Plastic and Restricted Heavy Metals

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Plastic has become an integral part of our daily life and its use is increasing. In 2014 the worldwide production has reached an all time high of 311 million tons. Single use-packaging, mainly food, accounts for almost 40% of the total production in the EU. Modern plastics for food packaging have to be safe (EU Commission Regulation, 2011), but is this always the case? In PET, used for instance in bottles and tea bags, a toxic leftover of the catalyst Sb_2O_3 can be found. These leftovers could migrate from plastic into the beverage. Could the inheritance of the past contaminate the future? Carbon-based plastics are thermodynamically metastable and will degrade over time. Heavy metals are firmly bound in plastic but degradation could accelerate migration of heavy metals. In the past the Life Cycle Assessment was linear: after usage plastic became waste and ended mainly as landfill or thermal recycling. Under consumer and political pressure the EU indicated that it has to become a circular economy. Plastics of durable applications, like cars, electronics, and crates, make recycling more difficult. During their functional life new regulations have been introduced. In the EU several regulations have been developed over the past decades, the recycled raw materials of recyclates could be contaminated with the inheritance of the past. Nowadays plastic is found littering the environment in large quantities. The ingestion of plastic by seabirds is best known and monitored, but the phenomenon of ingesting plastics is widespread among all marine biota (Kühn et al., 2015). New investigations prove that plastics loaded with heavy metals are found in the environment, which when ingested by wildlife may pose specific additional toxicity risks which we investigate in the JPI Oceans PLASTOX project.

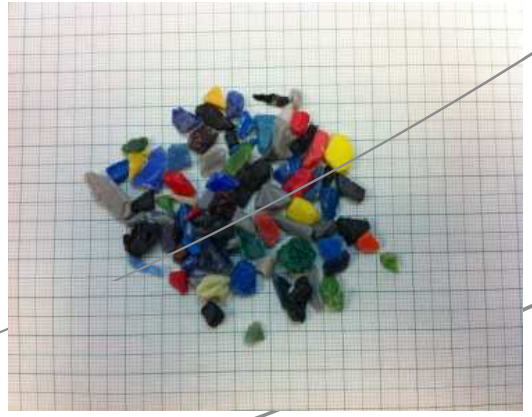
REFERENCES

EU Commision Regulation, (EU) No 10/2011 of 14 January 2011 on plastic materials and articles intended to come into contact with food. http://eur-lex.europa.eu/legal-content/EN/ALL/?uri = CELEX%3A32011R0010.

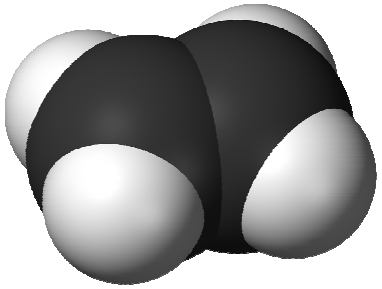
Kühn, S., Bravo Rebolledo, E.L., Van Franeker, J.A., 2015. Deleterious effects of litter on marine life. In: Bergmann, M., Gutow, L., Klages, M. (Eds.), Marine Anthropogenic Litter. Springer, Berlin, pp. 75–116, http://edepot.wur.nl/344861 (includes supplement).

MICRO 2016. Fate and Impact of Microplastics in Marine Ecosystems.

