B13

Environmental sustainability of the use of pesticides. A case study: "the Po River basin"

P. Paris | Institute for Environmental Protection and Research, ISPRA | Rome | Italy
L. Citro | Institute for Environmental Protection and Research, ISPRA | Rome | Italy
T. Cornetta | Institute for Environmental Protection and Research, ISPRA | Rome | Italy
D. Esposito | Institute for Environmental Protection and Research, ISPRA | Rome | Italy
S. Giardina | Institute for Environmental Protection and Research, ISPRA | Rome | Italy
S. Giardina | Institute for Environmental Protection and Research, ISPRA | Rome | Italy
G. Maschio | Institute for Environmental Protection and Research, ISPRA | Rome | Italy
E. Pace | Institute for Environmental Protection and Research, ISPRA | Rome | Italy
R. Pacifico | Institute for Environmental Protection and Research, ISPRA | Rome | Italy
D. Parisi Presicce | Institute for Environmental Protection and Research, ISPRA | Rome | Italy
D. Romoli | Institute for Environmental Protection and Research, ISPRA | Rome | Italy
S. Ursino | Institute for Environmental Protection and Research, ISPRA | Rome | Italy
DOI: 10.1481/icasVII.2016.b13c

ABSTRACT

Pesticides (plant protection products and biocides) are among the best regulated chemicals in Europe. An in-depth risk assessment is carried out before the placing on the market, also the final stage of the life cycle is regulated, with the definition of non-hazardous residues in food and environment. Recently it has also been regulated intermediate the life cycle stage, the use, with a series of measures to improve agricultural practices minimizing the use of chemicals, to protect water bodies and sensitive areas, to properly train the operators. Nevertheless, the monitoring shows a widespread pesticide contamination in surface and groundwater (GW). It seems, therefore, that the regulatory framework or at least its implementation is not fully adequate to protect the environment and human health.

The report presents a study of the contamination of the Po basin, the most important in Italy, both for its size and for the intense human activity, with particularly intensive agriculture with high input of pesticides. The considerable amount of data arising from an extensive monitoring network, allows to study pesticide contamination and its evolution since 2003.

Chemical pollution is one of the main factors considered in the approach "planetary boundaries", recently proposed. The "planetary boundaries" is identified as the boundaries that define the safe operating space for humanity with respect to the Earth system and are associated with the planet's biophysical subsystems or processes, (Rockström, J. et al. 2009). Unlike other anthropogenic pressures acting on a global scale, the complexity of chemical pollution has not yet possible to identify a sustainability limit.

Taking into account the fact that it is simplistic to analyze the problem on a regional scale, as large and important it may be, because you cannot ignore the long range transport of contamination, the study aims to contribute to understanding the capacity of' environment to respond to human disturbance, returning to the previous conditions (the phenomenon of resilience). For this purpose, the study focused on residual contamination of a banned pesticide in Italy and in Europe for several years (atrazine). A first analysis of the results suggests that the environmental response to a chemical stress is extremely slow and the return to the initial undisturbed conditions is not at all obvious. This requires a reflection on the actual environmental sustainability, which should not rely only on the comparison with the acceptable concentration limits.

Keywords: pesticides, planetary boundaries, water pollution

PAPER

1. Introduction

Pesticides are chemicals used to control weeds, insects and other pests in agricultural areas and as biocides in many other activities. Despite the acknowledged benefits, their use raises concerns in terms of possible adverse effects on human health and environment. Most of them are synthetic molecules conceived to kill harmful organisms and therefore they are generally hazardous to all living organisms exposed.

European regulatory framework addresses the risk raising in all life cycle stages of pesticides: production, use, residues in food and environment, nevertheless monitoring data show a diffuse pollution of surface water (SW) and groundwater (GW). Despite the well defined Regulatory framework, the national monitoring results, show a widespread contamination in water. In particular in 2014 pesticides were found in 63.9% of 1284 monitoring points, in surface waters and in 31.7% of 2463 points in groundwater as reported in the National report on pesticides in water (ISPRA, 2016).

