清华大学圆桌会议，2020.11.21

新关注污染物环境管理方式分析

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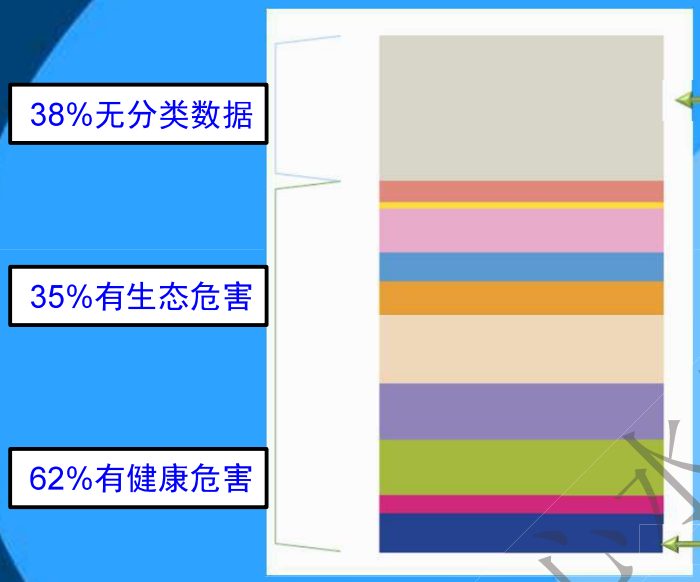
Aquality Technology

CASA 中科水质 www.casaet.com

Chemical space of known and unknown compounds

10^{60} possible chemicals <500 Da

10^{8} chemicals in CAS



38%无分类数据

35%有生态危害

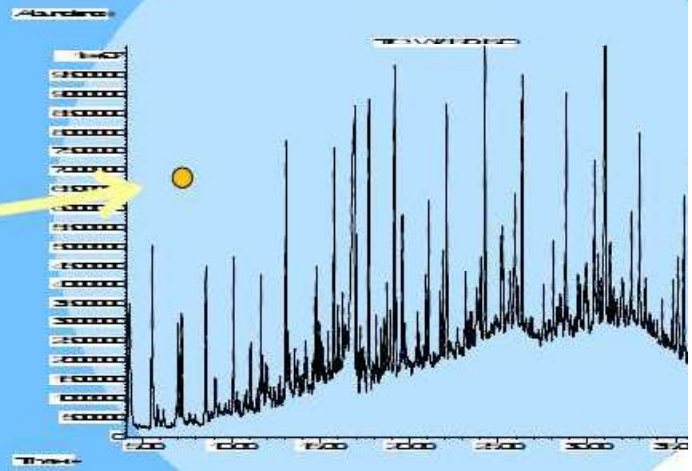
62%有健康危害

10^{5} chemicals in daily use

活跃化学品(2~4万)

三致/生殖毒性物质

10^{4} chemicals in environmental samples



45 priority pollutants (WFD)

资料来源：Werner Brake, 2016；GCO-II, 2018；EEA, 2018; C&L Inventory等

联合国教科文组织定义的新兴污染物
Emerging pollutants as defined by UNESCO

广义上的新兴污染物是指**缺乏环境监测数据**，或**尚未管控**、但是具有**已知或潜在有害生态和健康危害**的合成，或天然化学物质，或任何微生物。主要包括：

- 药品和化妆品中含有的化学物质
- 农药
- 工业化学品
- 日用化学品
- 金属
- 表面活性剂
- 工业添加剂和溶剂

对新兴污染物潜在人类健康和生态系统健康风险的认识非常稀缺，其在水源和污水中的存在情况、进入环境的途径和环境蓄积信息也十分有限。**大部分新兴污染物没有环境质量标准、水质和污水排放标准，属于当前的非管控污染物**。

UNEP-SAICM中的新关注政策议题(Emerging Policy Issues)

新关注议题	管理的理由
难降解药品类污染物(PPP)	持久性药物即使在很低浓度水平下也会导致环境和健康损害，最新研究表明许多PPP具有内分泌干扰作用，可能对生物多样性产生影响，如难降解激素类药物
高危害农药(HHP)	许多新的证据表明高危害农药对非靶标生物和普通人群和操作人员具有潜在的危害和风险，需要加快淘汰步伐
涂料中的铅	涂料中铅对人体健康有潜在危害，尽管市场上已经有许多替代产品，但是目前的政策措施不能保障其全面淘汰
产品中的化学品(CiP)	产品中的化学物质是一个多方关注的问题，需要不同国家交流产品中所含有的化学品，重点包括电子产品，玩具，建筑材料和纺织品
电子电气产品中有害物质的全生命周期管理	聚焦到电子电气产品中与鹿特丹、巴塞尔和斯德哥尔摩公约等化学物质公约有关限制性化学物质，包括产品绿色设计、电子产品的绿色制造和提高公众对电子产品危害的认识
纳米技术和纳米制造	议题目的是为合成纳米材料的健全管理开发国际化技术，管理方略和相关培训材料，提高这类材料的全球透明度。
全氟化合物及安全替代	收集和交流关于全氟化化学品的信息，并支持向更安全的替代品过渡
内分泌干扰化学物质	进一步本着开放、包容、透明的态度制定和落实OECD、UNEP和WHO关于环境内分泌干扰物的合作行动计划。
无需关注化学品	该平台是在SAICM项目的框架内创建的，得到全球环境基金资助，旨在为我们的环境和健康提供更安全的产品。

SAICM: Strategy Approach to International Chemical Management

美国环保署(OW)定义的水环境中新关注污染物
Contaminants of Emerging Concern as defined by US EPA Office of Water

美国环保署(US EPA) 采用的新关注污染物(Contaminants of Emerging Concern, CEC)这个术语是指目前尚没有环境标准，但是由于分析化学检测水平的提高而发现在自然环境中存在，并有可能在环境相关浓度下具有潜在的水生生物损害效应。

CECs是目前没有包含在常规监测项目中的污染物，但是可能是未来监管的候选对象，取决于其生态毒性、潜在的健康影响、公众认知以及在环境媒体中出现的频率。CEC不一定必须是新的化学物质。

新关注污染物(CECs)包括以下几类化学品:

- 持久性有机污染物（POPs），如多溴联苯醚(PBDEs)和全氟有机酸及其盐(PFOS/PFOA);
- 药品和个人护理产品（PPCPs），包括处方药（如抗抑郁药、控制血压用药）、非处方药（如布洛芬）、杀菌剂（如三氯生）、防晒霜、人造麝香;
- 内分泌干扰化学物质(EDC)，包括合成雌激素（如17α-乙二烯醇）和雄激素（如兽药中的特伦伯龙），自然产生的雌激素（如17β-雌二醇，睾酮），以及其他能够调节正常激素功能和在水生生物体内调节类固醇合成的化学物质（如有机氯农药，烷基酚）;
- 兽药，如抗菌素、抗生素、抗真菌剂、生长促进剂和激素;
- 纳米材料，如碳纳米管或纳米尺度的二氧化钛，对它们的环境归属或效应知之甚少。

新兴环境污染物/新关注环境污染物环境管理

环境管理者需要回答：

- 是否需要管理(对环境和人类具有不可接受的风险/社会经济代价可以接受？)
- 是否能够管理(监测方法/排放标准/质量标准/工程措施/成本效益？)
- 怎样有效管理(源头管理/过程控制/末端处理)?

- **在环境中普遍存在(环境监测技术/环境暴露数据/人群暴露数据)**
- **具有潜在环境/健康危害或风险(生态风险/健康风险/社会经济分析报告)**
- **环境管理的政策工具和控制措施(淘汰/限制/授权/标签/许可/标准/处理处置)**

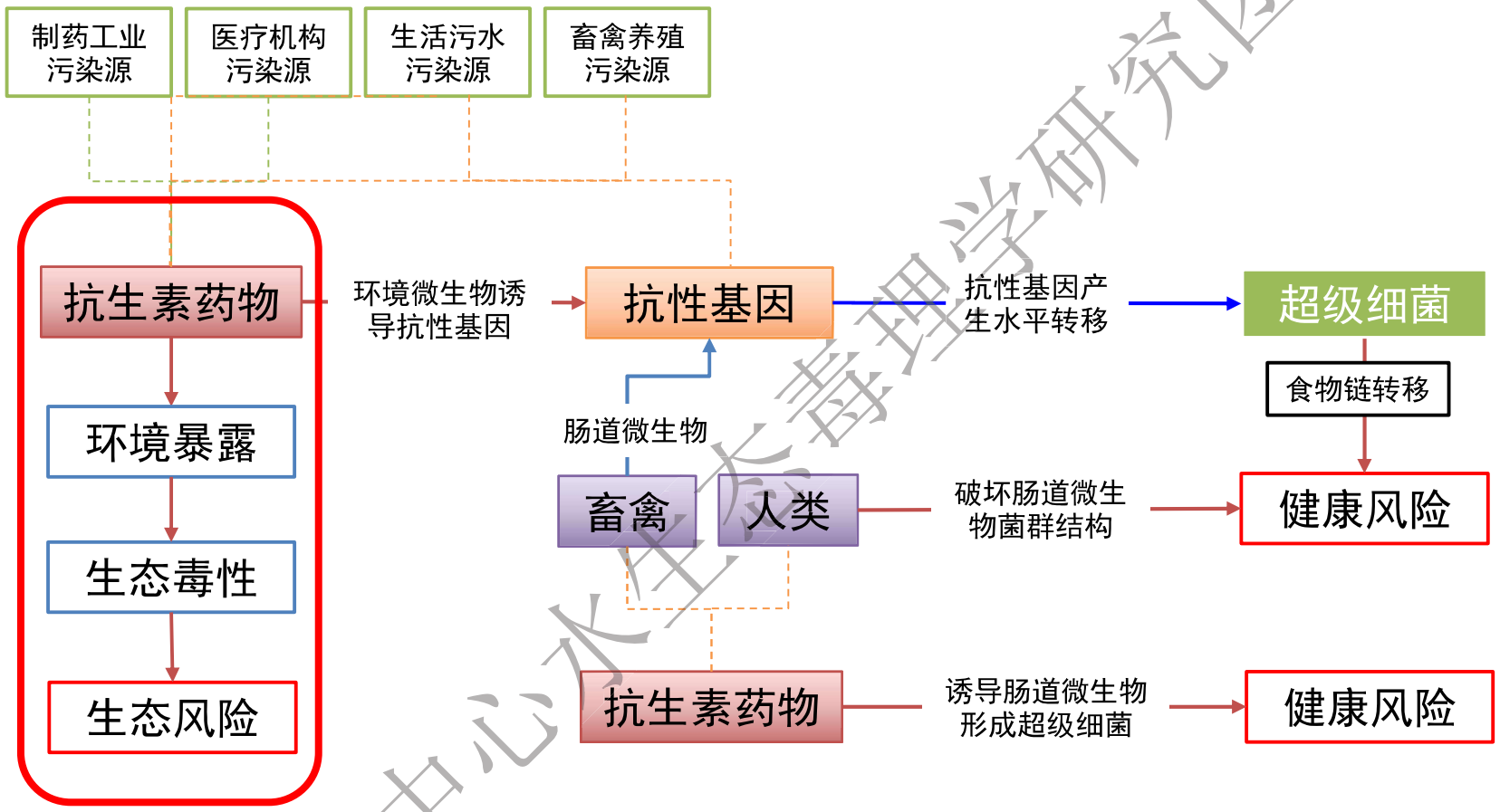
注：管理工具中的淘汰、限制和授权是化学品安全性管理的核心工具(如REACH 法规和TSCA法规)；标签制度包括地区和全球统一分类标签(如GHS和C&L)、行业组织标签(如RoHS)和绿色标签(如生态产品标签)；许可包括排放源许可(如NPDES许可证制度)和释放源登记制度(如TRI, ePRTR, jPRTR等)；标准包括环境质量标准、产品质量标准和环境表现准则(如ISO 14000)；处理处置包括废弃物处理处置、事故处理处置和环境责任法相关内容。化学品领域管理工具的选择依据风险评估报告(如RAC)和社会经济分析报告(*美国2016年新版“21世纪化学品安全法”中已经排除了社会经济报告要求)。

