different grades of rubber crumb. The SBR crumb of one field had only recently been applied and still smelled of rubber. Two fields had SBR crumb which had been applied at least a year ago, and one field contained rubber crumb which was not obtained by shredding tyres but had been produced specifically for sports pitches.

RIVM wanted to compare the results of the fieldwork with the work done earlier by HGM. Hence, the measurements were taken under circumstances similar to those during the earlier work. Consequently, the investigators waited for good weather to take the samples. Furthermore, some of the measurements were made while the pitches were in use for matches. The measurements were made at two different levels above the pitch: 30 cm and 100 cm. The higher level was used to get an impression of the concentrations which might be present in the breathing zone of the football players.

To check the measurements RIVM also took some blank samples. These samples were prepared in the same way as the samples taken at the football pitches but were not used for any measurements. Additionally, samples were taken upwind from the pitches. These were used to determine if any nitrosamine detected could have come from a separate source in the vicinity of the pitch. Finally, RIVM took additional samples which were sent to other laboratories for analysis.

2.2 MATERIALS ANALYSES

To investigate the properties of the rubber crumb RIVM collected pieces of rubber and loose crumb from six football pitches for analysis in the laboratory. Five to six samples were taken from various parts of each pitch (see Appendix 2).

In the laboratory the rubber crumb samples were exposed to several different treatments. This was to determine the extent to which the nitrosamines incorporated in the rubber crumb were released.

3 RESULTS

3.1 *AIR SAMPLES*

RIVM did not detect nitrosamines in any of the air samples taken above the various fields.

The first set of six back-up samples was submitted to the laboratory which had undertaken the earlier analysis for HGM. This laboratory detected the nitrosamine NMOR[3]. However, one of these samples was a blank and had not been used for any measurement.

As RIVM was aware that there might be a difference between its own analyses and that of the other laboratory, the second set of six back-up samples [4]was submitted to a laboratory in Germany accredited for nitrosamine analyses. This analysis confirmed the results obtained by RIVM: no nitrosamines were detected in the samples.

3.2 *MATERIALS ANALYSES*

Heating rubber crumb to 70 °C in a sealed container did not lead to detectable nitrosamine concentrations in the air within the container. Similarly, extraction of SBR did not lead to detectable nitrosamine levels in the extracted material. However, two migration tests (see Appendix 2) resulted in the release of minor quantities of nitrosamines from rubber crumb. The highest measured value was 4.5 µg/kg (see Appendix 2). Some of the samples did not lead to detectable nitrosamine levels. The analysis results are below the limits for rubber consumer products, such as balloons. The limit for consumer products is 10 µg/kg.

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3 N-(nitrosomorpholine) in two of the six samples.

4 For clarification: each of the three laboratories analysed identical sets of six tubes. Five of these samples were taken at the same level above the field and contained practically the same volume of air. The sixth sample was a blank.

4 DISCUSSION

RIVM investigation showed that no nitrosamines were detectable above the football pitches. These results were confirmed by the analyses carried out by the laboratory in Germany.

The laboratory which earlier detected nitrosamines in one analysis now detected another nitrosamine. However, this laboratory also detected this compound in a blank sample tube, i.e. one not used for air sampling. Hence RIVM doubts the results of the analyses undertaken by this laboratory.

Also in the materials analyses it was difficult to release nitrosamines from rubber crumb. Furthermore, the values obtained in the migration studies were well below the statutory limits for rubber consumer products such as balloons.

In a letter of 23 June 2006, RIVM concluded earlier that it is unlikely that anyone using these pitches will be exposed to a health hazard from polycyclic aromatic hydrocarbons (PAH) or plasticizers (phthalates).

During the earlier investigations (August 2006), HGM also analysed for heavy metals and PAHs in the air. HGM’s conclusion was that the inhalation of heavy metals and PAHs does not pose a health hazard to sportspeople.

However, in the letter of 23 June 2006, RIVM noted that rubber crumb contains a wide range of other chemicals. At present, RIVM does not have any information suggesting that there are potential health hazards. Once RIVM has more information about these products then it will be able to assess any health hazards which may be associated with the use of rubber crumb in artificial pitches. Companies producing and using rubber crumb in the Netherlands and other countries are currently providing additional information. Risk assessment reports are also being exchanged at the European level. This information will be used when advising on the potential health hazards associated with the use of rubber crumb in artificial pitches.

The current investigation into nitrosamines only concerned potential health hazards to the users of the pitches. RIVM’s letter of 23 June 2006 also addressed environmental hazards associated with rubber crumb. The letter identified substances associated with environmental hazards and made recommendations for further investigations.

5 CONCLUSIONS

No detectable concentrations of nitrosamines were found in air samples taken above the artificial pitches.

The materials analyses showed that nitrosamines can only be released from rubber crumb in small quantities.

Sports on artificial pitches containing rubber crumb are not likely to lead to any health hazard associated with exposure to nitrosamines.

RIVM has reasons to doubt the reliability of the analyses made by the laboratory used by HGM in August 2006, which did detect nitrosamines in the air samples.