The chemical pollution is one of the major anthropogenic factors used as reference in the recent years to develop the "planetary boundaries" approach, to identify a safe operating space for humanity with respect to the Earth system (J. Rockström et al. 2009) in which humans can continue to develop and thrive. Respecting these boundaries would greatly reduce the risk that anthropogenic activities could inadvertently drive the Earth System to a much less hospitable state. Since its introduction, the proposed approach has attracted interest and discussions within the policy, governance, and business sectors. A scientific debate is on-going on the criteria to identify the kinds of chemical substances that are likely to have influence at the global scale (Scheringer M. Et al. 2012; Strempel S. et al, 2012).

The paper aims to provide a contribute analysing the sustainability of pesticide pollution at regional scale. Bearing in mind that it is not possible to ignore the global impact, as e.g. the long range transport, the study analyses the contamination of the Po River basin, the most important in Italy, where intense industrial and agricultural activity are present. Data collected since 2003 through an extensive monitoring network allow to analyze the evolution of pesticide pollution. The study focused on residual contamination of atrazine, an herbicide banned from several years. This can be useful to understand the environment ability to respond to anthropogenic disturbance in restoring the previous conditions (resilience phenomenum).

2. Regulatory framework

The European regulatory framework covers the risk raising in all life cycle phases of pesticides. According to the Regulation (EC) No 1107/2009, substances are evaluated to prove the safety for humans and the environment before the placing on the market. Directive 2009/128/EC, on sustainable use of pesticides, aims to reduce risks in the use-phase with a series of measures to improve agricultural practices, minimizing the use of chemicals, protecting water bodies and sensitive areas, properly training the operators. Regulation (EC) No 396/2005 deals with the end of the life cycle of pesticides, establishing the maximum residue levels (MRLs) in foodstuffs, with the aim of limiting the exposure of consumers.

Moreover a number of other legislative acts regard pesticides. In particular, the Water Framework Directive (WFD) (Dir . 2000/60/EC) and daughter directives aim to ensure the water quality, identifying, among other things, a list of " priority substances " and setting limit values for environmental protection.

Despite the well-defined regulatory framework, monitoring data show a widespread pollution of surface and ground water. This highlights an inadequacy of the regulations or their implementation. In particular, a critical issue is the environmental exposure estimation. The forecasting models used in risk assessment do not always seem adequate to predict the environmental fate and exposure of substances. They lack of realism, as recognized by the scientific committees of the European Commission "to face the new challenges for risk assessment"(SCHER, SCENIHR, SCCS, 2013). Another critical aspect is the risk assessment of substances , such as persistent , bioaccumulative and toxic , or as endocrine disruptors,, which do not seem to have a threshold effect. In this case it is very difficult to recognize a safe level in the environment, and even very low concentrations could pose a risk. Furthermore, the regulatory risk assessment does not take into account the effects of mixtures.

Therefore, monitoring is a useful tool to check the real impact of pesticides on the environment and identify, through a retrospective analysis, the critical issues not properly addressed in the authorization process.

3. Case Study - Po river Basin

Po basin is the largest in Italy. The river (652 km length) flows through from west to east. The catchment area measures about 74,000 sq km of which approximately 71,000 are located in Italy, the rest in Switzerland.

Approximately 16,000,000 inhabitants live in the catchment area. Considering the density of the productive activities, the infrastructure and the water resources utilization, the Po Basin is the most important area in the Italian economy. Agriculture occupies over half of the basin area, with high chemical inputs (fertilizers, pesticides) in the lowland and in the hilly areas and part of the mountain "endovallive" areas.

The basin is divided essentially into three geomorphological areas: alpine area, in the north and north-west; the Apennines in the south; the plain area (Padana plain), which characterizes the entire course of the river, until the Adriatic Sea.

The average annual rainfall on the basin is 1,108 mm. The corresponding water volumes are therefore 77.7 x 109 m3/year. The average annual outflow corresponds at 664 mm, equivalent to about 46.5 x 109 m3/year, which represents 60% of inflow and is equivalent to 1,470 m3/s.

The river has 141main tributaries, coming from the Alps and the Apennines. The basin includes many lakes, the most important of which (Garda, Como and Maggiore) are located in the Lombardy region and are fed by alpine mountain streams.

The aquifers are fed mainly in the high plain near the mountain, whose geology consists mostly of coarse materials. In the pre-Alpine plains and in the Apennines the aquifer, in correspondence with impermeable barriers, emerges as springs ("risorgive"). The central part of the plain, both north and south, consists of fluvial deposits that gradually become finer and less permeable and host confined aquifer. The groundwater speed in the water table high plains may reach tens of meters per day, instead in the deep under pressure aquifers speeds are very low until the "stagnation " for certain very deep aquifers.

