Bundesanstalt für Materialforschung und -prüfung

Sicherheit in Technik und Chemie

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INVESTIGATION OF SORPTION OF ENVIRONMENTAL POLLUTANTS TO VIRGIN AND AGED MICROPLASTIC

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Motivation

- increasing plastic consumption, plastic products in our environment worldwide
- plastic fragments < 5 mm = Microplastics (MP)
- unknown sorption effects of environmental pollutants on microplastics

Creation of realistic sorption scenarios with relevant parameters

➡ choice of proper materials to simulate natural occuring MP

➡ extensive characterization of the materials

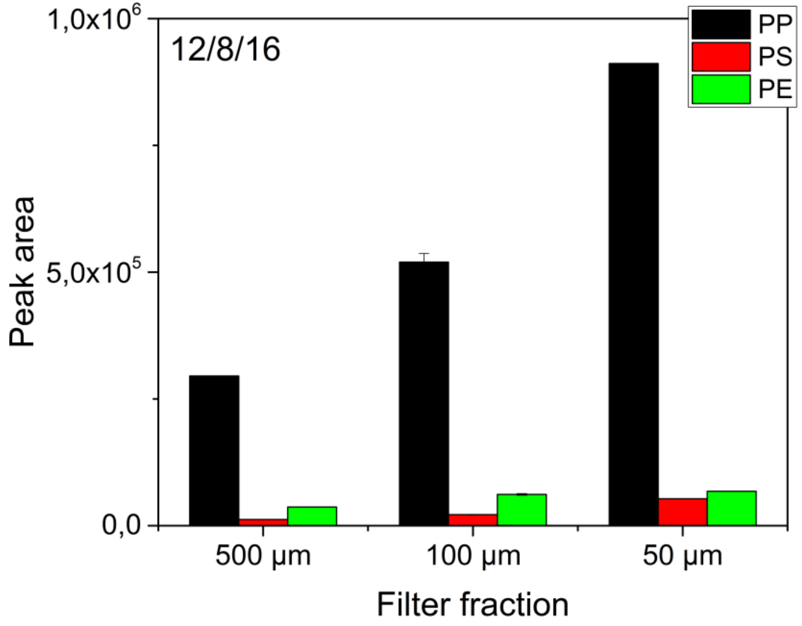
Identification of relevant polymer types

Sampling by M. Ricking, C.G. Bannick, German Environment Agency

detection of polymers in a sewage effluent

analytical method:
TED-GC-MS

screening for: PS, PP, PE, PET, PA



➡ **PP, PS, PE are of environmental relevance**

TED-GC-MS

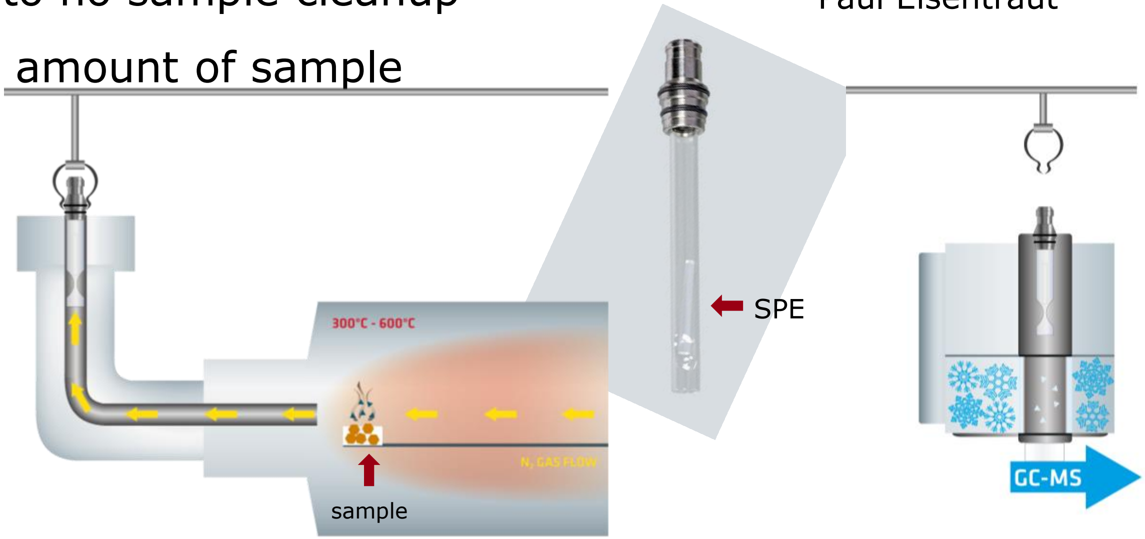
Thermal**E**xtraction**D**esorption-**GC-MS**