The conclusions stated in RIVM letter of 23 June 2006 can be maintained unreservedly. This letter (in Dutch) can be found at:
http://www.rivm.nl//bibliotheek/digitaaldepot/Briefrubbergranulaat.pdf

APPENDIX 1 AIR SAMPLES

1.1 FIELD WORK

The field work on the football pitches was undertaken on 11 and 15 October 2006. It was assumed that if any nitrosamines were indeed released this would primarily occur during dry, sunny weather. Hence, we waited for some time until the weather forecast was favourable. As during the first investigation, some of the measurements were undertaken while the pitch was being used for sports. Table 1 lists the sports facilities, time the samples were taken, and the weather at the time.

Table 1: Sports parks in Arnhem where samples were taken

Sports park	Date	Temperature	Wind
Bakenberg	11-10-2006	12-17 °C	South east 2-3 Bft
Rijkerswoerd	11-10-2006	18-20 °C	East 2-3 Bft
Bakenhof, main pitch	15-10-2006	11-16 °C	East 3 Bft
Bakenhof, Johan Cruijff Court	15-10-2006	11-16 °C	East 3 Bft

The pitch at Bakenberg had been laid around three weeks before the samples were taken and had only been played on for the first time the week before sampling. Although the pitch was wet during sampling, there was a clear smell of rubber. The Rijkerswoerd pitch was used for training by several teams in the afternoon of Wednesday 11 October. At the peak time there were about eighty football players and trainers on it. The main Bakenhof pitch was used by several young football players for some of the sampling period. The Johan Cruijff Court was intensively used by some twenty young players during the last two hours of sampling. Thus both the weather conditions and use of the pitches were comparable with those during the earlier HGM investigation.

1.2 MEASUREMENTS

The measurements were made in accordance with OSHA method 27. This is a validated method for the sampling and analysis of nitrosamines. According to OSHA, the detection limit for nitrosamines is approximately 30 ng/m^3. RIVM obtained lower detection limits during this investigation, ranging from 8.4 ng/m^3 for NDEA to 16 ng/m^3 for NDBA. HGM also used this method for its earlier investigation.

Several pumps and sampling tubes were set up on each pitch.

- One pump at 100 cm above ground level, upwind, close to the pitch, to detect any other nitrosamine sources in the vicinity.

- One pump on the pitch, 100 cm above the grass.
- Two pumps on the pitch, 30 cm above the grass.
- Two additional pumps on the pitch, 30 cm above the grass, for analysis by other laboratories.

Each sampling station was fitted with a pump with two ThermoSorb®N tubes connected in series to determine if there was any breakthrough or migration. The tubes were fitted below the pump, with the inlet opening pointing towards the field. Shortly before sampling, the pump flow (with the tubes fitted) was adjusted to 1000 mL/min using a Gilian soap bubble flow calibrator. This was done in the car park to prevent any influence from the pitch. The sampling periods were selected to obtain a total air intake of approximately 250 litres[5]. We also took field blanks at each pitch. These were obtained by placing a tube on a pump, adjusting the flow and then sealing the tube. As all tubes were treated identically before the measurements, any differences in concentration could only be due to the air samples.

1.3 ANALYSIS

In accordance with OHSA method 27, the received cartridges were eluted with 2 x 1 mL methanol/dichloromethane (25 : 75 v / v%). This was done by fitting a syringe needle to the cartridge inlet and then twice feeding 1 mL of eluent through the cartridge. The two fractions were collected in separate vials and then analysed with a gas chromatograph (GC) using a Thermal Energy Analyzer (GC-TEA) detector.

We noticed that the combination of methanol and dichloromethane attacked the stationary phase of the system. We concluded this because the system became less sensitive to the standards. For this reason we decided to transfer the samples to a keeper with hexane, after which the methanol/dichloromethane fraction was blown off. The remaining hexane fraction was then analysed using GC-TEA. On the basis of the sample chromatograms using methanol/dichloromethane, it was decided to determine only the first fraction (Fraction A) of the samples using hexane. If this was found to contain nitrosamines then the second fraction (Fraction B) would also be processed.

1.4 RESULTS

There were no detectable nitrosamines in the eluted material. The detection limits ranged between 2.1 ng/cartridge for NDEA and 4 ng/cartridge for NDBA (highest and lowest sensitivity). Hence there was little point in processing Fraction B.

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5 According to OSHA method 27 there are no losses when 280 L of air is sampled by two cartridges connected in series.

The nitrosamines covered by the analysis were:

NDMA	N-Nitrosodimethylamine
NMEA	N-Nitrosomethylethylamine
NDEA	N-Nitrosodiethylamine
NDPA	N-Nitrosodipropylamine
NMOR	N-Nitrosomorpholine
NPyR	N-Nitrosopyrrolidine
NpiP	N-Nitrosopiperidine
NDBA	N-Nitrosodibutylamine

The GC-TEA has previously been used for a number of samples from other sources. Hence, nitrosamines other than those listed above would also generate a signal.

The first set of six back-up samples was submitted to the laboratory which had undertaken the earlier analysis for HGM. This laboratory detected the nitrosamine NMOR in two of the six samples. This laboratory detected 35 ng in one tube and 25 ng in another. However, the latter tube was a blank which had not been used to sample air. Thus, there are reasons to doubt the value of these measurements. Thus, a comparison with the standard for NMOR (1 ng/m^3) is not useful.

