Project information

Keywords
Marine plastic pollution

Project title
Microplastics from artificial sports pitches: Composition, degradation and biological interactions (MARS)

Year
2017

Project leader
D.Herzke (NILU) & C. Halsband (APN)

Geographical localization of the research project in decimal degrees (max 5 per project, ex. 70,662°N and 23,707°E)
69.67°N 18.79°E

Participants

Andy Booth (SINTEF), Lisbet Sørensen (SINTEF)

Jan H. Sundet (IMR)

Flagship
Hazardous Substances

Funding Source

Flagship and NFR

Summary of Results

Test materials and characterization

A suite of tire granulate reference materials was procured for the study, as well as two field collected samples (Table 1). These included a sub-set of smaller sized materials (<1500 µm) which were generated by cryo-milling the larger materials. Initially, the materials were screened using a range of analytical chemical approaches to investigate the content of organic chemicals and metals. For analysis of organic chemicals two different methods were investigated, conventional GC-MS and pyrolysis-GC-MS. For conventional GC-MS analysis, rubber granulate samples were first subjected to a solvent extraction process (ethyl acetate, ultra-sonication and centrifugation). For pyrolysis GC-MS samples were analyzed directly without any pretreatment using thermal desorption and full pyrolysis methods. For analysis of metal content, rubber granulate samples were subjected to digestion in hydrofluoric acid prior to analysis by ICP-MS.

Table 1. Overview of tire rubber granulate reference materials used in the studies.

Material	**Source/Origin**	**Comments**
Coarse tire rubber granulate	Commercial supplier	'Pristine' consumer product in size range 2.5 – 4.0 mm
Medium tire rubber granulate	Commercial supplier	'Pristine' consumer product in size range 1.0 – 2.8 mm
Fine tire rubber granulate	Commercial supplier	'Pristine' consumer product in size range 0 – 1.2 mm
Collected field sample of rubber granulate	Sports field in Trondheim	Material has been in the environment for an unknown period of time. Represents material that may have undergone weathering and leaching.
Collected field sample of rubber granulate	Sports field in Tromsø	Material has been in the environment for an unknown period of time. Represents material that may have undergone weathering and leaching.
Medium rubber granulate	CARAT	Cryo-milled and sieved to obtain the <1500

cryo-milled fraction <1500 µm		µm fraction
Medium rubber granulate cryo-milled fraction <1000 µm	CARAT	Cryo-milled and sieved to obtain the <1000 µm fraction
Medium rubber granulate cryo-milled fraction <250 µm	CARAT	1000 µm fraction further sieved to obtain the <250 µm fraction
Trondheim rubber granulate cryo-milled fraction <1500 µm	CARAT	Cryo-milled and sieved to obtain the <1500 µm fraction
Trondheim rubber granulate cryo-milled fraction <1000 µm	CARAT	Cryo-milled and sieved to obtain the <1000 µm fraction

The total number of GC-MS identifiable compounds (>80% confidence to NIST library match) in the rubber extracts varied across the materials, with the course material containing 130, the medium material 123, the fine material 56, and the collected material containing 87 compounds. The compounds consisted of a range of chemical types, including known pollutants such as polycyclic aromatic hydrocarbons (PAHs), phthalates and rubber additives. A summary of the concentrations of identified PAHs in each sample is present in Table 2. The relative distribution and occurrence of all identifiable compounds is presented in Figure 1.

Table 3. Summary of identifiable PAH compounds and their concentration in the different rubber granulate reference materials.

PAH	**Concentration µg g^{-1}**			
	Fine	**Medium**	**Coarse**	**Collected**
Fluorene	0.6	0.7	0.7	0.5
Fluoranthene	8.7	3.6	6.4	6.4
Pyrene	18.5	6.2	15.1	16.0
Benzo(ghi)perylene	1.0	1.1	1.3	1.6
Other PAH	n.d.	n.d.	n.d.	n.d.

Figure 1. Relative distribution and occurrence of all identifiable compounds across the different rubber granulate materials

The results of thermal desorption and pyrolysis GC-MS analysis are demonstrated in Table 3. While the pyrograms provide an overall characterization of the materials, the thermal desorption analysis allows for identification of additives that may be potential leachates from the material, including e.g. benzothiazole.

Table 3 Results of direct thermal desorption (300 °C) or pyrolysis (600 °C) analysis of tire rubber samples

Sample	Thermal desorption analysis	Pyrolysis
Fine rubber, pristine		
Medium rubber, pristine		
Coarse rubber, pristine		
Collected rubber, Trondheim		

Seawater leachate production and characterization

A leaching study in seawater was conducted to investigate the influence of rubber size, concentration and natural weathering (field collected samples) on the chemical profile of the leachate water. Samples of rubber granulate (0.1 – 1 g) were shaken in 10 mL of sterile filtered (0.22 µm) seawater at ambient temperature (dark) for 14 days. The leachate was filtered through a glass fiber filter (0.7 µm) and sub-sampled for metal and organics analysis. Metals were analysed using ICP-MS. Organic compounds were extracted using 1:1 DCM-*n*-hexane, and the extract concentrated prior to analysis by GC-MS. The quantity of PAHs in the leachate was very low, but a number of GC-amenable additives and other compounds could be identified at levels far exceeding background, including *n-tert*-butylacetamide, c6-acetamide, benzoic acid, benzothiazole, *n*-cyclohexyl acetamide, *n*-phenyl-acetamide, diethyl phthalate, 2-(methylthio)-benzothiazole, 2(3H)-benzothiazolone (> 90 % match to NIST libraries). Mn, Fe, Co, Zn, Sr and Pb were among the metals identified in the leachates, where Zn, Sr and Co were the most abundant.