典型新关注(新兴)环境污染物环境管理方式分析

- 抗生素类
- 微塑料
- 全氟辛酸及其盐(PFOA)

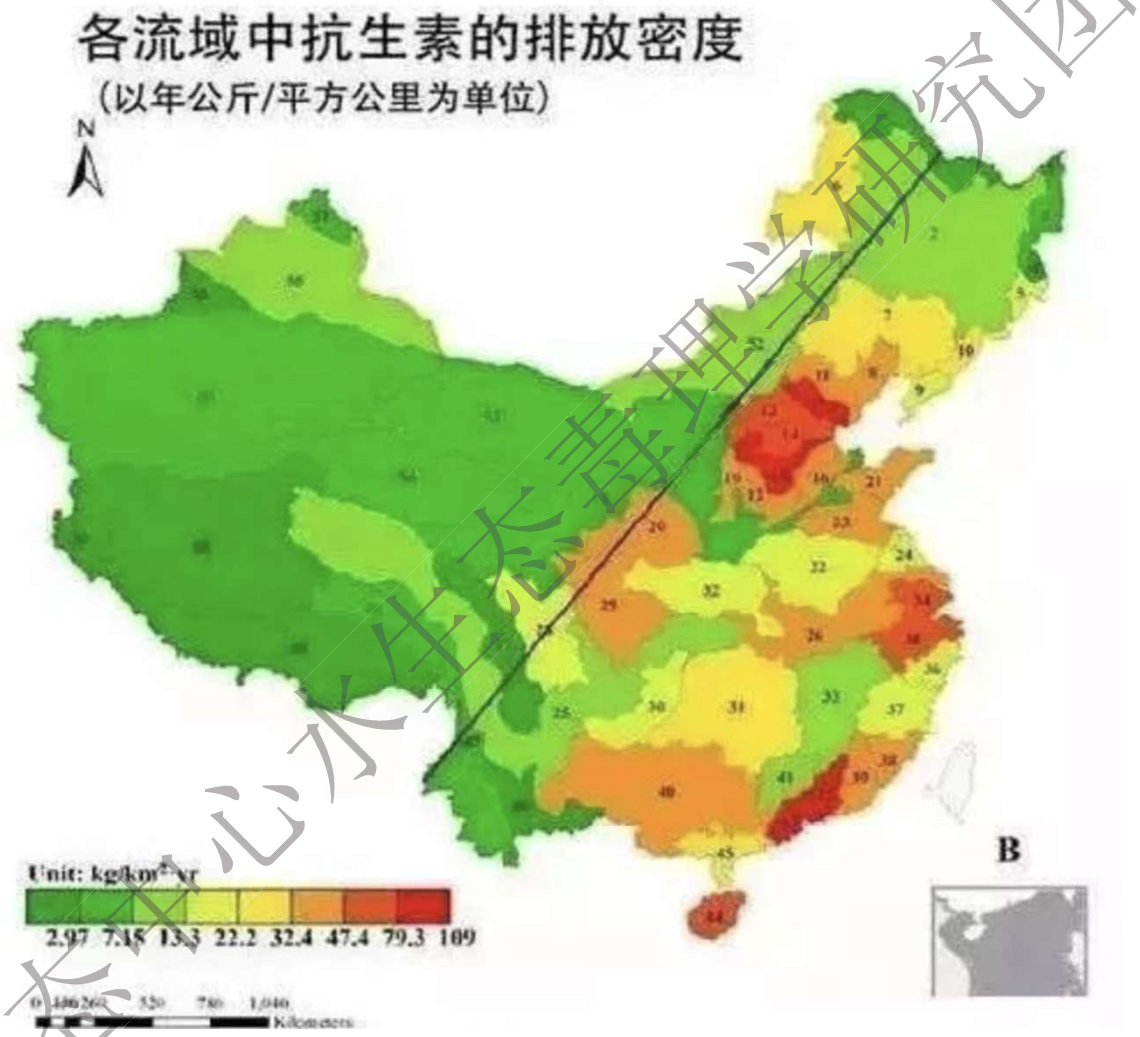
注：选择这三类新关注污染物是因为其代表性。抗生素类物质研发初期是人类用药，通常经过了大量动物实验和三期临床，因此总体上对人类是安全的，但是对野生动物的安全性数据严重缺乏；同时抗生素相关的抗药性问题很早之前就已经被发现(如四环素耐药性)，现在被抄热了。纳米材料和微塑料这类物质基本没有可用的毒性数据，因为所有规范化的测试都没有包含难溶物质，也没有标准化的环境监测方法可以遵循，因此主要是科学界撰写文章的体裁，环境管理工具的选择难度很大；全氟和多氟类物质是可能面临全面淘汰的一大类物质，也是中国化学工业主要生产和出国的大宗产品，其社会经济意义一定程度上超过了环境意义(个人观点)。

抗生素类污染物：生态和健康危害特征和风险途径分析



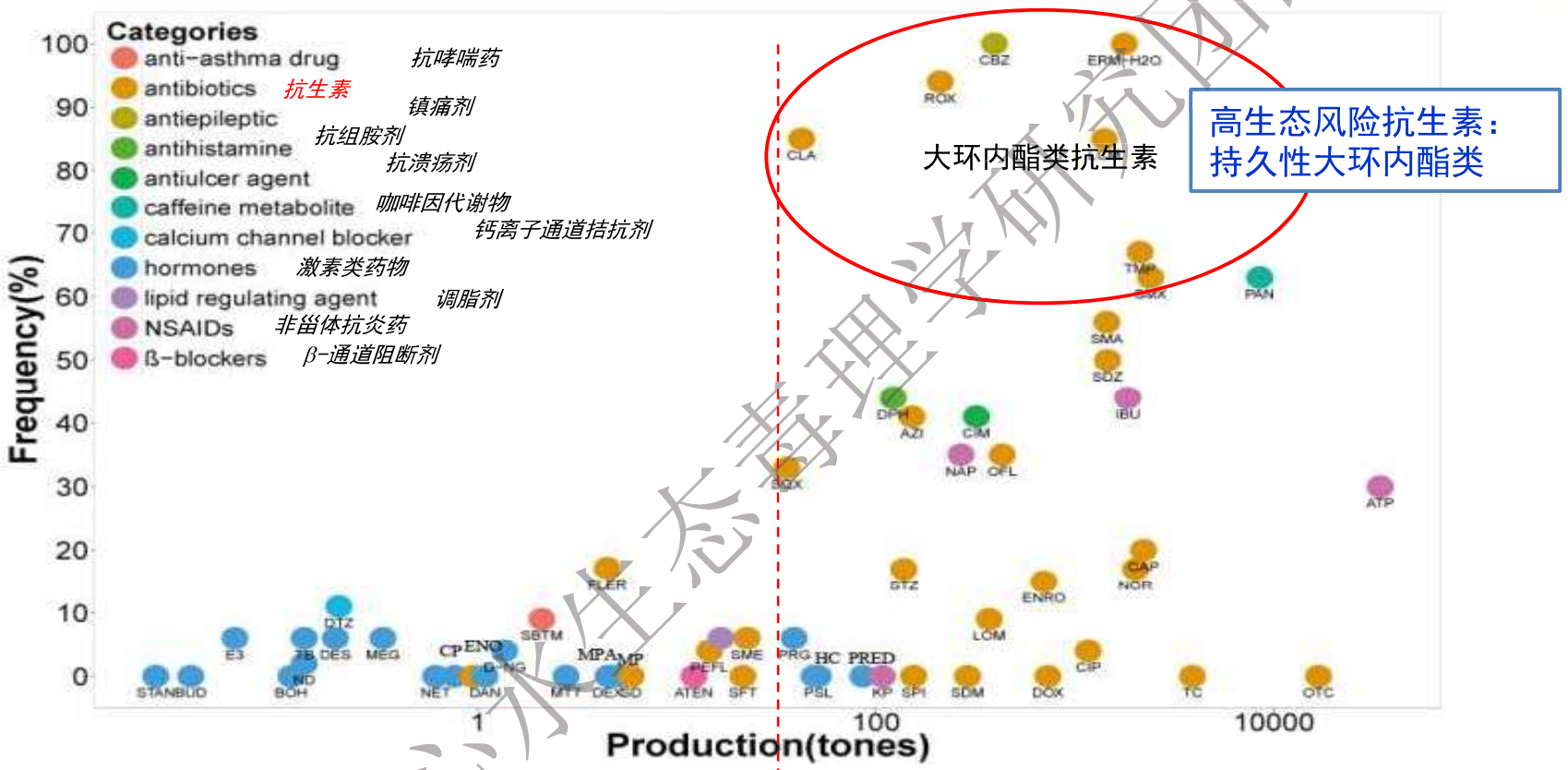
生态风险：对野生生物的生态毒性和生态风险问题(风险特征为直接危害)
健康风险：抗生素相关抗药基因和超级细菌问题(风险特征为间接危害)