As RIVM was aware that there might be a difference between its own analyses and that of the other laboratory the second set of back-up samples was submitted to a laboratory in Germany with an accreditation for nitrosamine analyses. This analysis confirmed the results obtained by RIVM: no nitrosamines were detected in the samples.

APPENDIX 2 MATERIALS ANALYSES

2.1 PITCH SAMPLES

On 28 August 2006, an RIVM official, accompanied by personnel of the municipality of Arnhem, visited several artificial pitches to obtain samples of rubber crumb. A knife was used to cut out sections of approximately 20 x 20 cm^2 and rubber crumb was then collected with a hand-held vacuum cleaner. It was estimated that at most 5% of the total layer thickness (several centimetres) was removed. Five to six locations along a diagonal line across the pitch were sampled until sufficient rubber crumb had been obtained for the materials analysis.

Samples were taken from the following pitches:

1. Bakenhof Sports Park: large football pitch. A different sampling method was used for this pitch. A bucket of bulk material was taken from spare crumb stored in a Big Bag. This pitch was created about two years ago.
2. Bakenhof Sports Park: Johan Cruijff Court. This pitch was created this summer and officially opened in September. It contains a different material, a light-yellow crumb (Thiolon® Infill Pro) and is only a few weeks old.
3. Malburgen West Sports Park (opposite the Gelredome stadium). This was created in 2005.
4. Rijkerswoerd Sports Park. This is the field where HGM undertook measurements in August 2006. This pitch is about one year old.
5. Elden Sports Park, Eldenia Football Club. This pitch was created in 2004.
6. ’t Cranevelt Sports Park. This was the first pitch in Arnhem where SBR crumb was used. It was created in 2003 and the crumb is slightly finer.

2.2 LABORATORY TESTS

The materials analyses comprised three steps.

1. Heating SBR rubber crumb was heated to 70 ^{0}C in a sealed bottle. The headspace (the air above the crumb) was then analysed for a range of components including nitrosamines. Additionally, nitrosamine was added to rubber crumb and the headspace of this mixture was investigated.
2. Extraction. The rubber crumb was extracted with dichloromethane which was then analysed for the presence of nitrosamines.
3. Migration. Rubber crumb was brought in contact with a special fluid which simulates human saliva. The simulated saliva was then analysed with GC-TEA for the presence of nitrosamines.

The first two methods are experimental, and therefore uncertain, methods to detect nitrosamines. The third method is standardised (NEN-EN 12868) and is used to determine the safety of rubber consumer products such as balloons. This method is routinely used by RIVM.

The first method was used to increase the likelihood of the release of components such as nitrosamines. Obviously, the results of these analyses could not be used to assess the risk for users of the field, given that:

a) heating to 70 ^{0}C is quite different from the conditions during a game;
b) the air above a pitch is continuously replaced by fresh air;
c) this method does not consider the height of the breathing zone above the pitch.

The second method is widely used to release compounds for analysis. However, it was uncertain if it could be used to detect nitrosamines.

The third method was used to get an impression of the extent to which nitrosamines can be released from the material, compared with other consumer products such as balloons. The migration tests with artificial saliva give an impression of the amount of nitrosamines which might be released if the material was sucked for some time. Obviously, unlike with balloons, this is not a realistic exposure route for rubber crumb.

2.3 RESULTS

Method 1: No nitrosamines were detected when SBR was heated to 70 ^{0}C in a sealed bottle and the headspace was analysed. (They were detected in the test where the sample was spiked with nitrosamines.)

Method 2: No nitrosamines were detected in the extract when SBR was extracted with dichloromethane.

Method 3: Nitrosamines were detected when rubber crumb was exposed to simulated saliva, but only after a minor modification to the method. This was necessary because it was found that rubber crumb released smaller amounts of nitrosamines than balloons, for example.

The results are listed in Table 2, expressed in μg/kg. Three nitrosamines were detected: N-nitrosodiethylamine (NDEA), N-nitrosodimethylamine (NDMA) and N-nitrosomorpholine (NMOR). The last of these three compounds was not detected earlier in rubber crumb but was found in the largest quantity in these experiments.

Table 2: Nitrosamines released from different types of rubber crumb by migration tests, in µg/kg.

Sample	NDMA	NDEA	NMOR
Pitch 1 Bakenhof	0.6 ± 0.1	< 0.2	4.0 ± 0.5
Pitch 2 Cruijff Court	< 0.2	0.7	2.5
Pitch 3 Malburgen West	0.3 ± 0.2	< 0.2	1.4 ± 0.4
Pitch 4 Rijkerswoerd	< 0.2	< 0.2	1.2 ± 0.2
Pitch 5 Elden	<0.2	< 0.2	1.5 ± 0.5
Pitch 6 ’t Cranevelt	< 0.2	< 0.2	1.8 ± 1.1

The release of these nitrosamines was limited compared with consumer products. For example, the maximum amount of nitrosamines which may be released from balloons using this method is 10 µg/kg. The values obtained for the rubber crumb were far below this.

APPENDIX 3 NITROSAMINE LIMITS

3.1 NDMA AND NDEA

NDMA and NDEA are proven carcinogens in animals based on extensive animal carcinogenicity tests. These compounds are also proven genotoxins. Given the laboratory-animal evidence, NDMA and NDEA are classified as suspected human carcinogens (IARC group 2A). The majority of animal tests used oral exposure. RIVM recently undertook a quantitative risk assessment for NDMA based on this exposure route. This resulted in an estimated additional risk of one per million per lifetime at a dose of 23 ng NDMA/person/day over a whole lifetime. In a combined risk assessment for NDMA and NDEA, the NDEA risk was scaled on the basis of TD_{50} values[6] for both substances. Hence the potential effect of NDEA was estimated to be 3.6 times that of NDMA.