Ecotoxicity studies

Rubber leachate was produced by mixing 100 g of crumb rubber, collected in situ from a local sports field, with 2L of filtered seawater on a shaker at room temperature for 2 weeks. A brownish discoloration of the resulting solution was clearly visible. A pilot study was conducted with 24 individuals of two coastal arctic species (*Acartia longiremis* and *Calanus finmarchicus*) sorted from field samples collected near Tromsø (Håkøybotn). These were exposed to 50% and 100% leachate solution in 5mL wells on 12-muliwell plates. Survival was monitored over/after 24 h. Mortalities of both species were 100% in both treatments within this time. In a second experiment, adult copepods (n=10) were incubated in 3 replicate 500 mL bottles containing filtered seawater, microalgae food (*Tetraselmis* sp.) and a range of leachate concentrations (5 to 35%), in addition to a control (with copepods, algae and filtered seawater). The bottles were strapped onto a plankton wheel (Fig. X) and rotated slowly submersed in seawater at ambient temperature (8°C) until mortality of the copepods reached ≥95%. Mortality was clearly dose-dependent and reached ≥95% at all concentrations (except controls) and in both species (Fig. Y). Some mortality occurred also in the control treatments. Species-specific differences were also evident, where *A. longiremis* individuals died much faster than *C. finmarchicus* individuals at the same concentration.

Fig. X: Bottle incubation with arctic coastal copepods on a plankton wheel

Fig. Y: Survival of adult copepods of the species Acartia longiremis (A) and Calanus finmarchicus (B) in a rubber leachate exposure experiment

Characterization of chemical body burden in Acartia and Calanus

Pooled samples of *Acartia* and *Calanus* were collected for analysis of body burden after exposure to tire rubber. A miniaturized solid-liquid extraction followed by extract purification (removal of biogenic material) was applied for this purpose, and samples analyzed for PAHs and screened for unknowns (including additives). These analysis are currently ongoing, but will help to identify which rubber-derived chemicals are contributing to the severe toxicity of the leachate.

Master and PhD-students involved in the project

Master student: Håkon Stenersen (UiT)

Student: Otto Storan (GMIT Galway, Ireland/Akvaplan-niva)

For the Management

Crumb rubber is widely used as recycled material in pavements, playgrounds and sports fields. The toxicity of both the rubber itself and its leachate in arctic marine environments is thus highly relevant. A large number of potentially harmfull compounds was identified in the rubber crumb, able to leach out into the sorrounding water (metalls, PAHs, bisfenols and others). The exposure experiments conducted here represent extremely high concentrations of leachate that are not expected to be found under natural conditions due to fast dilution with seawater in waterways and fjords. The severity of the observed effects, however, warrants further studies with lower, sublethal concentrations and including fitness endpoints such as reproductive success and offspring survival. The nature of the underlying toxicity of the chemical mixtures present in crumb rubber, i.e. which physiological processes are affected by which (combination of) contaminants, also needs to be investigated further. The invovlement of schools all over Norway to identify the major rubbertypes used on Norwegian artificial turfs, resulted in valuabel insights into type of rubber used, amount of rubber transported by each player from the turf as well as how many and which kind of turfs can be found in Norway.

Published Results/Planned Publications

ESSAS poster (Tromsø, June 2017): "Potential risks from microplastics in a warming Arctic"

Poster presentation SETAC NA in Minneapolis, US in November 2018.

Poster presentation SETAC Europe 27th Annual Meeting, Brussels, 7-11th May 2017.

Report: Results from the national school experiments are planned to be published and presented in early 2018.

Paper: Contaminants and effects of rubber crumb leachate will be submitted to the special issue "Microplastics: Hazards to Environmental and Human Health" of the *International Journal of Environmental Research and Public Health* by 15th Dec 2017.

Communicated Results

Workshop for Alta Videregående skole, Januar 2017 at Framsenteret og NILU laboratories

Arctic Frontiers 2017 side event (workshop)…

Launch of the "Tavaha" plastic whale in front of Polaria (https://www.mynewsdesk.com/no/akvaplan-niva/news/kunst-av-plast-241006)

Presentation at 'Farlig avfall konferanse http://www.farligavfallskonferansen.no/program2.cfm ', Stavanger, Sep 2017

Miljødir workshop on microplastics 18.9. in Oslo, incl. 2 presentations (Claudia & Andy)

Radio interview https://www.deutschlandfunknova.de/beitrag/plastikmuell-vom-kunstrasenfeld-ins-meer with German public station DRadio Wissen.

First ever scientific session on the topic of rubber crumbs from artificial soccer turfs as a source of pollution was initiated and chaired by Dorte Herzke, NILU, at SETAC NA. First data [CH3] on pollutants measured in rubber crumbs were communicated at the SETAC NA in Minneapolis, US in November 2017.

Interdisciplinary Cooperation

Cooperation between chemists (Sintef, NILU), ecotixicologists (Sintef) and ecologists (APN). Cooperation with schools and educators from Miljølærere and Forskningsrådet.

Budget in accordance to results

yes

Could results from the project be subject for any commercial utilization

No

Conclusions

Rubber crumbs from used car tires contain a broad range of inorganic and organic pollutants. A potentially large amount of rubber crumbs is lost from soccer fields, entering the environment directly or through the waste water stream and subsequently the ocean. A broad variety of harmfull contaminats was identified in both rubber and leachate. The marine leachate is toxic to plankton, and the main additives are currently undergoing identification in 1) the crumb rubber, 2) the leachate and 3) the exposed copepods. Effects on crabs will be investigated in 2018.