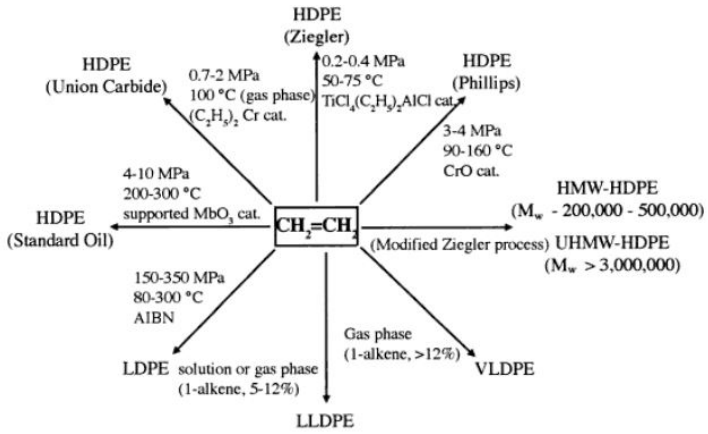
Plastic and restricted heavy metals



Modern Plastics: Tailor made



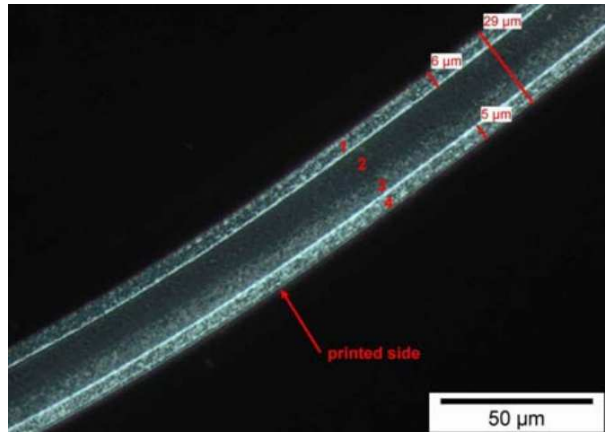
Polyethylene is the most common plastic. More than 80 million tons are produced yearly. Polyethylene is a versatile product.



By adjusting the reaction conditions and catalyst, many subclasses can be produced with special properties.
Modern plastics are tailor made

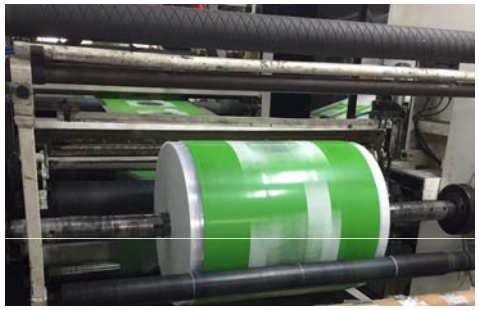
Modern equipment can produce foil of several layers (up to 13 or more).

In the example each layer consists of a special modified LLDPE (Linear Low Density Polyethylene).



Printing pristine foil

Often the pristine foil is printed. Modern inks are often based on metals. A small part, the edges becomes waste and will be recycled (post-industrial recyclates).



ICP-OES analyses were carried out of the pristine and recycled pellets:

Element	Conc. (ppm)	Element	Conc. (ppm)
Ca	10	Ti	6
S	16	Zn	4

Element	Conc. (ppm)	Element	Conc. (ppm)	Element	Conc. (ppm)
Al	279	K	63	S	223
Ba	371	Mg	178	Sb	5
Ca	6836	Na	113	Ti	171
Cu	16	Ni	16	Zn	387
Fe	50	P	50	-	-

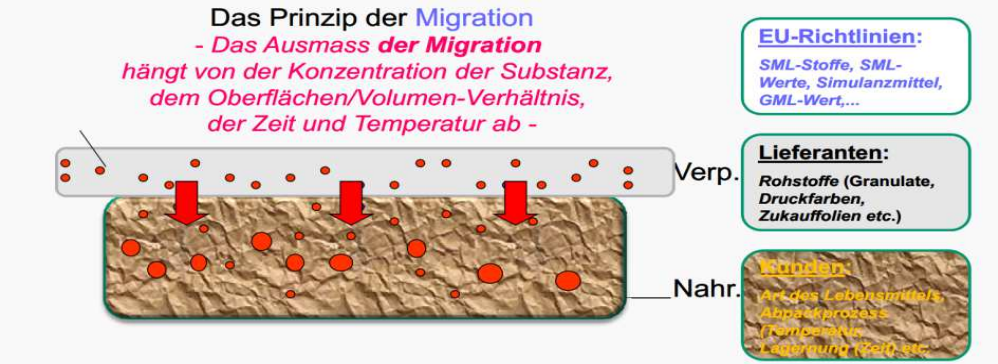
The recycled pellets aren't re-usable for food packaging.