Some carcinogenicity tests based on inhalation are available for NDMA. The Health Council of the Netherlands used these studies for a quantitative cancer risk assessment for workplace exposure (Gezondheidsraad, 1999). In a study of rates by Klein et al. (1991) an increased incidence of nasal tumours (13/36, compared with 0/36 in controls) was observed at the lowest test concentration, 120 $\mu g/m^3$. However, this report does not clearly define the exposure schedule (hours per week, weeks of exposure). Thus, it is unclear if the specified exposure period of 4 - 5 hours per day, four times per week, was maintained over a period of 207 days or 362 days. For these two periods the Health Council has determined the *unit risks* to be $1x10^{-1}$ per $\mu g/m^3$ and $0.57x10^{-1}$ per $\mu g/m^3$, respectively. These unit risks relate to continuous exposure over a full lifetime. In its recommendation the Health Council used the lowest unit risk of $1x10^{-1}$ per $\mu g/m^3$. This unit risk corresponds to the following risk-specific concentrations: one per million per lifetime at 0.01 ng/m^3, one per hundred thousand at 0.1 ng/m^3 and one per ten thousand at 1 ng/m^3. The risk level of one per ten thousand per lifetime is the maximum acceptable risk.

There are no usable inhalation studies for NDEA. It is expected that NDEA will have the same effect as NDMA. For oral exposure, the carcinogenic potency of NDEA is actually higher than that of NDMA (3.6 times, see above). Assuming that this difference in potency is also relevant to exposure by inhalation, the above risk-specific concentrations of NDMA can be used to determine the values for NDEA: one per million per lifetime at 0.003 ng/m^3, one per hundred thousand at 0.03 ng/m^3 and

6 Tumorigenic dose, the dose at which 50% of the animals develop some form of cancer

one per ten thousand at 0.3 ng/m^3. The risk level of one per ten thousand per lifetime is the maximum acceptable risk.

CONCLUSION

Risk-specific NDMA concentrations:

1 per 10^6 per lifetime:	0.01 ng/m³	(VSD: Virtual Safe Dose - negligible risk)
1 per 10^5 per lifetime:	0.1 ng/m³	
1 per 10^4 per lifetime:	1 ng/m³	(maximum acceptable risk)

Risk-specific NDEA concentrations:

1 per 10^6 per lifetime:	0.003 ng/m³	(VSD: Virtual Safe Dose - negligible risk)
1 per 10^5 per lifetime:	0.03 ng/m³	
1 per 10^4 per lifetime:	0.3 ng/m³	(maximum acceptable risk)

3.2 NMOR

Nitrosomorpholine (NMOR) (CAS 59-89-2) has not been subject to the same level of toxicological study as NDMA and NDEA. IARC classifies this substance as Group 2B (possibly carcinogenic to humans) based on adequate evidence from laboratory experiments with animals (IARC, 1978). NDMA and NDEA are classified as Group 2A. There are no comprehensive toxicological assessments of NMOR by rivm or other recognised bodies such as the WHO, US-EPA or ATSDR.

The available toxicological data were assessed by IARC (1978), NTP (2004) and HSDB (2003). NTP (2004) lists the following carcinogenicity studies: orally in drinking water (rats and mice), subcutaneously (hamsters) and intravenously (rats). The drinking water study of rats showed liver tumours (cellular carcinoma, cholangio carcinoma and hemangiosarcoma), neoplasia of the tongue and oesophagus and epithelial kidney tumours. The drinking water study of mice only resulted in benign liver cell tumours and lung tumours. Subcutaneous injection in hamsters resulted in various tumours of the respiratory system. Intravenous injection in rats resulted in hepatocellular carcinoma and ethmoturbinal carcinoma. The only inhalation study of NMOR which we were aware of was a limited experiment undertaken by Klein et al. (1990). They exposed rates (n = 24) to an NMOR concentration of 7.7 mg/m^3 NMOR for four or five days per week, during a period of only six weeks, followed by observation up to week 124. One nose tumour was observed, compared with 0/17 in the controls. The incidence of liver tumours was also clearly higher in the exposed group (Klein et al., 1990).

The available genotoxicity studies were positive in several in-vitro systems. The available NMOR tests in in-vivo systems were also positive (conclusions based on the data presented in HSDB, 2003).

The only inhalation study available is too limited for a meaningful comparison with the NDMA inhalation experiment undertaken by the same group (Klein et al., 1991). Hence, for exposure to NMOR by inhalation, the carcinogenic potency can not be estimated directly and one has to rely on oral data (using the same approach as for NDEA). For rats the Berkeley Cancer Potency Database gives an oral TD_{50} for rats of 0.109 mg/kg bw/day. This database gives an oral TD_{50} of 0.0959 mg/kg bw/day for NDMA in rats. These TD_{50} values for oral exposure suggest that both substances have approximately the same carcinogenic potency. Assuming that the potency is also similar for exposure by inhalation, we can use the maximum acceptable risk of NDMA to estimate that of NMOR. Assuming equipotency, this results in a maximum acceptable risk of NMOR which is the same as that of NDMA, i.e. 1 ng/m^3.