Monitoring network of pesticides in the Po basin includes 1,035 sites in groundwater and 570 in the surface water. Samples were collected every month in surface water and at least twice a year on the groundwater.

4. Atrazine

Before the ban, atrazine was one on the most widespread herbicide used in Italy, applied on corn and sorghum, but also for urban and industrial areas. A reasonable estimate of the quantities used in the Po valley is about 1,000 tons /year, for about 25 years. The substance is an herbicide of the triazine class; it has a selective, systemic action with residual and foliar activity and inhibits photosynthesis.

Atrazine was detected in the atmosphere, also far away from the use areas. In the atmosphere it tends to exist more in the particulate and precipitation is the primary mechanism for removal. Volatilization from water surfaces is not expected to be an important fate process based on a Henry's Law constant value.

It is expected to have high to slight mobility in soil, based upon a log Koc range of 1.96 to 3.38. Soil pH may affect the transport of atrazine (sorption to soils increases with pH decreasing). Atrazine is not expected to volatilize from dry soil, if released into water may adsorb to suspended solids and sediment based on the Koc value range.

According to Mackay I model (Finizio A., 1997), atrazine mainly distributes in water (about 90% of the amount released to the environment), fractions of the order of 4% are distributed both in soil and in sediment, little significant percentages in air and in biomass.

According to Regulation (EC) No 1272/2008, atrazine is very toxic to aquatic life, both acute and chronic effects (Aquatic Acute 1 – H400, Aquatic chronic 1 – H410), may cause damage to organs through prolonged or repeated exposure (STOT RE 2 - H373) and may cause an allergic skin reaction (Skin Sens. 1 - H317).

Atrazine is in the priority list within the EU-Strategy (EC, 1999; EC, 2000) for Endocrine Disruptors (ED); it is considered ED Category 1 (evidence in organism). In particular, the substance (Norwegian Pollution Control Authority, 2005) may induce hermaphroditism and demasculinize the larynges of frogs (Hayes TB et al. 2002).

The substance is persistent and toxic, but it is not considerd bioaccumulative. According to WFD, il has been identified as "priority hazardous substance" on the basis of ED concern.

Atrazine was banned in Europe since 2004, because of widespread groundwater contamination at concentrations exceeding the drinking water limit of 0.1 µg/L. For the same reason, in Italy it had been banned since the early 90s.

Metabolites

Desethylatrazine is formed in the environment through the N-dealkylation of atrazine.

Desethylatrazine is expected to have very high to slight mobility in soil, based upon Koc values of 24 to 3000. In water, some adsorption to suspended solids and sediment is expected. Desethylatrazine has been shown to biodegrade in soils under aerobic conditions, but it is generally stable in groundwater microcosms under anaerobic conditions. According to the classification provided by companies to ECHA the substance is harmful if swallowed, causes serious eye irritation and is harmful if inhaled.

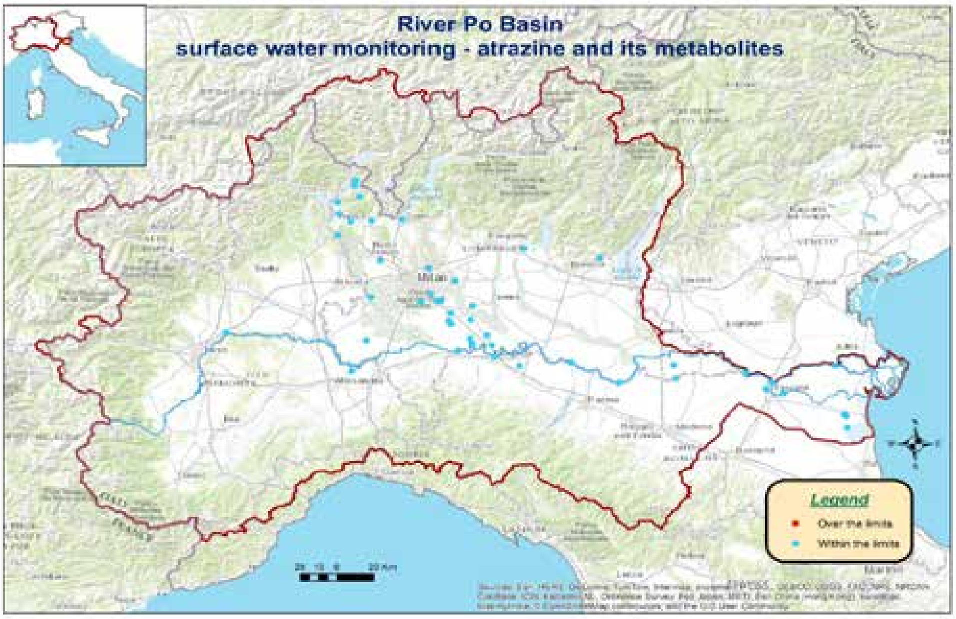
Deisopropylatrazine is formed in the environment through the N-dealkylation of atrazine. Deisopropylatrazine is more soluble than parental compound and less than deethylatrazine. The substance is not persistent to persistent in soil (half-life ranges from 32 to 172 days)and it is expected to have very high to moderate mobility based upon Koc values ranging from 28 to 130. Field studies show that it does not accumulate in the soil (Crobe A., et al, 2002). According to the classification provided by companies to ECHA the substance is harmful if swallowed, causes serious eye irritation and is harmful if inhaled.