抗生素类物质在中国的生产(排放)状态分析



网络下载的地图来源：中科院广州地化所应光国课题组，2017

重点流域水源水中的PPCPs及其检出率与产量之间的关系(2012~2013)

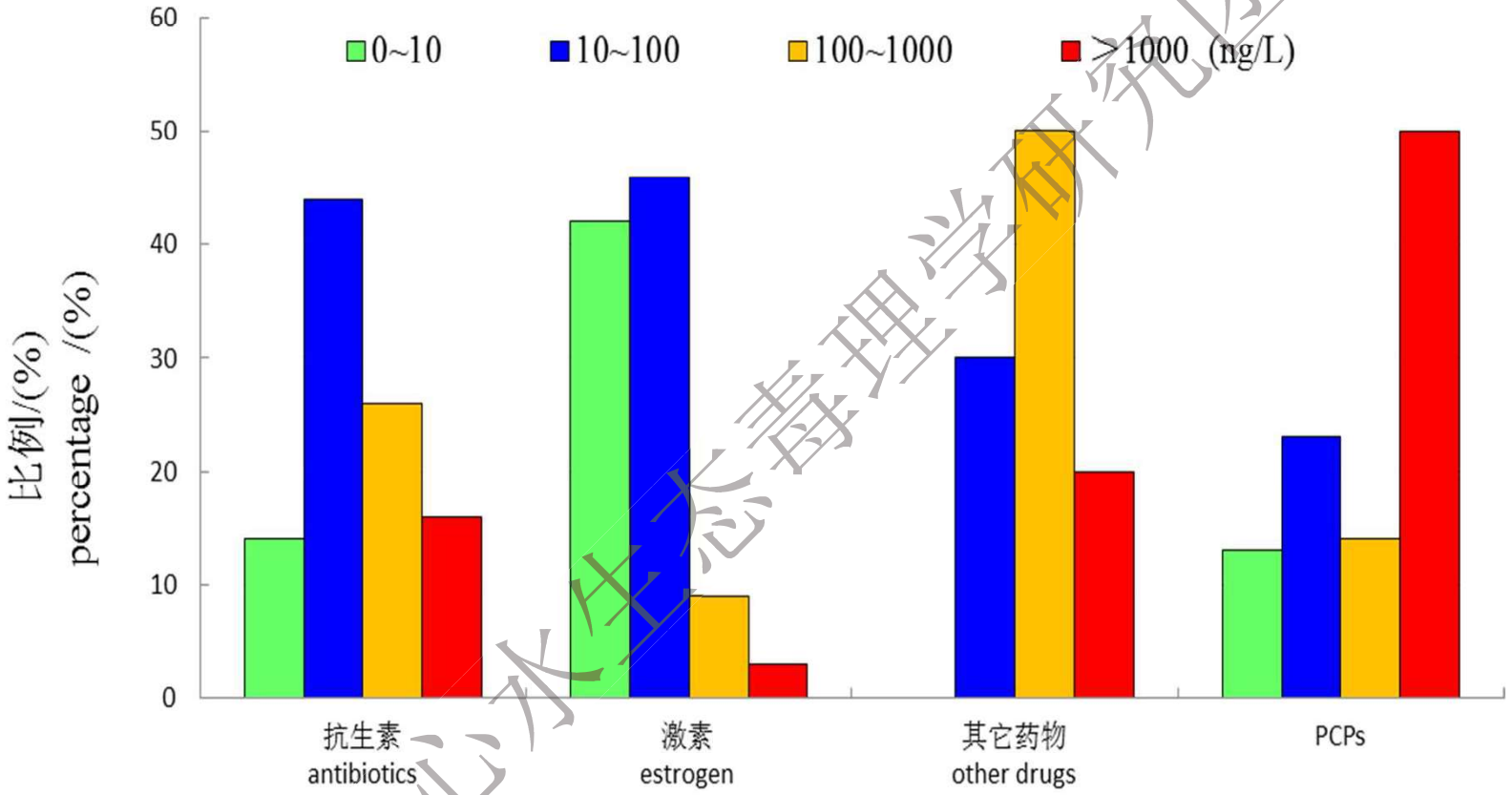


磺胺类抗生素（22种）：主要磺胺甲恶唑、磺胺嘧啶和降解产物苯磺酰胺, 未超过10 ng/L。
喹诺酮类抗生素（12种），主要萘啶酸、氧氟沙星、诺氟沙星、氟罗沙星等，浓度低于10 ng/L。
大环内酯类抗生素（5种）：与产量/使用量关系密切，浓度低于5 ng/L；
林可霉素属于林可酰胺类抗生素。均有检出，浓度低于1.4 ng/L 。
氯霉素(酰胺醇类抗生素): 主要在黄河和长江流域有检出, 最高不超过1.4ng/L。

资料来源：王子健等，水利部水源水质调查公益项目报告，2013

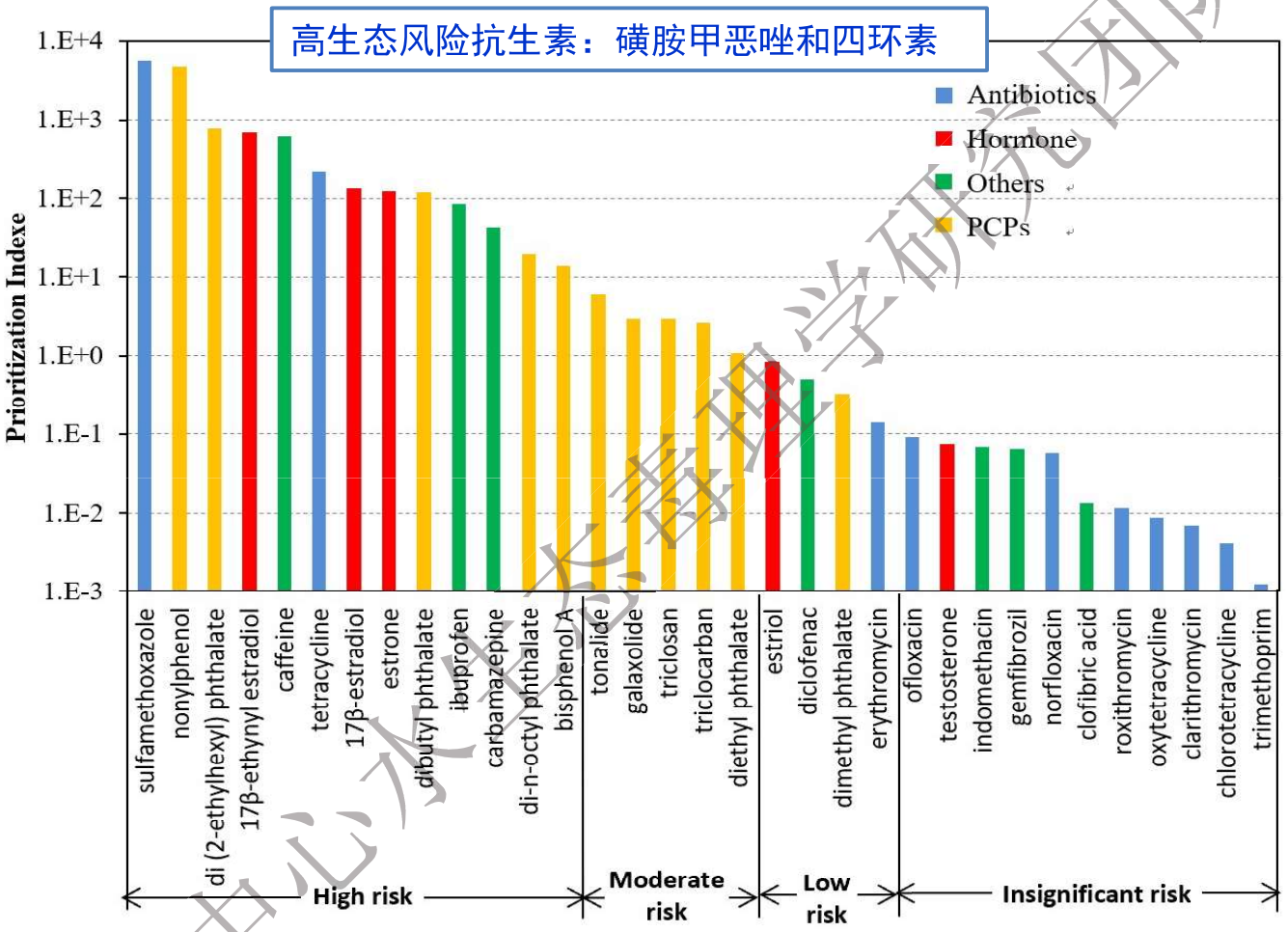
中国内陆水体中PPCPs浓度及其生殖毒性的生态风险评价

Ecological Risk Assessment of PPCPs in China In-land Waters based on Reproductive Toxicity



按照对野生动物生殖毒性的生态风险评估方法，有16个PPCPs类的生态风险熵大于1，包括1种抗生素，5种激素，3种人类用药和7种其他类型的PPCPs。其中风险最大的是乙炔基雌二醇，其次是烷基酚和酞酸丁苄酯。(刘娜等，生态毒理学报，2015)

中国内陆水体中PPCPs生态风险的优先指数(PI)