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APPENDIX 4 NITROSAMINES

4.1 INTRODUCTION

Nitrosamines are created by the reaction between secondary amines and nitrite in an acidic environment. Under certain conditions, tertiary and quarternary amino compounds may be nitrosated to nitrosamines, for example to a limited extent in the alimentary canal of humans and animals. In the workplace, nitrosamines may be formed from nitrous vapours. These are found in combustion engine exhaust fumes, hence their presence in the workplace is practically unavoidable. Rubber in particular contains certain amines (naturally and as additives) which can react with nitrite or nitrate during salt bath vulcanisation. This reaction leads to the formation of nitrosamines such as nitrosodimethylamine (NDMA), nitrosopiperidine (NPIP), nitrosomorpholine (NMOR), nitrosodiethylamine (NDEA) and nitrosopyrrolidine (NPyR). The formation of nitrosamines is a recognised problem in the rubber industry, and a range of measures have been taken to reduce the formation of these substances or exposure to them.

Most of the available data relate to workplace measurements. There are no measurements of the atmosphere in urban or rural areas in the Netherlands. Atmosphere measurements in other countries, in so far as these are available, generally relate to the atmosphere in the vicinity of suspected or confirmed industrial sources. Exposure to nitrosamines is not limited to inhalation. We will also consider other exposure routes, i.e. through food and consumer products.

4.2 WORKPLACE

Spiegelhalder and Preusmann (1983) reported average concentrations of 1 to 10 $\mu g/m^3$ NDMA and NMOR based on air samples from 19 operations in the rubber and tyre industry. Personal monitoring indicated concentrations from 0.1 to 380 $\mu g/m^3$. The highest NDMA concentration was 1060 $\mu g/m^3$. For the rubber industry, HSDB (2005) reported NDMA concentrations from 0.1 to 47 $\mu g/m^3$ in the period from 1979 to 1983, while the concentrations after that were generally lower. The observed NDEA concentrations in these studies were lower (0.025 to 1.4 $\mu g/m^3$) (HSDB, 2003).

Five nitrosamines were detected during a series of measurements in 24 French rubber production plants, from 1992 to 1995. NDMA was the most common compound (98% positive), followed by NDEA (55%). The maximum and median concentrations were

99.9 and 0.25 µg/m^3 for NDMA and 5.6 and 0.12 µg/m^3 for NDEA. The highest concentrations were found during salt bath vulcanisation. Measurements in tyre factories resulted in relatively low concentrations, less than 2.5 µg/m^3. The authors ascribe this to the introduction of 'safe amines' in this industry since 1990 (Oury et al., 1997).

At an American factory producing rubber strips, several nitrosamines were found in the breathing zone. NDMA was found in the highest concentration: 0.47 to 11.44 µg/m^3 (Reh and Fajen, 1996). Rogaczewka and Wroblewska (1996) found similar concentrations in a Polish tyre factory. Monarca et al. (2001) tested the atmosphere in four rubber production companies and found NDMA concentrations ranging from 0.10 to 0.98 µg/m^3. More recently, Iavicoli and Carelli (2006) undertook measurements at four plants producing rubber drive belts for automotive engines and only found low nitrosamine concentrations (generally below the detection limit of 0.06 µg/m^3).

The available data for the Netherlands are extremely limited. In a presentation to the European rubber industry, De Vocht (2005) only found NDMA measurements for the Netherlands for one year, 1998. For tyre production he quoted average concentrations of approximately 0.04 µg/m^3. In countries where there are more measurements available, the trend from 1980 to 2000 was clearly downwards.

4.3 ATMOSPHERE

There are no data for the Netherlands on representative concentrations in urban areas, near motorways, etc. The only known report on outdoor atmosphere measurements in the Netherlands is of measurements undertaken in 1981 by the then RIV (National Institute for Public Health). This was in response to concerns of residents in the vicinity of a company based in Maastricht which processed inner and outer tyres for reuse by the rubber industry. No nitrosamines were detectable in five 24-hour air samples taken at five locations in the vicinity of the site (NDMA <0.03 µg/m^3, NMOR <0.06 µg/m^3). The NDMA and NMOR emissions (µg/second) were calculated on the basis of measurements inside the factory and the dispersion was then calculated with the Dutch national model. The highest average concentration expected over a longer period in the residential area around the factory was 0.01 ng/m^3 NDMA and 0.12 ng/m^3 NMOR (RIV, 1981).

Similarly, only limited information is available for other countries. Some American measurements made between 1975 and 1980 in the vicinity of industrial sources resulted in NDMA concentrations of approximately 1 µg/m^3. Some measurements in urban areas without known sources resulted in concentrations from 0.01 to 0.8 µg/m^3

(ATSDR, 1989). Spiegelhalder and Preusmann (1987) undertook measurements in the industrial region around Linz, Austria in 1983-1984. The took 363 samples, 6% which were found to contain low levels of nitrosamines, with concentrations ranging from 0.01 to 0.04 μg/m^3 NDMA, NDEA and NMOR. Ziebarth (1994) took over one thousand air samples in industrial areas in the former GDR from 1992 to 1994. Nitrosamines were detected in 4.4% of these samples, in concentrations from 0.01 to 0.38 μg/m^3. Khesina et al. (1996) reported NDMA concentrations in the centre of Moscow from 0.03 to 0.06 μg/m^3, and in the industrial areas of the city several tenths μg/m^3 (unspecified) and 0.1 μg/m^3 or higher (unspecified) near major roads.