- identification via decomposition products
- fast analysis
- little to no sample cleanup
- large amount of sample

E. Dümichen, Fast identification of microplastics in complex environmental samples by a thermal degradation method, 2017, *Chemosphere*, 174, 572–584.

Dr. Erik Dümichen

Paul Eisentraut



Selection of the sorption materials

detected polymers in sewage effluent: PP, PE, PS

density below water: PE, PP
close to water: PS
above water: PA, PET, PVC

PP, PS,
PA instead of PE

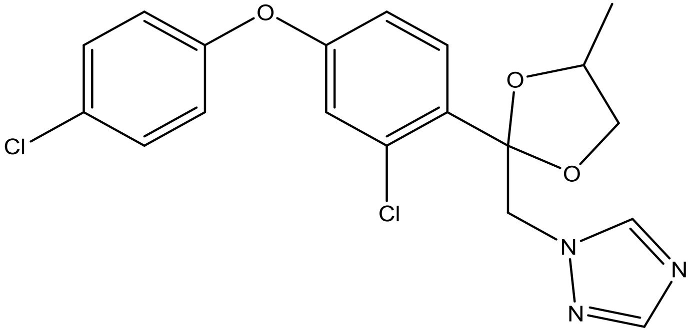
literature confirmed foundings

source	sampling	analytics	Identified polymer species
Gregory 1978	Pacific Ocean (NZ)	FTIR	PE, PP
Thompson 2004	Atlantic Ocean (UK)	FTIR-microscope	PE, PP, PA, PES, Acryl
Reddy 2006	Indian Ocean (Ind)	FTIR	PU, PA, PS, PES
Frias 2010	Atlantic Ocean (P)	FTIR-microscope	PS, PE, PP
Browne 2011	various	FTIR	PES, PP, PE, PA, Acryl
Claessens 2011	Atlantic Ocean/ North Sea (B)	FTIR	PS, PP, PA, PE, PVAL
Hirai 2011	Pacific Ocean	NIR	PE, PP
Murray 2011	Atlantic Ocean (UK)	RAMAN	PE, PP
Imhof 2013	Lake Garda (I)	RAMAN	PE, PP, PS, PVC, PA
Nor 2014	Singapore	FTIR	PP, PVC, PA
Lusher 2014	North East Atlantic Ocean	RAMAN	Viscose, PES, PA

Selection of the analyte-triacole fungicides

- one of the most used organic fungicides (market share 20 %)
- chiral
- non-polar
- percieved as persistent in soil