4. Monitoring Results

Monitoring results show a widespread pesticide contamination of the Po valley, pesticides have been found in more than 70% of surface water sites and in more than 40% of groundwater sites. The triazine herbicides (atrazine, simazine, terbuthylazine and atrazine – desethyl, atrazina desisopropil, metabolites and desethyl - terbuthylazine) are among the substances most frequently detected in surface water and groundwater, often above the legal limits. With the exception of terbuthylazine, all other substances are no longer permitted in Europe.

The maps (Figure 1) shows the contamination level of atrazine and its main metabolites (atrazinedesethil, atrazine desisopropil) in the study area.

Figure 1 - surface water and groundwater contamination level of atrazine and its metabolites in Po basin (2014).



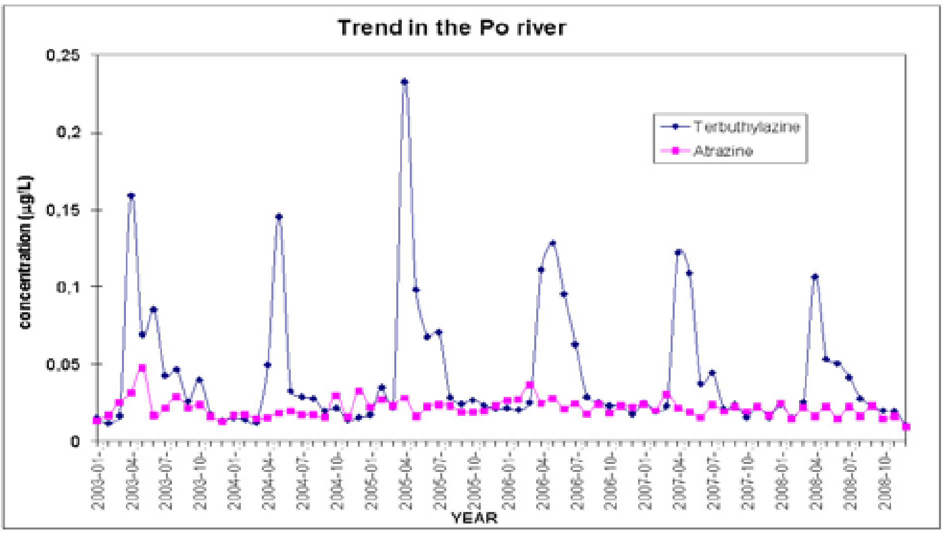
The contamination levels are referred to the limit value for the drinking water (0.1 g/L).

In 2014, atrazine has been detected in 46 sites of the surface waters (10.2% out of 453) and in 104 sites of the groundwater (10.8% out of 968). The concentration is never over the limit in the surface water and it is over the limit in the 0.7% of groundwater sites.

Taking into account that the substance has being banned for many years, the monitoring highlights a residue of a historical contamination, due to the widespread use in the past and to the environmental persistence. The detection of the its metabolites at levels generally greater than the parental substance supports the conclusion of a long-standing pollution.