Kataoka et al. (1997) investigated the presence of nitrosamines in the smoke of burnt food, hair, wood, rubber, plastic, etc. Minor amounts of nitrosamines (NDMA, NMOR, NPyR, NPIP) were detected in practically all the items investigated. High concentrations (up to 45 μg/g) were found in smoke from black pepper, dried squid, hair and rubber. Cigarette smoke contained approximately 0.3 μg/g NDMA. The authors concluded that these results indicated that nitrosamines are widely distributed in the environment and that human exposure to them is frequent.

IPCS (2002) reported some measurements for the Canadian province of Ontario. Eight air samples from five cities did not contain detectable amounts of NDMA (detection limit 0.0034 to 0.0046 μg/m^3). In the vicinity of a chemical works in one city, NDMA was detected in 20 out of 41 samples (detection limit 0.0029 to 0.0048 μg/m^3). The highest concentration, 0.23 μg/m^3, was found close to the chemical works and 0.079 μg/m^3 was measured at a slightly greater distance.

4.4 INDOOR ATMOSPHERE

As far as we are aware, cigarette smoke is the main source in the indoor atmosphere. In the US, the atmosphere in a pub contained 0.24 μg/m^3 NDMA while the substance was undetectable in the living room of a nonsmoker (<0.003 μg/m^3) (Brunneman and Hofmann, 1978). According to IPCS (2002) the average NDMA concentration in indoor air polluted by cigarette smoke is 0.01 to 0.1 μg/m^3.

Rounbehler et al. (1980) undertook measurements in new cars. NDMA was present in 37 out of 38 cars. The concentrations ranged from 0.07 to 0.83 μg/m^3 (average: 0.29 μg/m^3). NDEA was detected in 17 out of 37 cars in concentrations ranging from 0.04 to 0.39 μg/m^3 (average: 0.11 μg/m^3).

4.5 INTAKE THROUGH FOOD AND CONSUMER PRODUCTS

Nitrosamines are found in food, cosmetics and some other consumer products. These compounds are also formed in the body after eating certain foods containing their precursors. This endogenic formation of nitrosamines is influenced by parameters such as physiology, general health and age, which are difficult to quantify. All in all, the human population is exposed to a broad range of N-nitrosamines, many of which can not be identified.

RIVM Basic Document on Nitrate estimated the average exposure to all nitrosamines through food in the Netherlands at several hundred nanograms per day (RIVM, 1989). Measurements as part of 24-hour duplicate diet studies (Ellen et al., 1990) suggested an intake of 100 ng/day of nitrosamines by adults. In other European countries, values of around 200 ng/person/day have been reported (Domanska and Kowalski, 2003). Passive smoking can increase the exposure by a factor ten.

Endogenic formation can occur during combined exposure to nitrate and secondary or tertiary amines, which are primarily found in fish. In-vivo volunteer studies (Vermeer et al., 2000) and in-vitro studies by RIVM (Zeilmaker et al., 2004), indicate that the additional exposure due to endogenic formation can greatly exceed external exposure on the days the subject eats fish.

Cosmetics are a further source of nitrosamines. Here it is primarily the formation of nitrosodiethanolamine (NDELA) which can lead to human exposure. To prevent the formation of NDELA in cosmetics there are regulations addressed to the manufacturers concerning the use of raw materials which do not contain relevant precursors. Similarly, standards have been set for potential exposure to nitrosamines from rubber dummies (pacifiers). Consumers may occasionally be exposed when using rubber consumer products such as washing-up gloves, balloons and condoms (RIVM 2003, 2006).