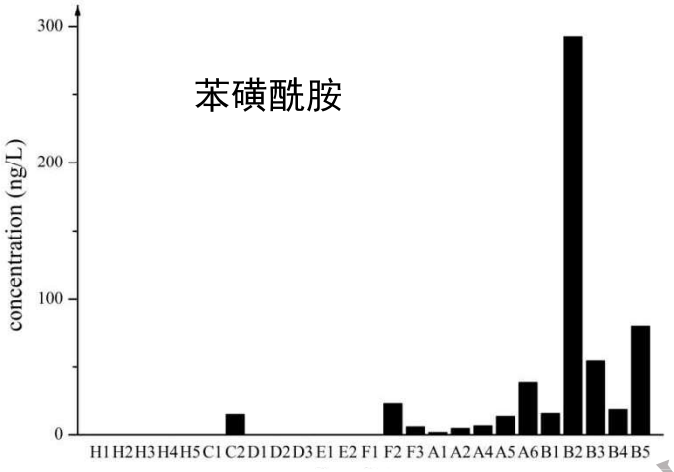


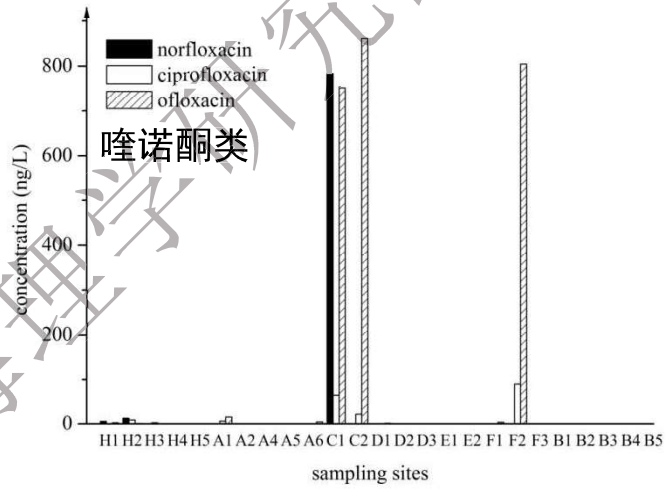
PI(Prioritization Index) = RQ x F(超PNEC频次)，其中RQ = PEC/PNEC和F = n/N

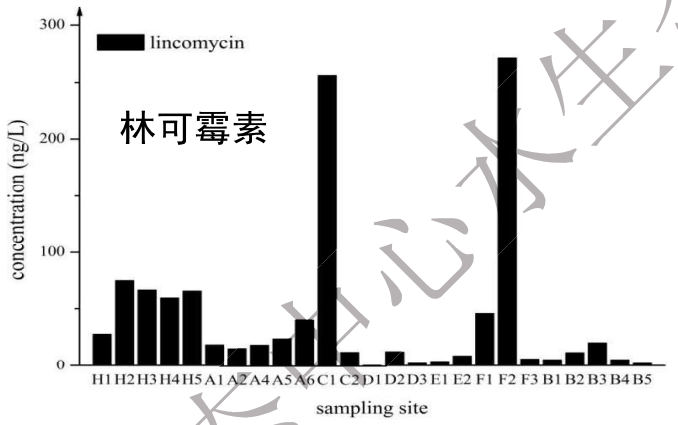
数据来源：2006~2017年国内学者发表的科学论文和环境监测数据

资料来源：Na Liu et al.，Environmental International, 2019

重点流域27个国控断面的抗生素类污染物浓度及其健康危害属性 (2014)



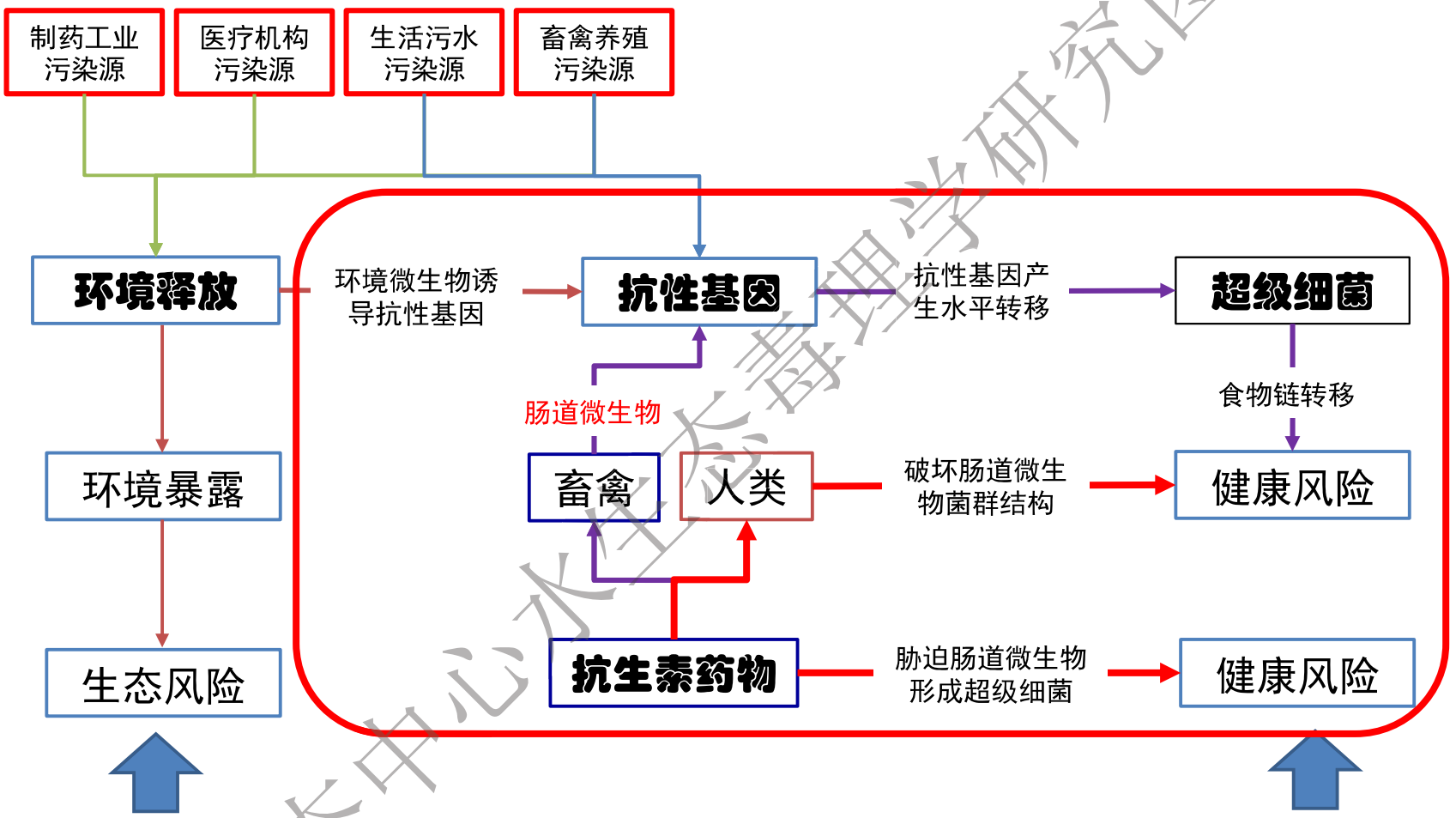




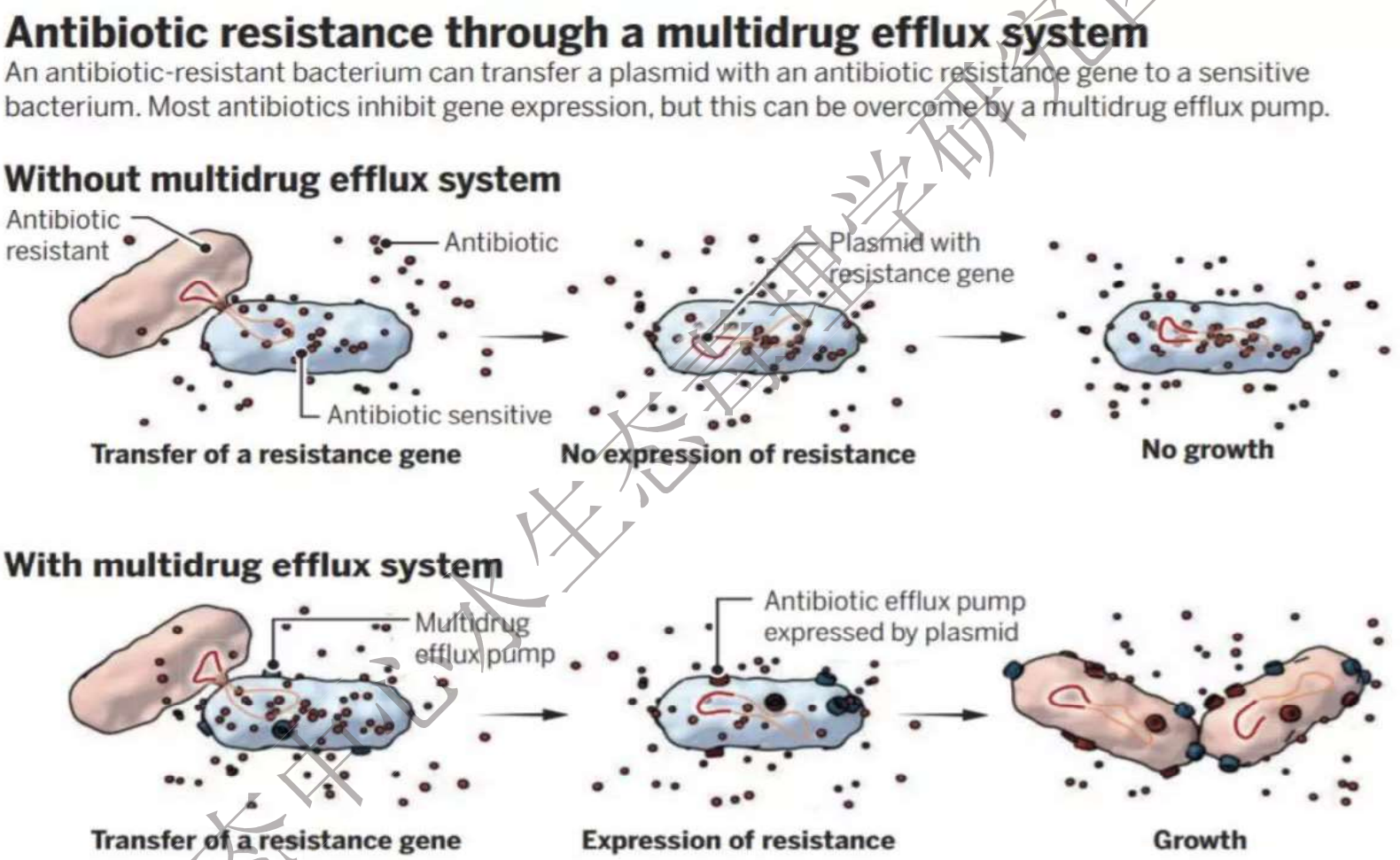
危害属性	检出抗生素种类
致癌性	磺胺甲恶唑, 磺胺二甲嘧啶, 磺胺二甲氧嗪,氯霉素
致畸性	磺胺二甲嘧啶，磺胺醋酰，磺胺间甲氧嘧啶，磺胺嘧啶，磺胺胍，磺胺二甲氧嗪，磺胺甲氧哒嗪，诺氟沙星，氧氟沙星。氯霉素
致突变性	磺胺甲恶唑，磺胺醋酰，磺胺，诺氟沙，环丙沙星，洛美沙星，氧氟沙星，氟罗沙，氯霉素
内分泌干扰物	磺胺二甲嘧啶，磺胺甲恶唑

结论：所有抗生素类污染物的健康风险水平均在可接受范围之内，存在个别高污染点源需要单独管理。
资料来源：王东红等，典型流域水环境风险污染物筛选与分析研究报告。生态环境部水司委托任务，2014.