Difenoconazole



Specification

pKa	1.07
logP	4.36
water solubility	15 mg L^{-1}
analysis	GC-MS

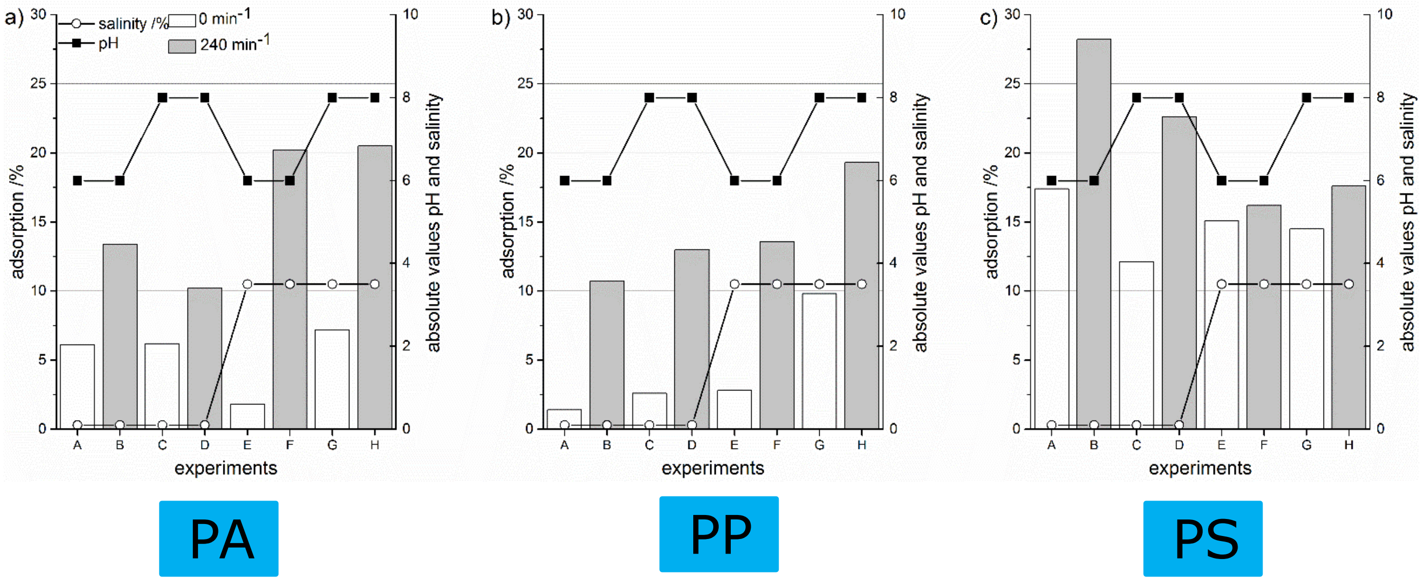
➡ **Investigation of sorption of difenoconazole on PP, PS and PA**

Sorption experiments of difenoconazole

	pH	salinity	agitation
a	6	0.1 %	0 min^{-1}
b	6	0.1 %	240 min^{-1}
c	8	0.1 %	0 min^{-1}
d	8	0.1 %	240 min^{-1}
e	6	3.5 %	0 min^{-1}
f	6	3.5 %	240 min^{-1}
g	8	3.5 %	0 min^{-1}
h	8	3.5 %	240 min^{-1}

- full factorial design
- **1 g MP**, V=50 mL, c=0.02 mg L^{-1}
- adsorption time **24 h**
- sorption has been **corrected with blank values** (Sorp. on glass etc.)
- 2-3 replicates per point
- quantification of difenoconazole via GC-MS

Adsorption of Difenoconazole on virgin MP

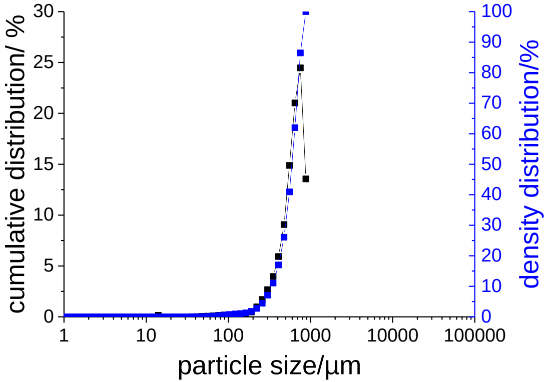


- high effect of agitation
- pH and salinity of minor importance
- highest adsorption on PS