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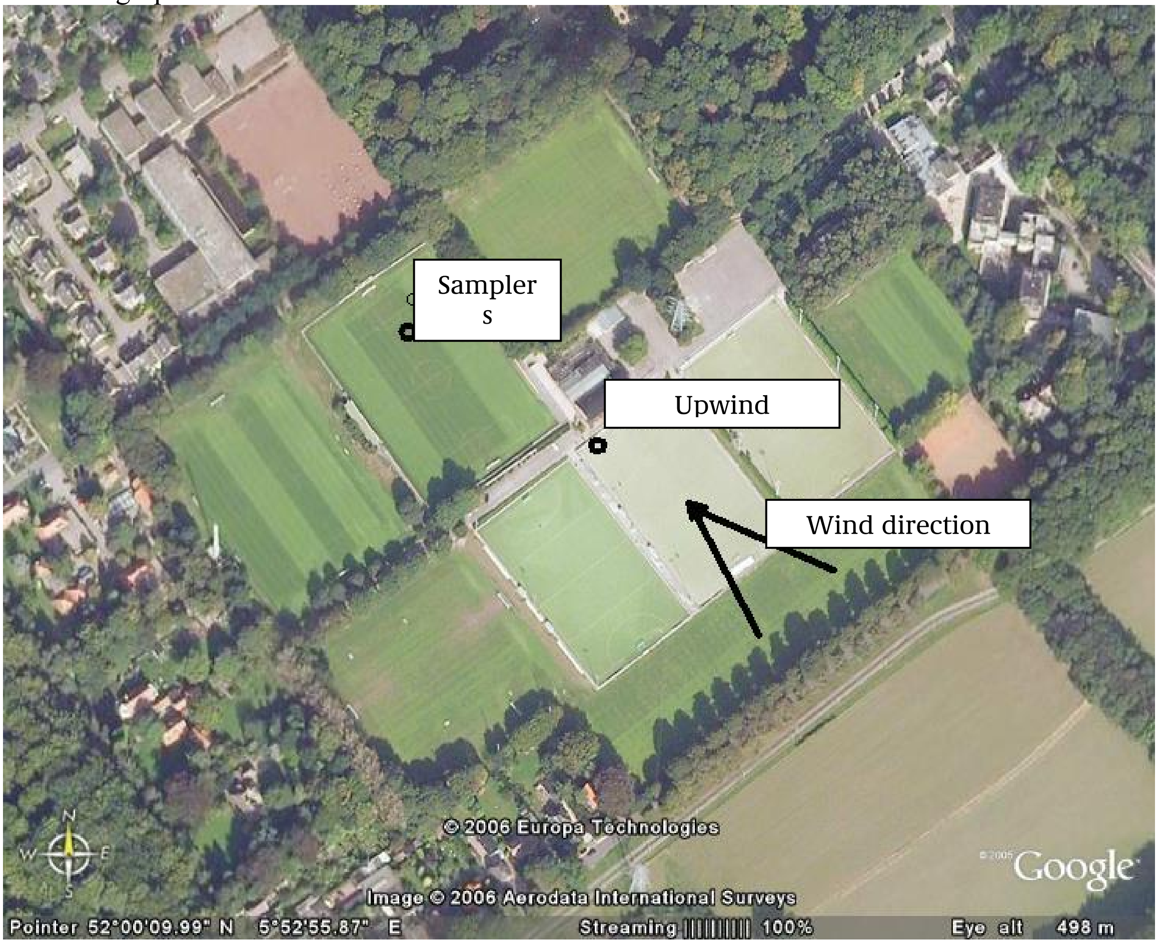
APPENDIX 5 PHOTOGRAPHS

Photograph 1 Taking a material sample

Photograph 2 Pump with dust filter and two ThermoSorb-N cartridges

Bakenberg Sports Park



Photograph 4 Five pumps at Bakenberg

Photograph 3 Upwind sampling

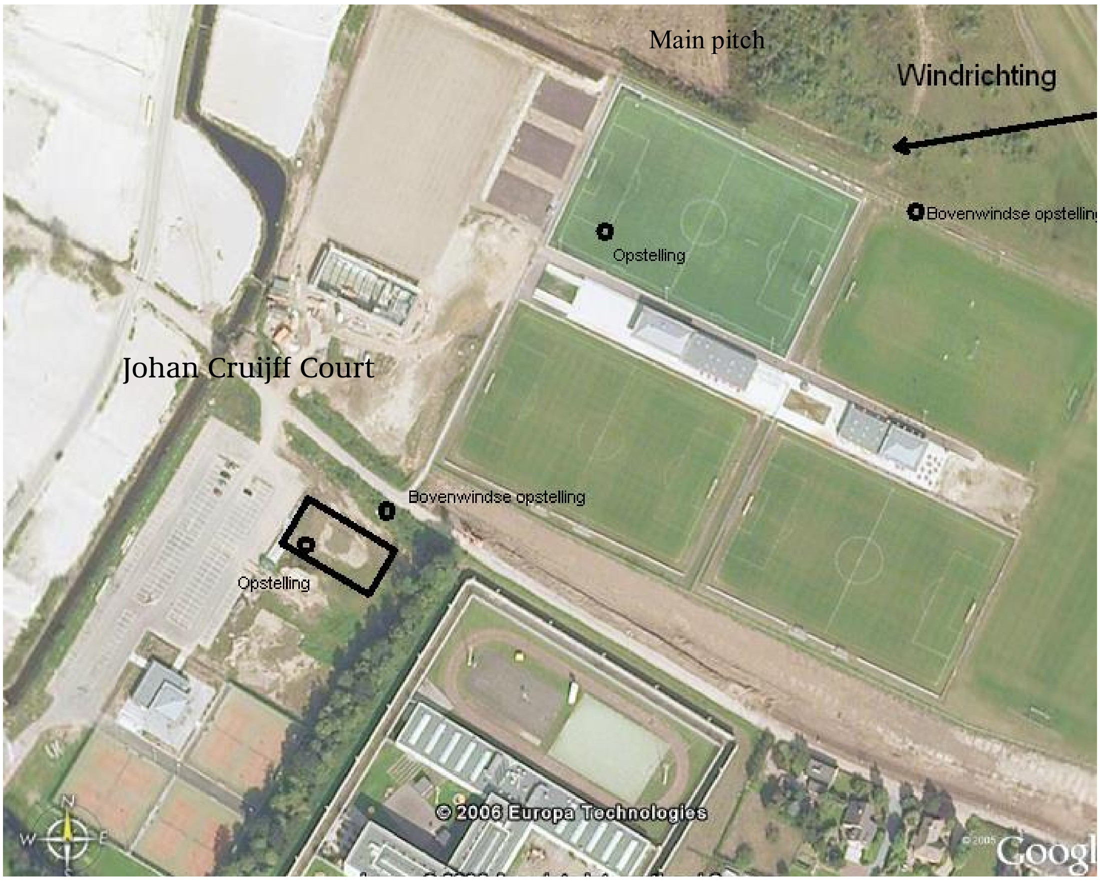
Rijkerswoerd Sports Park

Photograph 6 Five pumps at Rijkerswoerd

Photograph 5 Upwind sampling

Bakenhof Sports Park

Opstelling = Samplers
Bovenwindse opstelling = Upwind sampler
Windrichting = Wind direction