抗生素类污染物：健康和生态危害和风险的影响途径分析

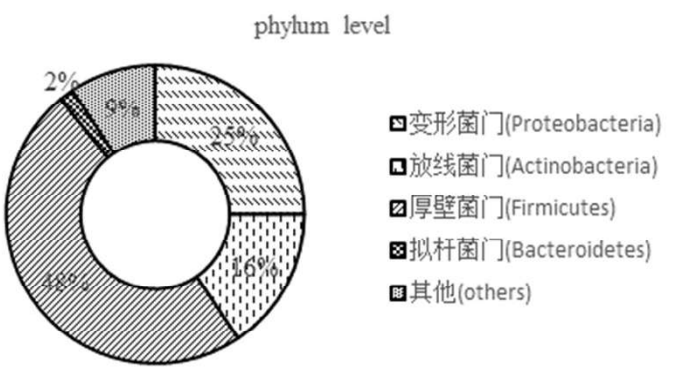


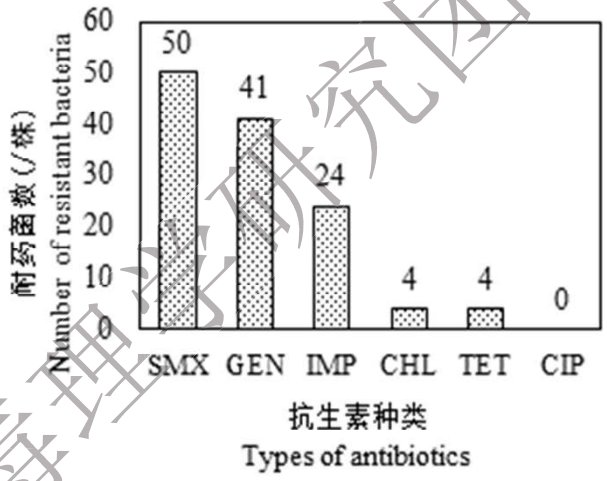
采用荧光标记，人类第一次直接观察到抗性基因的转移过程。将两种大肠杆菌混在一起培养，其中一种能被四环素杀伤，另一种则对四环素有耐药性。结果**仅过了3个小时，就有70%的细菌从不耐药变为了耐药**。图中解释了携带抗药基因的四环素菌体会携带多重抗药的“通用解毒泵”的质粒水平转移到非抗性细菌时，荧光标记的抗性就会在进入的位置富集，产生几个小亮点，宣告“传功”的开始((Science， 2019；资料来源：学术经纬 原创)。

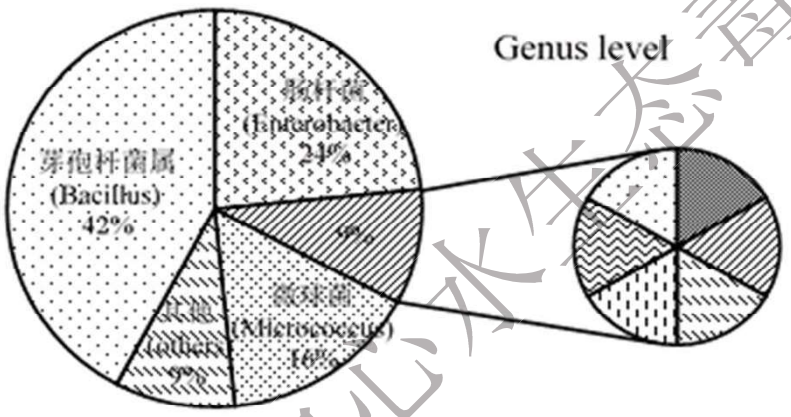


▲《科学》杂志为本研究做了专文评述，指出抑制“通用解毒泵”的重要意义（图片来源：参考资料[2]）

空气污染证据：机舱空气中环境耐药基因及耐药细菌的污染特征研究

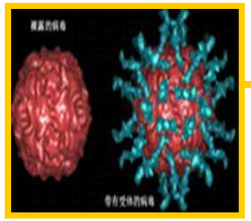






对分离出的64株细菌进行耐药表型检测发现，具有磺胺甲恶唑耐受性的细菌为50株（78.1%），具有庆大霉素耐受性的细菌为41株（64.1%），具有亚胺培南耐受性的细菌为24株（37.5%）。其中61株菌至少含有两重耐药性。(李鹏等，生态毒理学报，2019)

水源中重点关注的病原微生物：需要关注饮用/娱乐水体中细菌的耐药性！



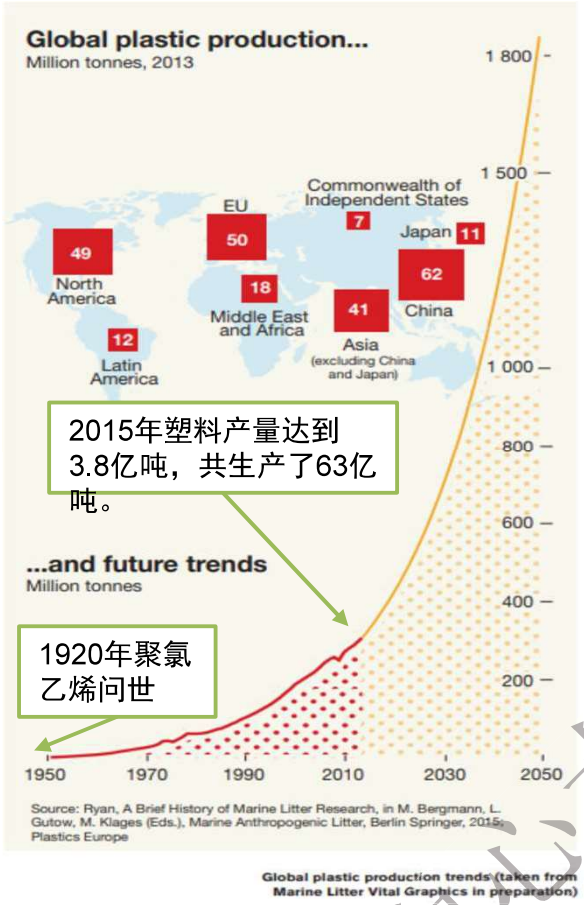
分类	病原微生物	引发的疾病
细菌	志贺氏菌	痢疾
	沙门氏菌	肠胃炎
	霍乱弧菌	霍乱
	肠致病性大肠杆菌	多种肠胃疾病
	耶尔森氏菌	肠胃炎
病毒	肝炎病毒	传染性肝炎
	诺沃克病毒	急性肠胃炎
	轮状病毒	急性肠胃炎
	脊髓灰质炎病毒	急性骨髓灰质炎
	柯萨奇病毒	流感
	埃可病毒	流感
原生动物	内阿类已属	阿米巴病
	兰氏贾第鞭毛虫	肠胃炎
	隐孢子虫	肠胃炎
寄生虫	蛔虫	蛔虫病
	绦虫	绦虫病
	线虫属	钩口线虫病
	鞭虫属	鞭虫病

美国、欧洲水体病原体主要评价指标：大肠杆菌(E.Coli)、肠球菌(Enterococci)、各种病毒、二虫等

典型新关注(新兴)环境污染物环境管理方式分析

- 抗生素类
- 微塑料
- 全氟辛酸及其盐(PFOA)

全球和中国的塑料生产及其环境影响(GCO-II， UN-Environment, 2018)



Global plastic production trends (taken from Marine Litter Vital Graphics in preparation)

全球环境展望-6中关于废弃塑料的评论：

- **海洋塑料垃圾可以因为缠绕鱼类和被鱼类吞食而造成重大生态影响，并且还可以成为入侵物种和其他污染物迁移的载体。(成立但证据不充分)**
- **废弃、丢失或以其他方式丢弃的渔具是海洋垃圾的重要来源，不 仅十分有害，而且由于它们能破坏海洋船舶、渔业和生态系统服务，因而导致鱼类数量减少，并构成重大的经济威胁。(成立且证据充分)**

树脂和纤维的全球产量从1950年200万吨增加到2015年的3.8亿吨, 平均8.4%的复合年增长率(CAGR)，**中国占全球28%的聚合物树脂和68%的全球聚合物纤维产量(Geyer et al . 2017年)**。

截止到 2015年，全球共产生的 63亿吨塑料废物，不到 9%被回收， 12%被焚化，79%进入垃圾填埋场或进入环境(GCO-II, 2018)，480~1270万吨废弃塑料进入海洋(Jamback, 2015)。

聚合物环境管理：化学品登记中聚合物登记管理的法规差异分析

法规	登记要求	低关注聚合物(PLC)
欧盟REACH法规	• 聚合物不进行登记; • 如果单体或反应物体量超过1 t/y，则需要注册单体或当反应物>2% w/w需要登记;	• 不界定PLC
美国TSCA法规	• (未列入1976年TSCA清单)的新聚合物按照PMN登记； • 界定PLC并对符合PLC条件的聚合物豁免登记和报告；	• 聚合物的平均分子量(MW)在1000 ~ 10000 Da之间。同时分子量<500的低聚物重量百分比小于10%，分子量<1000的低聚物重量百分比小于25%，不符合对反应性官能团的附加限制; • 聚合物的平均分子量(MW)大于10000 Da。同时，分子量<500的低聚物的重量百分比小于2%，分子量<1000的低聚物重量百分比小于5%; • 不包括某些阳离子聚合物；能够降解、分解或解聚的聚合；由不在TSCA清单中的单体或其他反应物形成的聚合物；数均分子量大于10000 Da的吸水性聚合物；以及含有CF3或较长链全氟烃基组分(非杂质)的聚合物。
中国环境部-7号令(2016版)	• 未列入中国化学品名录(IECSC)按新物质登记 • PLC(简易申报） • 非PLC(< 1t/a)简易申报和(> 1t/a)简化常规申报	• 聚合物的平均分子量(MW)在1000 ~ 10000 Da之间。同时分子量<500的低聚物重量百分比小于10%，分子量<1000的低聚物重量百分比小于25%。此外，这些聚合物不能含有“明显含量”的活性官能团，如重金属、氰基异氰酸酯、异硫氰酸酯、乙烯基等； • 聚合物的平均分子量(MW)大于10000 Da。同时，分子量<500的低聚重量百分比小于2%，分子量<1000的低聚物的重量百分比小于5%。
日本CSCL法规	• 未列入日本现存/新化学物质清单(ENCS/ISHL)按新物质登记 • 豁免PLC • 非PLC合规登记	• 聚合物的数均分子量>1000 Da； • 物理和化学性质稳定； • 符合: (a)不溶于水、有机溶剂及酸或碱，或不溶于水、有机溶剂且具有特定分子结构；或(b)可溶于水和有机溶剂，但低聚物的重量百分比(MW<1,000) <=1% w/w，无资料表明高积累; • 不含重金属或具有阳离子性质; • 不是政府已经得出可能对人类健康或环境有负面影响结论的聚合物； • 需通过规范化的PLC测试流程确认PLC。