Unknown are the migration effects of the inks.

Migration of catalyst Sb_2O_3

PET is a much used material in food packaging. For the polymerisation of PET Sb_2O_3 is the most used catalyst (cheap).

Usually the leftover of Sb_2O_3 in PET is 200 – 250 ppm.



Sb_2O_3 isn't chemically bound in the plastic matrix and can migrate into the food of beverage.

Among other things heat accelerates the migration.
First experiments showed that the migration of Sb2O3 of PET teabags exceed the drinking water standard[1].

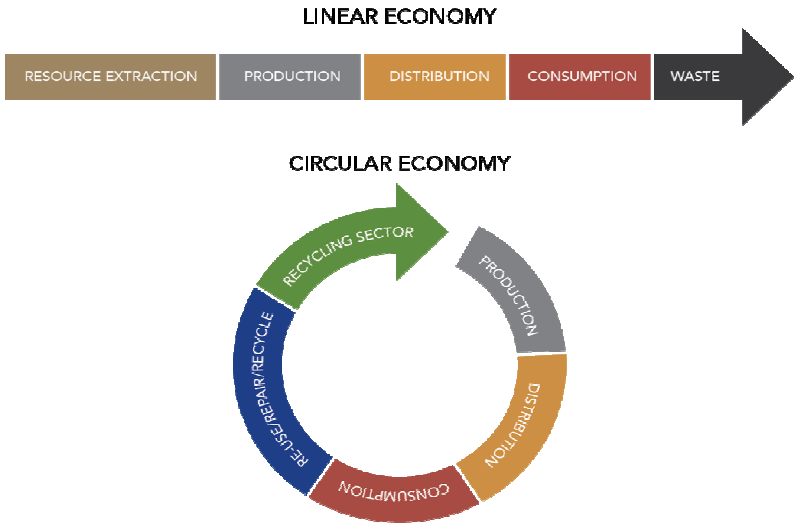
[1]*Antimony in breakfast tea; M. Egelkraut-Holtus, J. Knoop, M. Ortlieb*

EU Regulations and circular economy

Worlwide the following heavy metals are nowadays limited:

Cadmium: max. 100 ppm
Lead: max. 1000 ppm
Mercury: max. 1000 ppm
Chrom VI: max. 1000 ppm

In the EU these limitations are described in REACh (1907/2006 and RoHS /2015/863)



Almost 40% of the produced plastic in the EU is used for packaging. The plastic becomes waste after usage. The EU wants to change from a linear economy to a circular. More than 65% of the plastic has to be reused in 2030[2].

[2]*Closing the loop New circular economy package; European Parliament*

Recycling and the inheritance of the past

Recycling of more durable post consumer apllications: crates:

This yellow crate contains about 2000 ppm cadmium (limit 100 ppm).

Solution of the recycling industry:

dillution with other materials without cadmium.

Element	Conc. (ppm)	Element	Conc. (ppm)	Element	Conc. (ppm)
Al	183	Fe	223	S	168
Ba	173	K	15	Se	10
Ca	1208	Mg	87	Sr	6
Cd	116	Na	107	Ti	102
Co	7	Ni	7	Zn	45
Cr	29	P	18	-	-
Cu	10	Pb	50	-	-

Recycling and the inheritance of the past

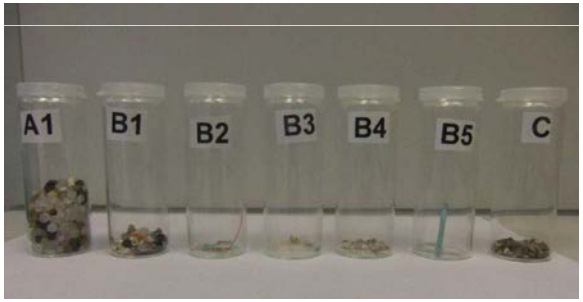
Automotive: the recycled material contains more than 1100 ppm lead (limit 1000 ppm).