Simulation of aging processes

cryo-milling of PP

particle size distribution

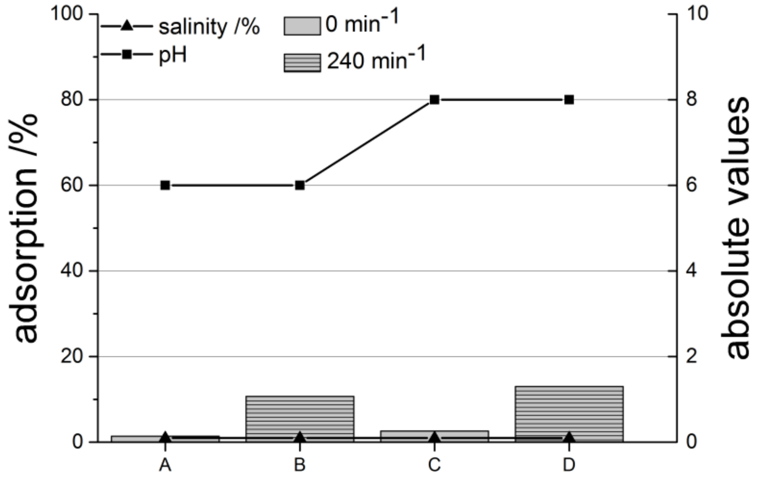


➡ enlargement of the surface: factor 5-14

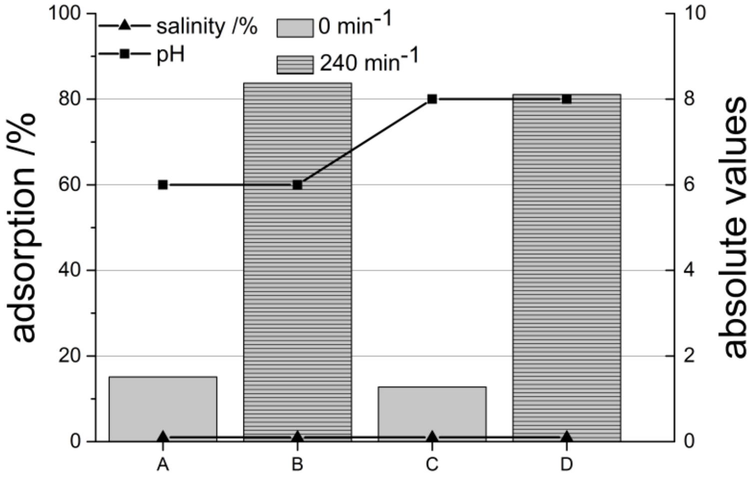
➡ environmental relevance of the sizes

Influence of particle size

virgin PP



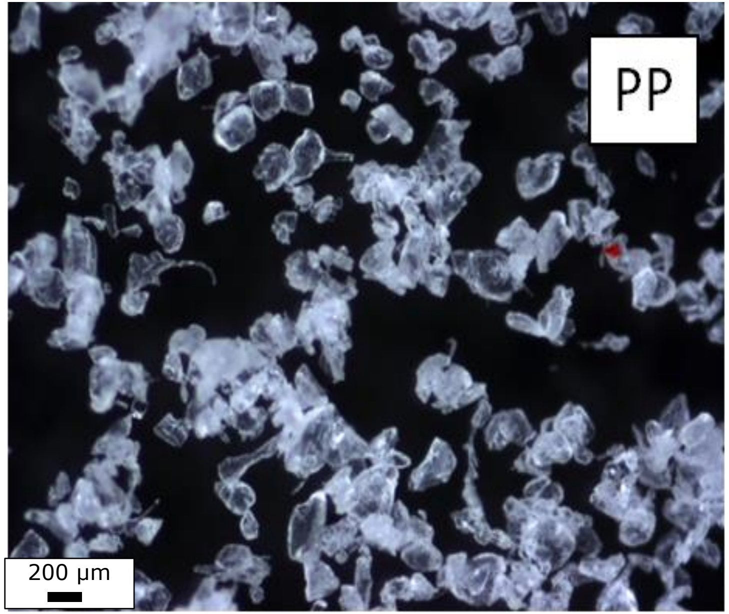
milled PP



- smaller particle size leads to higher sorption effects (factor of ~4)
- minor effect of pH and salinity

Characterization of the particles

Photomicrograph of milled PP



- high shape inhomogenity after milling
- spheric & non-spheric particles)
- **low T_{glass} of PP (0-20 °C)**

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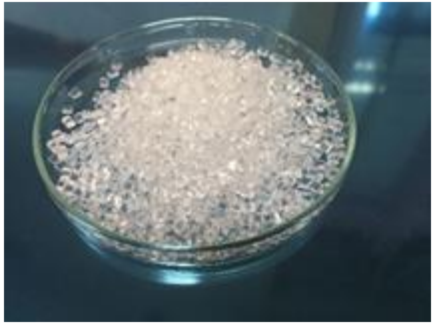
- both particle size and shape affect sorption behaviour

Simulation of aging processes

- PA easy to age through breaking of polymer chains
- aging by UV-radiation time consuming