资料来源：ChemSaftyPro, 2016

欧盟委员会环境董事会和ECHA的微塑料环境管理策略(Valentina, 2018)

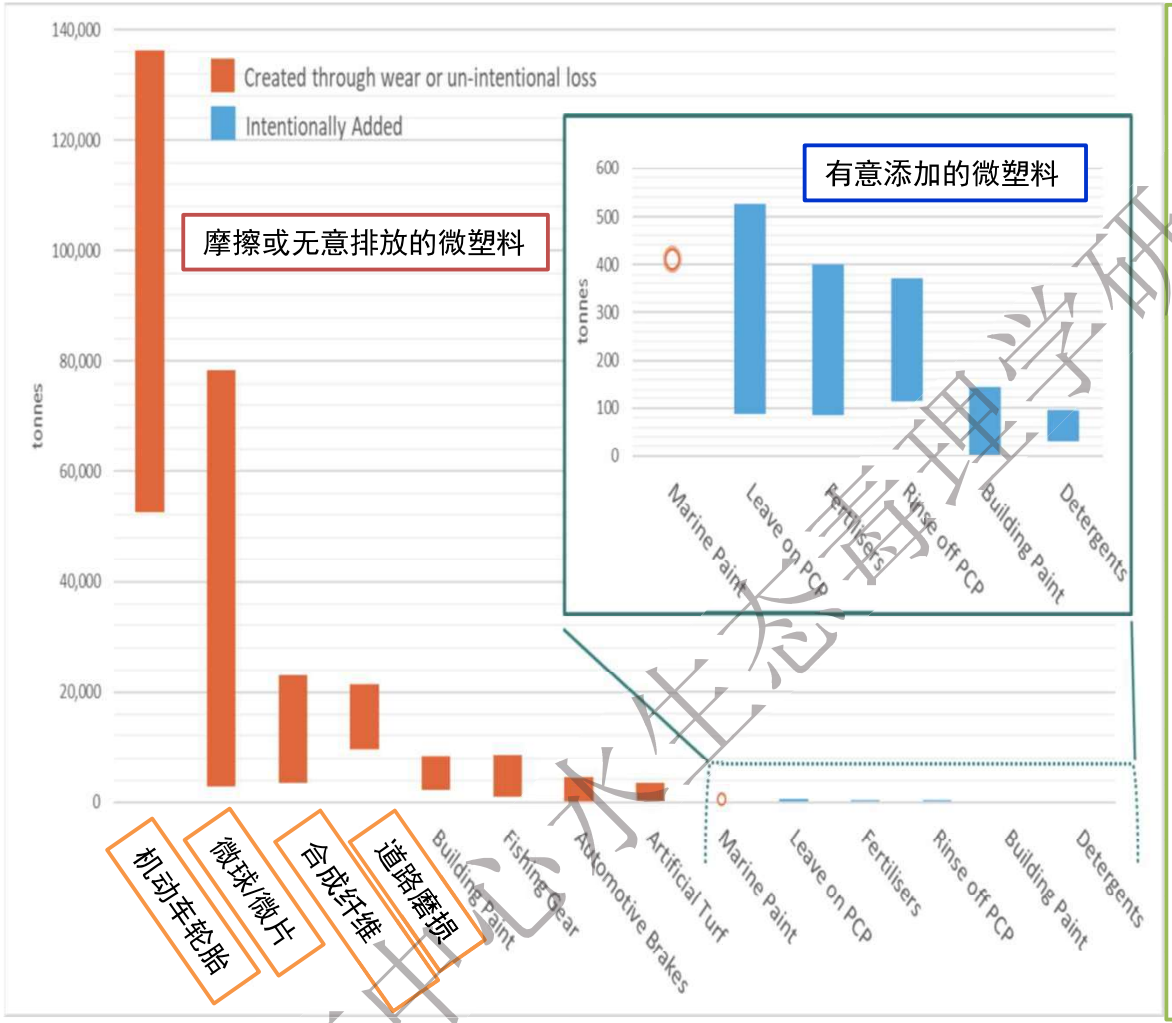
微塑料作为化学品环境风险管理的认知差距：

1. 微塑料进入环境的途径和环境行为(缺乏统一规范的监测方法/环境暴露数据)
2. 环境和健康危害(尚没有针对不溶解物质的毒性测试规范/仅有vP无法分类)
3. 风险评估缺少数据支撑(几乎不存在可用的剂量-效应关系)

- 欧洲委员会董事会提出针对微塑料环境管理的政策选项：
  1. 通过化学品管理法规(REACH)
     - ✓ 信息和分类标签警示制度，引入恰当的关注措施；
     - ✓ 限制或禁止全部或部分特定用途和有意生产使用的塑料微珠；
  1. 通过其他环保措施管理所有微塑料释放源，包括：
     - ✓ 通过工业排放指令/市政污水处理指令处理或去除微塑料；
     - ✓ 通过饮用水法规中引入微塑料监测项目(目前没有数据证明混凝工艺效果)；
     - ✓ 在固废法规中引入必要的塑料产品生态设计要求(资源化方案)。

- ECHA应委员会的要求根据REACH Annex XV提交了一项议案(高关注物质: 有意添加的微塑料，包括微珠和微粒)，相关文档的公众咨询将持续到2019年9月20日。
- ECHA的提案将微塑料定义为由直径小于5mm的固体聚合物颗粒组成的材料，限制范围是有目的添加(fit-for-purpose)，注明其中可能添加了多种添加剂或其他物质。
- REACH的ANEEX XV管理对象包括聚合物在内的物质和混合物(法规定义没有微塑料或塑料微珠)及其在使用过程中可能导致环境和健康风险的物质或具体用途。
- 提议一旦通过，ECHA可以沿用ANEEX XVII实施限制，该条款允许对”具有不可接受风险”化学物质采取限制行动，因此可以”极大推动针对为塑料的其他管理行动“。

环境中不同来源微塑料及其进入地表水环境的途径和排放量(EUNOMIA, 2018)



环境微塑料来源分析：

车辆轮胎：包括天然橡胶、聚异戊二烯橡胶、丁苯橡胶和顺丁橡胶摩擦形成的超细颗粒；

塑料微球：包括PVC、PE、PA和PS塑料制成的实心和空心颗粒；

合成纤维：包括碳链合成纤维，如聚丙烯纤维(丙纶)、聚丙烯腈纤维(腈纶)、聚乙烯醇缩甲醛纤、合成纤维吊环、合成纤维吊环维(维尼纶)和杂链合成纤维，如聚酰胺纤维(锦纶)、聚对苯二甲酸乙二酯(涤纶)等；

塑料地面：包括各种人工合成树脂、塑胶跑道、塑料地砖和“先进”、”环保”的塑料道路；

塑料涂料：主要品种有：热塑性丙烯酸酯树脂涂料、热固性丙烯酸酯-聚氨酯树脂改性涂料、氯化聚烯烃改性涂料，改性聚氨酯涂料等。

机动车轮胎主要成分还包括：黑炭、硅、树脂、金属氧化物、尼龙纤维。合成橡胶轮胎生产过程中会产生多种致癌物质，包括亚硝胺和二苯并吡喃(Spiegelhalder, B. 1983; Sadiktsis, I. 2012)。轮胎摩擦产生超细颗粒(PM2.5)对健康影响依然未知，但是职业病调查发现橡胶行业工作的职业暴露是导致口腔癌和口咽癌高发的潜在因素。

中国55个沿海地级城市机动车轮胎磨损产生的微塑料释放量估算

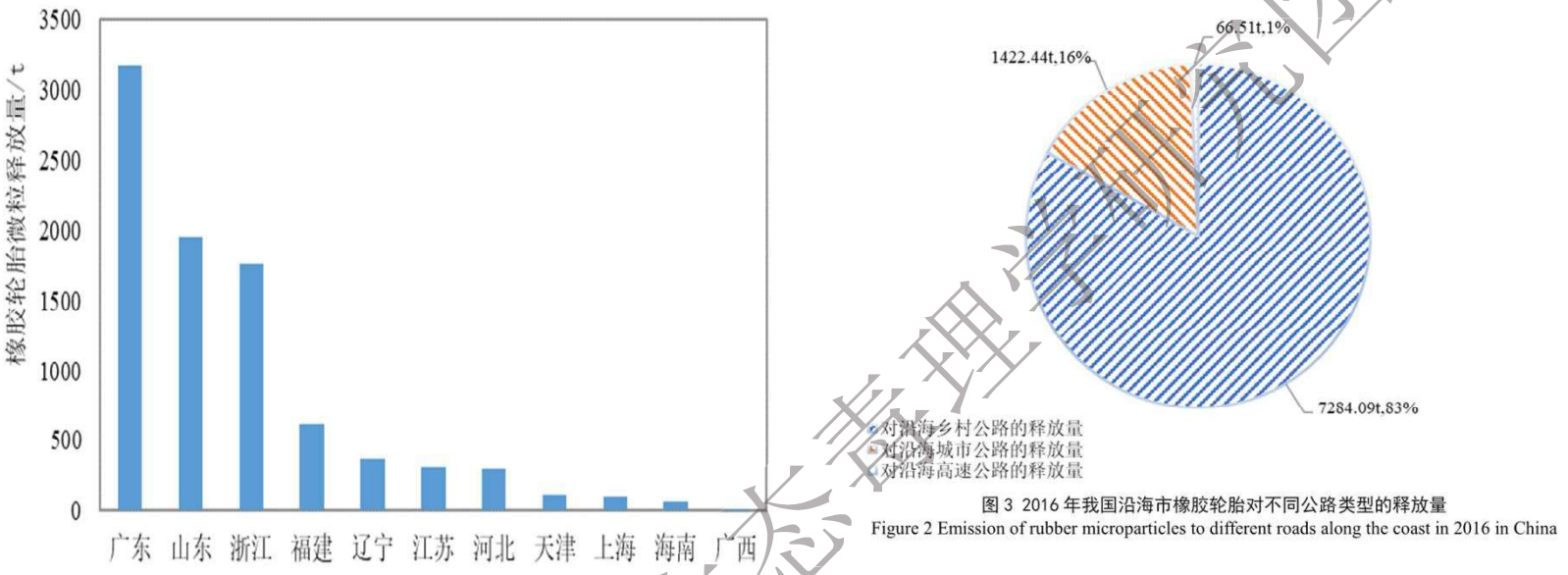


图 3 2016 年我国沿海市橡胶轮胎对不同公路类型的释放量

Figure 2 Emission of rubber microparticles to different roads along the coast in 2016 in China