Figure 2 compares the concentration trend in the Po river of atrazine and terbuthylazine, that replaced the use of atrazine after the ban. Terbuthylazine concentrations highlights a seasonal use related to an application in the spring (March–May) repeated year by year. Differently, the occurrence of atrazine shows a stable trend clearly indicating a residual contamination.

Figure 2 - Trend in the Po river of terbuthylazine and atrazine



Analysis of the Contamination Trend

The graph in Figure 3 shows that atrazine concentration (90%-ile of the medium values) in the river is significantly lower than the basin groundwater. Moreover it is highlighted that the concentration in the river decreases regularly with an asymptotic trend, while the concentration in the groundwater does not indicate any trend but ranges around a roughly constant value.

The purpose of the trend analysis is to follow how the pesticide and its main metabolites occurrence in surface and groundwater is changed over the last decade. From figure 3, it is possible to identify with a good correlation a well defined trend curve in the River and it allows to derive an half-time of about 8 years for disappearance of the parental substance. This value would trigger to a re-calculed average concentration referred to the period of the ban (early 90s) equal to ca. 1.0 g/L. This value seems to be consistent to the current average concentration of terbuthylazine in the river.

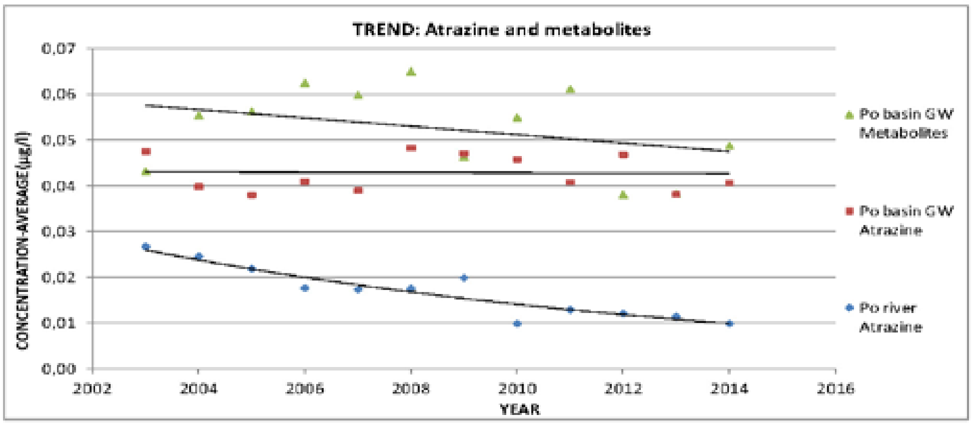
The possible explanations of the gradual decrease of the concentration in the river and the stable occurrence in the ground water are the following: the degradation of the parental substance in the groundwater is slow because lacks the degradating agents abiotic and biotic. Another possibility is that surface contamination is mainly due to the exchange with groundwater, which mainly concerns the shallow aquifer than the deep ones , well separated from the river, where the concentration is almost constant.

The stable trend of atrazine in groundwater, reasonably indicates that same situation is foreseeable for the future due to the very slow movement of the groundwaters, particularly, in the deep aquifers. The metabolites trend confirm the contribute of the overall stable contamination of the substance, once reached groundwaters.

In the surface water the contamination levels are lower than the regulatory thresholds and the Environmental Quality Standard (EQS). Nevertheless the hazourdous properties, in particular the ED property, (no-treshold) makes significant also the low measured concentrations.

The importance of very low concentration is also related to the concern for the mixture detected in the samples, for which it is still not well known the relevance for the Human Health and the environment. Infact in some samples there are mixtures up to tens of substances.

Figure 3 - Trend of atrazine and its metabolites (desethylatrazine, deisopropylatrazine)



5. Conclusion

The environmental sustainability of chemicals should be based on the capability of the environment to respond to anthropogenic stressors in restoring the previous conditions.

The present study allows to conclude that the regulatory framework does not comply the above general principle, as following summarised.

The regulatory framework seems not completely adequate to prevent a diffuse contamination of pesticides. In particular one of the critical issue is related to the exposure estimation in the authorization process. The estimations derived by models are not always representative of the real environmental behaviour of chemicals, at least on a large scale. A particular attention should be given to the substance persistence assessment. Standard information utilised seems not representative of the real persistence in the environment. Once the substances reach groundwaters, the degradation processes are very slow due to the lack of the biotic and abiotic degradation mechanisms.