➡ simulation via chemical treatment

virgin PA

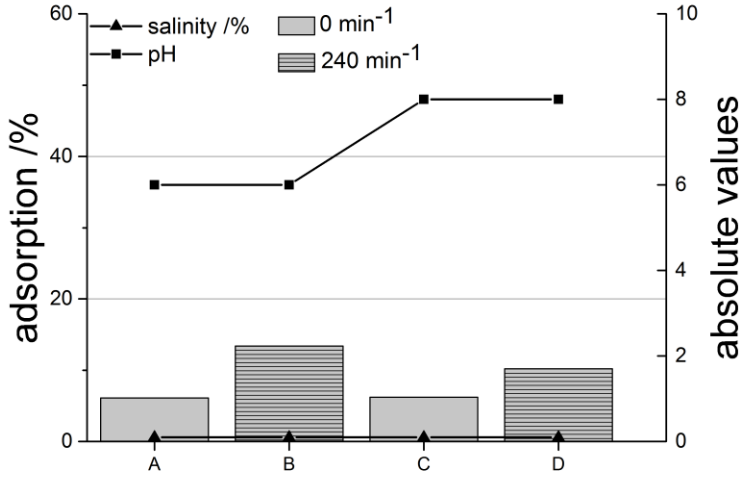


12 % HCl,
20 % acetone

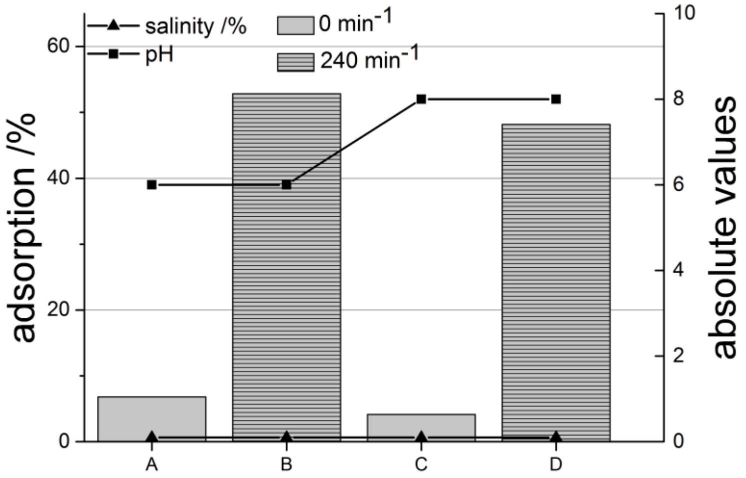
PA flakes after treatment

Results of sorption on aged PA

virgin PA



acid treated PA

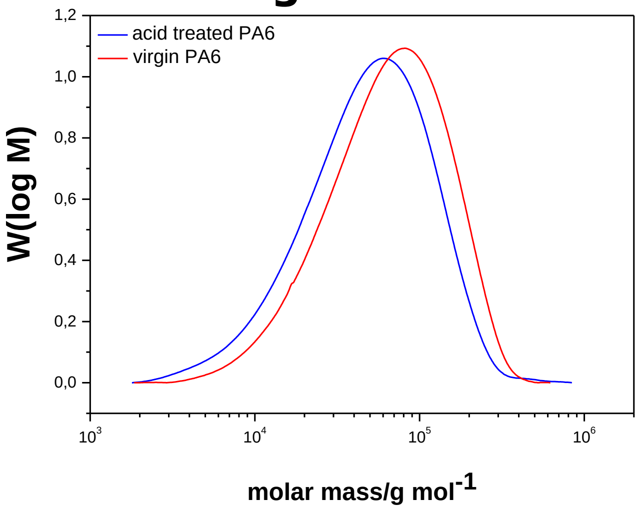


- aging leads to higher sorption effects (factor of ~3)
- small effects of pH and salinity