……全球轮胎磨损排放的微塑料约占海洋微塑料排放总量的5%-10%，空气中$PM_{2.5}$颗粒的3%～7%。我国2016年我国轮胎产量为94697.7万条。模型估算，中国55个沿海城市轮胎磨损释放的橡胶颗粒为8773 t/a，与荷兰机动车轮胎磨损橡胶微粒释放量(8834 t/a)相近，高于丹麦机动车轮胎磨损橡胶微粒释放量(6721 t/a)。轮胎磨损排放的颗粒物质主要进入土壤环境，其次是城市下水道和地表水体….(资料来源：凌玮等，生态毒理学报，2019)

废旧轮胎回收利用的方式之一是生产橡胶粉，是指废旧橡胶制品经粉碎加工处理而得到的粉末状橡胶材料(微塑料)，广泛用于体育塑胶运动场、游乐场、橡胶地砖、防水卷材、防水涂料、公路改性沥青、橡胶制品、变性淀粉、阔高等领域，问题最大！(资料来源：百度百科)

有意生产和使用的微塑料及化学品环境管理技术问题分析

ECHA proposes to restrict intentionally added microplastics

ECHA/PR/19/03

ECHA has submitted a restriction proposal for microplastic particles that are intentionally added to mixtures used by consumers or professionals. If adopted, the restriction could reduce the amount of microplastics released to the environment in the EU by about 400 thousand tonnes over 20 years.

Helsinki, 30 January 2019 – ECHA has assessed the hea and environmental risks posed by intentionally added microplastics and has concluded that an EU-wide restriction ld be justified. If adopted, the restriction could result in a reduction in emissions of microplastics of about 400 thousa nes over 20 years.

ECHA's assessment found that intentionally added microplas most likely to accumulate in terrestrial environments, as the particles concentrate in sewage sludge that is frequently ap rtiliser. A much smaller proportion of these microplastics is released directly to the aquatic environment.

The persistence and the potential for adverse effects or bioa microplastics is a cause for concern. Once released, they can be extremely persistent in the environment, lasting ears, and practically impossible to remove. Currently it is not possible to determine the impact of such long-term nvironment.

Data available on effects is limited, particularly for the terres hich makes risk assessment difficult. Due to their small size, microplastics and nanoplastics – even smalle eated from the further degradation of microplastics – may be readily ingested and thereby enter th tial effects on human health are though still not well understood.

Ov y controlled.

E evitably be released to th 5mm), synthetic polymer P hal products in multiple se uction materials and m s sectors.

E on is likely to result in d cted to be cost-effective in ally added m

Several EU Member States have already introduced bans on the use of microplastics in certain types of products, largely concerning wash-off cosmetic products.

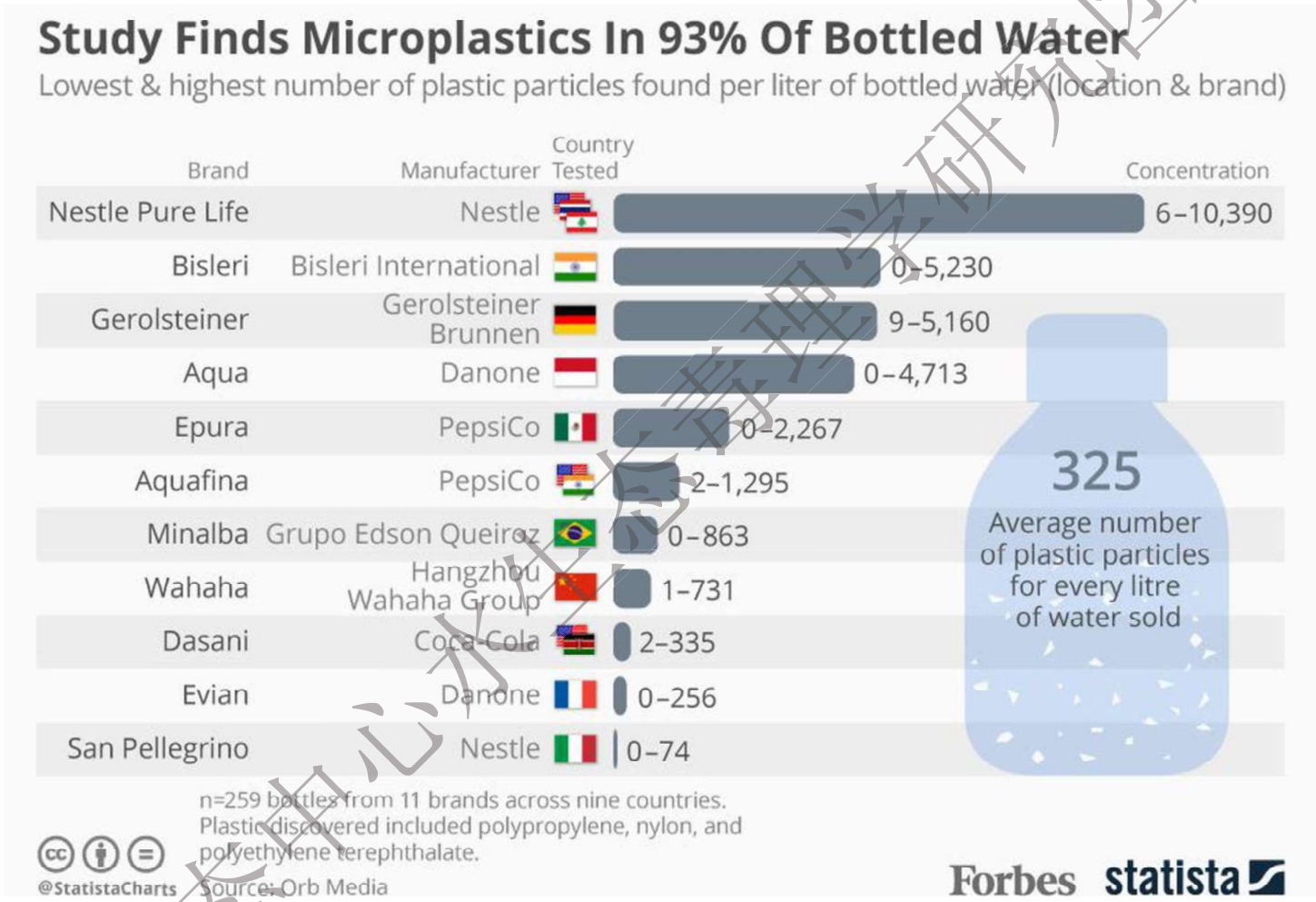
ECHA has published the restriction proposal on microplastics at the same time as its restriction proposals for formaldehyde and for siloxanes D4, D5 and D6.

ECHA已经提出限制有意添加到消费品或专业用品混合物中微塑料的议案。该限制令可以在20年内减少超过40万吨的微塑料环境释放量。

- **ECHA微塑料限制：**包括有意生产和使用的塑料微珠和无意产生的塑料碎片。ECHA限制令主要针对部分“有意添加(fit-for-purposes)到产品中并含有合成聚合物、粒径小于5毫米的塑料小球”；
- 按照PBT或vPvB原则的危害评估，则所有聚合物均符合BPT危害属性中的P，学术争议点在B和T；
- (数均计算的)微塑料是主要的污染指标。尽管已经有分离、鉴定和计数方法，但是规范化的监测或暴露评估方法依然缺失；
- 危害评估的主要质疑来自微米或纳米级颗粒物是否能够通过血液传输、在脏器中蓄积和能否进入细胞；
- 在风险评估中有关环境暴露和暴露~剂量效应关系数据严重缺失；
- 国际社会普遍赞同的管理原则是”合理的禁用、有条件的限制和最大限度的资源化利用”。

注：REACH法规中并没有”微塑料”的定义，限制令(Annex XVII)只能针对3(5)条款定义的“聚合物”

安全饮用水：微塑料的人体暴露--93%的瓶装水均能够检出塑料微粒



欧洲化学品局关于公众要求对人为添加微塑料实施限制的回复，2018

……描述微塑料可能对人类健康或环境造成各种危害的科学文献正在迅速增长，报告了从物理危害、炎症或微塑料作为其他环境污染物“载体”进入有机体(包括持久性有机污染物) 的潜在影响。**重要的是：文献资料所获得的毒性数据很可能与实验材料(塑料基质)中的“添加剂”有关，而并非聚合物本身的各种“毒性”。**