Electronics: recycled material contains more than 250 ppm cadmium. Also a flame retardant, based on bromine and synergist Sb2O3, was found in high concentrations.

In addition to PE and PP, we find heavy metals mainly in styrene copolymers (including ABS) and PVC.

The inheritance of the past: environment, beached

Regulary on the beaches pellets and other plastic waste is found.

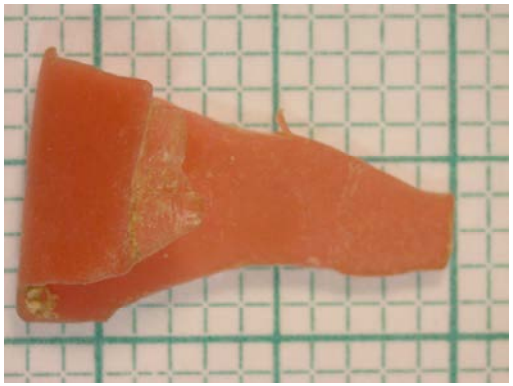


Some of these pellets were investigated on heavy metals. The yellow pellets contain about 3800 ppm cadmium.

The black pellets are likely the so called Bio Beads, used in wastewater treatment (mainly USA and some in the UK).

The inheritance of the past: environment, eaten

The stomach content of beached fulmars is further investigated with FTIR-ATR and EDX-RF. Both methods are non-destructive. Some remarkable results:

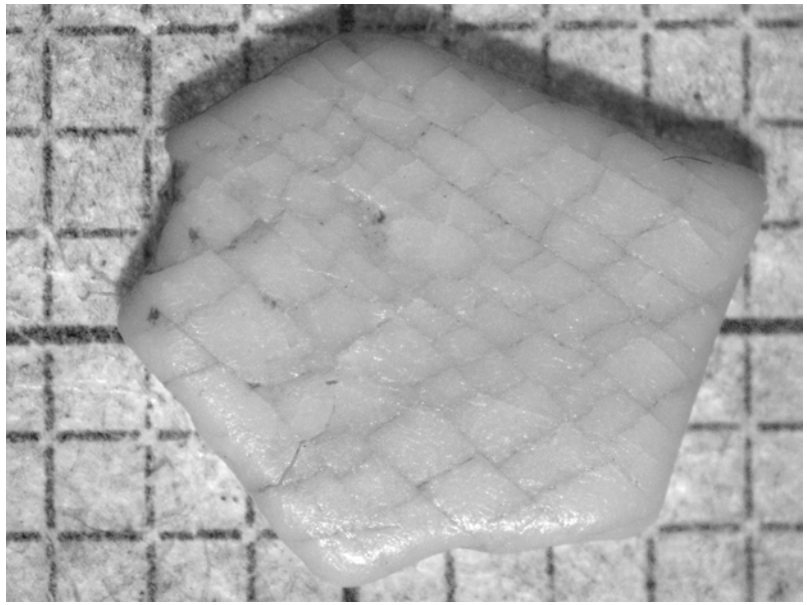


Red fragment:
2171 ppm cadmium

Blue fragment:
130 ppm lead

A lot is unknown……..

Known is that heavy metals like cadmium and lead, for normal use, are firmly bound in the plastic matrix.



Unknown is the migration of heavy metals into the environment of degradating plastic.