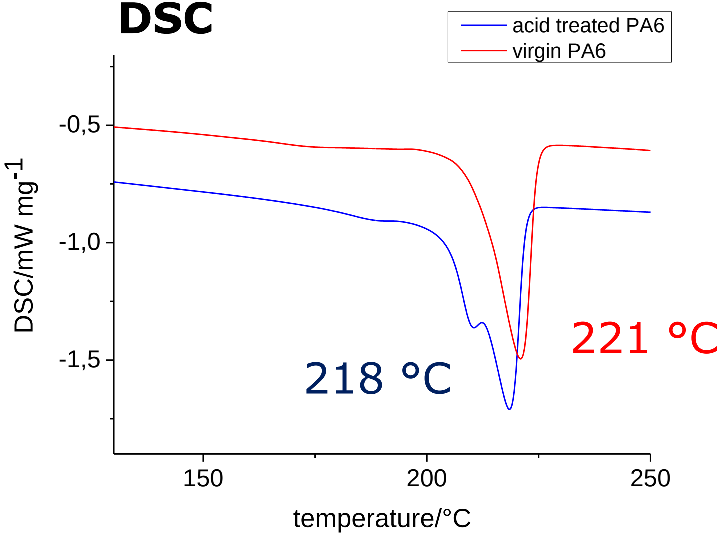
Characterization of PA6

comparison of virgin PA & acid treated PA6

GPC-elugrams



DSC

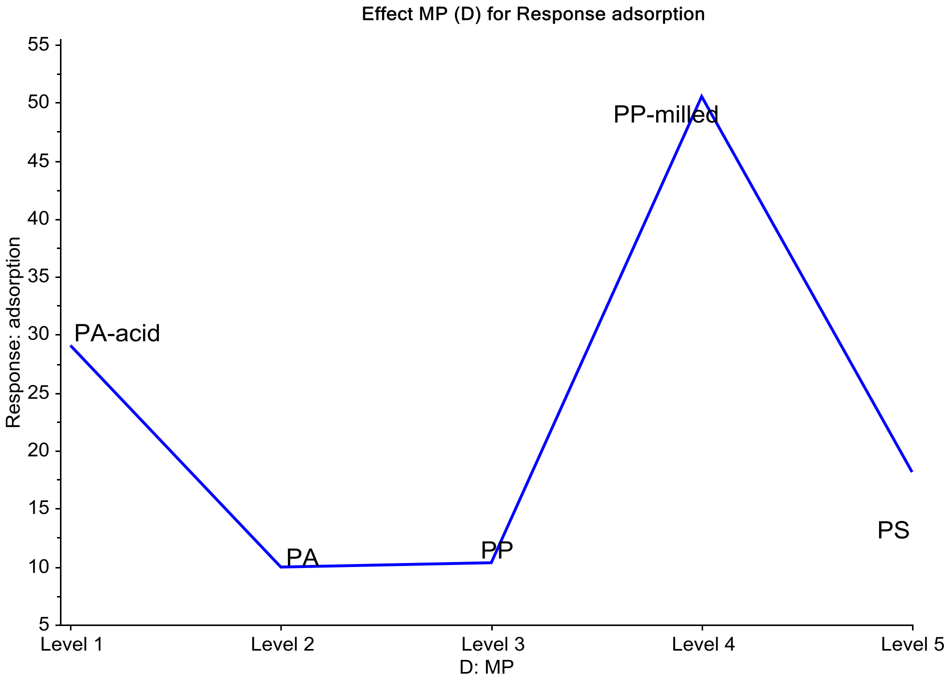


reduction of molar mass

melting peak ➡ changed crystal morphology

➡ **more sorption, but effect less significant than particle size**

Results of ANOVA



design „treatment"

- **milling of PP:** strongest effect
- **acid treatment** on PS and PA-acid: similar

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results of ANOVA confirm results of graphic evaluation

Summary

- sorption of difenoconazole on all selected polymers
- effects of pH, salinity and agitation were evaluated by factorial design
- strongest effect of agitation, whereas pH and salinity are negligible
- relevant: choice of polymer type and characteristics:
    - amorphous PS sorbs stronger than semi - crystalline PP and PA
    - small PP particles sorb more difenoconazole than granulate - but difficult to characterize in model experiments
    - aged PA sorbs more than fresh, because of changed material morphology and possible increased absorption

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Parts of this presentation are already published:

Goedecke C, Mülow-Stollin U, Hering S, Richter J, Piechotta C, et al. (2017) A First Pilot Study on the Sorption of Environmental Pollutants on Various Microplastic Materials. J Environ Anal Chem 4: 191.

Thank you all for your attention!