The trend analyses of the occurrence in the Po basin of no more used herbicide, demonstrates that substances can persist in the environment longer than how estimated Evaluation of substances under authorization process may underestimate their ability to contaminate the environment, in particular the water compartment. It is necessary to take due account of the available measured information, considering the available monitoring data also on similar chemically substances.

Probably it is not enough cautelative to base the authorization process on the regulatory acceptable limits: e.g. concentrations in drinking water and EQS. This because some substances are considered "non-treshold" and it is not possible to define a safe concentration. Moreover the mixture concern is up to now an unsolved issue.

The reported results related to a herbicide banned since several years as atrazine can be useful to foresee the future critical issues of similar triazine substances still in use.

References

Berger J. (1990) Robust Bayesian analysis: sensitivity to prior, Journal Statistical Planning and Inference, 25, 303-328.

Cooper M. C., Milligan, G. W. (1988) The effect of measurement error on determining the number of clusters in cluster analysis, in: Data, Expert Knowledge and Decision, Gaul, W. & Shader, M. (Eds.), Springer, 3 19-328.

Crobe A., Bottoni P., Fava L., Orrù M.A., Funari E. (2002) Istituto Superiore di Sanità. Rischio di contaminazione delle acque sotterranee: schede monografiche di alcuni metaboliti di prodotti fitosanitari . Rapporti ISTISAN 02/37.

EC (1999) - Communication from the Commission to the Council and the European Parliament -Community Strategy for Endocrine Disrupters. COM (1999) 706 final

EC (2000) Directive of the European Parliament and of the Council establishing a framework for Community action in the field of water policy. Dir. 2000/60/EC.

EC (2000) - Towards the establishment of a priority list of substances for further evaluation of their role in endocrine disruption: preparation of a candidate list of substancesas a basis for priority setting. BKH Consulting Engineers, Delft, The Netherlands (on behalf of European Commission DG ENV). EC (2009) Directive of the European Parliament and of the Council of 21 October 2009 establishing a framework for Community action to achieve the sustainable use of pesticides. Dir. 2009/128/EC EC (2009) Regulation concerning the placing of plant protection product on the market. Reg. 1107/2009/EC

EC (2008) Regulation on classification, labelling and packaging of substances and mixtures.Reg. No 1272/2008/ EC.

Finizio A. (1997) Definizione di criteri di classificazione del rischio ambientale di prodotti fitosanitari, conparticolare riferimento agli effetti su organism non bersaglio. RTI 2/97-AMB-NOCS. ANPA ECHA: http://echa.europa.eu

Hayes T.B., Collins A., Lee M., Mendoza M., Noriega N., Stuart A.A., Vonk A. (2002) - Hermaphroditic, demasculinized frogs after exposure to the herbicide atrazine at low ecologically relevant doses. Proc Natl Acad Sci U S A. Apr 16;99(8):5476-80 Hansch, C., et al Leo, A., D. Hoekman (1995). Exploring QSAR - Hydrophobic, Electronic, and Steric Constants. Washington, DC: American Chemical Society. ISPRA, (2016) Rapporto nazionale pesticidi nelle acque. Dati 2013-2014. Rapporti ISPRA 244/2016

Norwegian Pollution Control Authority (2005) - A study of the priority substances of the Water Framework Directive: Monitoring and need for screening. Bergfald & Co

Po Basin Authority (2006) Caratteristiche del bacino del fiume Po e primo esame dell'impatto ambientale delle attività umane sulle risorse idriche. Po Basin Authority institutional website www.adbpo.it

Rockström J., et al. (2009) Planetary boundaries: Exploring the safe operating space for humanity, Ecology and Society 14, 32 SCHER, SCENIHR, SCCS, (2013) Addressing the New Challenges for Risk Assessment. ISSN 2315-0106. European Union, 2013. Scheringer M., Strempel S., Hukari S., Ng C. A., Blepp M., Hungerbuhler K. (2012) How many persistent organic pollutants should we expect? Atmospheric Pollution Research 3, 383–391

Steffen W., et al.(2015) Planetary boundaries: Guiding human development on a changing planet, Science

Strempel S., Scheringer M., Ng C. A, Hungerbühler K., (2012) Screening for PBT chemicals among the "existing" and "new" chemicals of the EU. Environmental Science & Technoogy. 46, 5680–5687.