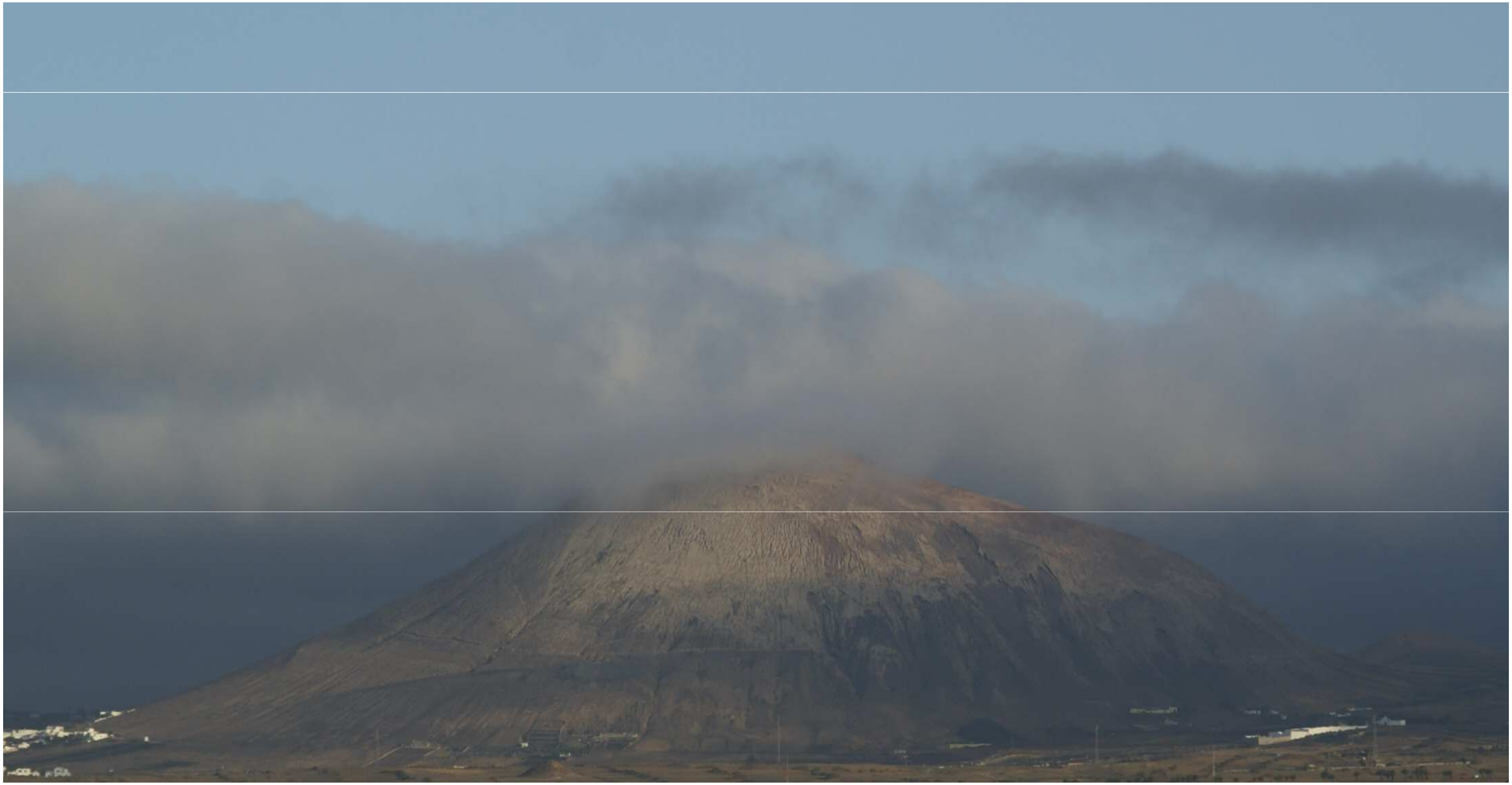
This moment these effects are more closely investigated by the PLASTOX Project (JPI Oceans) see also Poster 95410.

SHIMADZU

IMARES WAGENINGEN UR

CARAT

Thank you!



Questions?