Photograph 8 Johan Cruijff Court

Photograph 7 Bakenhof main pitch

APPENDIX 6 LIST OF ALL SAMPLES

Nitrosamine samples										
				Date	11-10-2006					
Location	Rijkerswoerd									
Position	Sample code	Cartridge	Start time	End time	Start flow	End flow	mL/min	Pump code	min.	litres
Upwind	IMD1110006.11A and B	G51594 and G51595	14:32	18:38	1031	1019	1025	6516331	246	252
Pitch, 100 cm	IMD1110006.12A and B	G51596 and G51597	14:25	18:27	997	1032	1015	6516323	242	246
Pitch, 30 cm	IMD1110006.13A and B	G51598 and G51599	14:25	18:27	1023	1050	1037	451245	242	251
Pitch, 30 cm	IMD1110006.14A and B	G51600 and G50441	14:25	18:27	997	1062	1030	6516336	242	249
Pitch, 30 cm	IMD1110006.15A and B	G50442 and G50443	14:25	18:27	991	1346	1169	6516328	242	283
Pitch, 30 cm	IMD1110006.16A and B	G50444 and G51595	14:25	18:27	990	552	771	6516327	242	187
Blank, RIVM	IMD111006.BL2	G50446								
Blank, Lab A	IMD111006.BL3									
Blank, Lab B	IMD111006.BL5									

Nitrosamine samples

Date 15-10-2006

Location	Bakenhof, Cruijff Court									
Position	Sample code	Cartridge	Start time	End time	Start flow	End flow	mL/min	Pump code	min.	litres
Upwind	IMD1510006.31A and B	G51481 and G51247	11:49	16:10	994	997	995.5	6516324	261	260
Pitch, 100 cm	IMD1510006.32A and B	G51256 and G51248	11:50	16:05	1007	925	966	6516331	255	246
Pitch, 30 cm	IMD1510006.33A and B	G51484 and G51485	11:50	16:05	994	906	950	6516332	255	242
Pitch, 30 cm	IMD1510006.34A and B	G51495 and G51494	11:50	16:05	1003	1013	1008	6516334	255	257
Blank, RIVM	IMD151006.BL14	G51463								

Nitrosamine samples								Date	11-10-2006		
Location	Bakenberg										
Position	Sample code	Cartridge	Start time	End time	Start flow	End flow	mL/min	Pump code	min.	litres
Upwind	IMD111006.1A and 1B	G51581 and G515182	9:12	13:17	1019	1134	1077	6516335	245	264
Pitch, 100 cm	IMD111006.2A and 2B	G51583 and G515184	9:07	13:08	1016	1052	1034	6516325	241	249
Pitch, 30 cm	IMD111006.3A and 3B	G51585 and G515186	9:07	13:08	1025	1063	1044	6516337	241	252
Pitch, 30 cm	IMD111006.4A and 4B	G51587 and G515188	9:07	13:08	1000	1062	1031	6516332	241	248
Pitch, 30 cm	IMD111006.5A and 5B	G51589 and G515190	9:07	13:08	1010	1085	1048	6516324	241	252
Pitch, 30 cm	IMD111006.6A and 6B	G51591 and G515192	9:07	13:08	1002	1015	1009	6516334	241	243
Blank, RIVM	IMD11106.BL1	G51593								

Nitrosamine samples						Date	15-10-2006			
Location	Bakenhof									
Position	Sample code	Cartridge	Start time	End time	Start flow	End flow	Flow mL/min	Pump code	min.	litres
Upwind	IMD1510006.21A and B	G51487 and G51492	10:57	15:46	1018	1078	1048	6516325	289	303
Pitch, 100 cm	IMD1510006.22A and B	G51491 and G51490	11:54	15:40	1024	1029	1027	6516329	226	232
Pitch, 30 cm	IMD1510006.23A and B	G51488 and G51489	11:00	15:40	1020	1002	1011	4512459	280	283
Pitch, 30 cm	IMD1510006.24A and B	G51462 and G51461	11:00	15:40	1022	1079	1051	6516323	280	294
Pitch, 30 cm	IMD1510006.25A and B	G51465 and G51467	11:00	15:40	1007	1004	1006	6516330	280	282
Pitch, 30 cm	IMD1510006.26A and B	G51249 and G51468	11:00	15:40	1020	1047	1034	6516335	280	289
Blank, RIVM	IMD151006.BL11	G51463								
Blank, Lab A	IMD151006 .BL12	G51464								
Blank, Lab B	IMD151006 .BL13	G51469								