风险管理希望科学界的研究数据能够有效区分不同尺度、聚合物种类，添加剂种类和添加方式，以及环境释放/危害场景的数据。

典型新关注(新兴)环境污染物环境管理方式分析

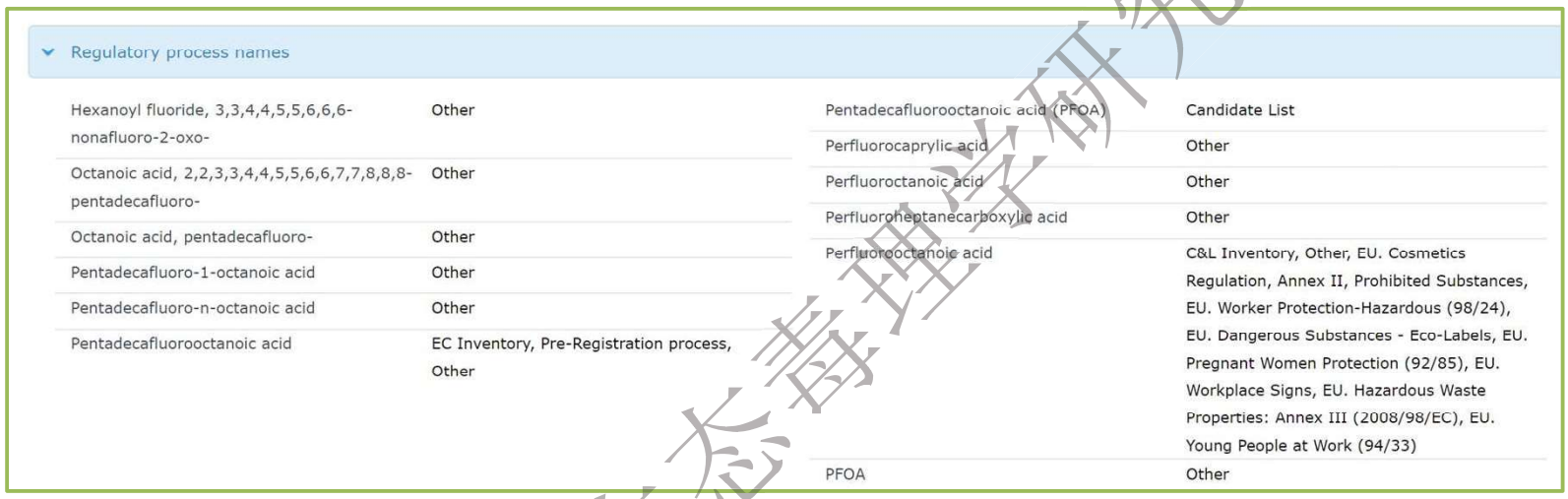
- 抗生素类
- 微塑料
- 全氟辛酸及其盐(PFOA)

全卤代或多卤代类物质是当前国际社会化学品环境管理的热点，其中的氟化工在中国也被称为“黄金产业”，是化工产品出口大户。

全球范围内PFOA的生产/供应和使用情况分析

根据2020年ChemBook数据，全球一共有187个PFOA生产/供应商，其中中国有101个均是生产/供应商，是全球主要生产商。该化学物质在4个化学品登记数据库中备案，有4个MSDS报告。

化学品管理进程：REACH法规下PFOA的登记、评估和管理进程分析



Regulatory process names

Hexanoyl fluoride, 3,3,4,4,5,5,6,6,6-nonafluoro-2-oxo-	Other
Octanoic acid, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-	Other
Octanoic acid, pentadecafluoro-	Other
Pentadecafluoro-1-octanoic acid	Other
Pentadecafluoro-n-octanoic acid	Other
Pentadecafluorooctanoic acid	EC Inventory, Pre-Registration process, Other
Pentadecafluorooctanoic acid (PFOA)	Candidate List
Perfluorocaprylic acid	Other
Perfluoroctanoic acid	Other
Perfluoroheptanecarboxylic acid	Other
Perfluorooctanoic acid	C&L Inventory, Other, EU. Cosmetics Regulation, Annex II, Prohibited Substances, EU. Worker Protection-Hazardous (98/24), EU. Dangerous Substances - Eco-Labels, EU. Pregnant Women Protection (92/85), EU. Workplace Signs, EU. Hazardous Waste Properties: Annex III (2008/98/EC), EU. Young People at Work (94/33)
PFOA	Other

- 已经列入REACH法规中的高关注物质清单；
- 已经按照CLP法规要求完成了分类并进入分类数据库(C&L Inventory)
- 在属于欧盟化妆品法规中ANNEX II规定的禁止添加物质
- 在欧盟职业个人保护和孕妇保护法规中生态标签中是危险化学物质
- 在欧盟工作场所标志法规中的ANNEX III有害废弃物。

欧盟CLP法规中关于PFOA的危害属性信息(C&L Inventory)

Name	EC / List no.	CAS no.	Criteria (indication)
Pentadecafluorooctanoic acid CAS number: 335-67-1	206-397-9	335-67-1	Suspected acutely toxic via the oral route Harmonised classification for acute toxicity Harmonised classification for carcinogenicity Harmonised classification for effects on or via lactation Harmonised classification for eye damage Harmonised classification for reprotoxicity Harmonised classification for specific target organ toxicity Suspected bioaccumulative Suspected carcinogen Suspected hazardous to the aquatic environment Suspected persistent in the environment Suspected toxic

- 统一分类为急性毒性；
- 统一分类为致癌性；
- 统一分类为对哺乳期妇女本人或通过哺乳对婴幼儿有健康影响
- 统一分类对眼睛有伤害作用；
- 统一分类为生殖毒性物质；
- 统一分类为特定靶器官毒性物质；
- 疑是经口急性毒性物质；
- 疑是致癌物；
- 疑是生物蓄积性物质；
- 疑是持久性污染物；
- 疑是对水生生物具有毒性；
- 疑是具有各州毒性属性。

风险评估进程：ECHA在REACH框架内执行PFOA限制政策的RAC/SEAC报告

Committee for Risk Assessment (RAC)

Opinion

on an Annex XV dossier proposing restrictions on

Perfluorooctanoic acid (PFOA), its salts and PFOA-related substances

ECHA/RAC/RES-O-0000006229-70-02/F

Adopted

8 September 2015

RAC报告：RAC倾向于对混合物和成品中PFOA的限制上限是25 ppb，PFOA相关物质的限制上限是1000 ppb。

Committee for Socio-economic Analysis (SEAC)

Opinion

on an Annex XV dossier proposing restrictions on

Perfluorooctanoic acid (PFOA), its salts and PFOA-related substances

Draft

10 September 2015

SEAC报告：除了在REACH下施加限制措施外，没有其他可预见的选择在可接受的时间和范围内大幅减少排放。

管理进程：ECHA在REACH附录XV下的限制政策提议(Intention until outcome)

The registry of restriction intentions until outcome lists the intentions and Annex XV restriction proposals received by ECHA.

A restriction proposal may be prepared by a Member State or by ECHA at the request of the Commission or on its own initiative for substances in the Authorisation List. It is a legal requirement for a Member State to notify ECHA of its intention to prepare a restriction dossier. The advance notice enables interested parties to plan and prepare for commenting later on.

Interested parties can follow the progress of a proposal through the restriction process, from the notification of the intention to the adoption of the final opinions by the Committee for Risk Assessment (RAC) and the Committee for Socio-economic Analysis (SEAC), and the adoption of the restriction by the European Commission.

Stakeholders are encouraged to submit any relevant information to the dossier submitters during the preparation of the restriction proposal and during the public consultations. Information to motivate any exemptions to the scope described in the intention is particularly useful to receive in the preparatory phase of the dossier.

SEE ALSO

- Submitted restrictions under consideration
- Substances restricted under REACH
- Support on restriction

REACH附录XV是提议化学物质限制生产和使用的条款，包括限制或禁止生产、投放进入市场(含进口)和各种用途添加。

perfluorooctanoic acid (PFOA), its salts and PFOA-related substances

EC / List no: - **CAS no:** -

附录XV提议的公开征求意见：提议通过ANNEX XVII限制的物质包括全氟辛酸/盐和相关化合物；C9~C14全氟羧酸/盐和相关化合物。

CLP Annex VI Index number	
Further substance information	The following groups of substances are covered by this intention: Perfluorooctanoic acid (PFOA), its salts and PFOA-related substances; C9-C14 perfluorocarboxylic acids (C9-C14 PFCA), their salts and C9-C14 PFCA-related substances
Submitter(s)	ECHA
Details on the scope of restriction	Revision of derogations from proposed restrictions on perfluorooctanoic acid (PFOA), its salts and PFOA-related substances; C9-C14 perfluorocarboxylic acids (C9-C14 PFCA), their salts and C9-C14 PFCA-related substances.
Reason for restriction	
Remarks	Stakeholders are requested to provide relevant information in a call for evidence.
Status	Intention
Date of intention	30/04/2020
Expected date of submission	09/10/2020
Withdrawal date	
Reason for withdrawal	
Start of Call for Evidence public consultation	06/05/2020
Deadline for comments on the Call for Evidence	06/07/2020

- 管理方式(通过REACH法规)：对PFOA进行限制的提议由德国(可能是杜邦公司)和芬兰于2013年首次提交给ECHA。
- ECHA于2015年将完成后的限制意图报告提交给RAC和SEAC，后者当年完成2份评估报告；
- ECHA于2020年4月30日正式提起附录XVII的限制，向公众征求意见截止到2020年7月6日。

PFOA限制政策通过欧盟议会批准后于2020年7月4日发布(限制令68号)

ANNEX XVII TO REACH – Conditions of restriction

Restrictions on the manufacture, placing on the market and use of certain dangerous substances, mixtures and articles

Entry 68

Perfluorooctanoic acid (PFOA)

CAS No 335-67-1

EC No 206-397-9

and its salts.

Any related substance (including its salts and polymers) having a linear or branched perfluoroheptyl group with the formula C_7F_{15}- directly attached to another carbon atom, as one of the structural elements.

Any related substance (including its salts and polymers) having a linear or branched perfluorooctyl group with the formula C_8F_{17}- as one of the structural elements.

The following substances are excluded from this designation:

— C_8F_{17}-X, where X = F, Cl, Br.

— C_8F_{17}-C(=O)OH, C_8F_{17}-C(=O)O-X′ or C_8F_{17}-CF_2-X′ (where X′ = any group, including salts).

Conditions of restriction

1. Shall not be manufactured, or placed on the market as substances on their own from 4 July 2020.

2. Shall not, from 4 July 2020, be used in the production of, or placed on the market in:

(a) another substance, as a constituent;

(b) a mixture;

(c) an article,

in a concentration equal to or above 25 ppb of PFOA including its salts or 1 000 ppb of one or a combination of PFOA-related substances.

3. Points 1 and 2 shall apply from:

(a) 4 July 2022 to

- 禁止在半导体生产设备中使用
- 禁止用于乳胶涂料

(b) 4 July 2023 to:

(i) textiles for the protection of workers from risks to their health and safety;

(ii) membranes intended for use in medical textiles, filtration in water treatment, production processes and effluent treatment;

(iii) plasma nano-coatings.

(c) 4 July 2032 to medical devices other than implantable medical devices within the scope of Directive 93/42/EEC.

4. Points 1 and 2 shall not apply to any of the following:

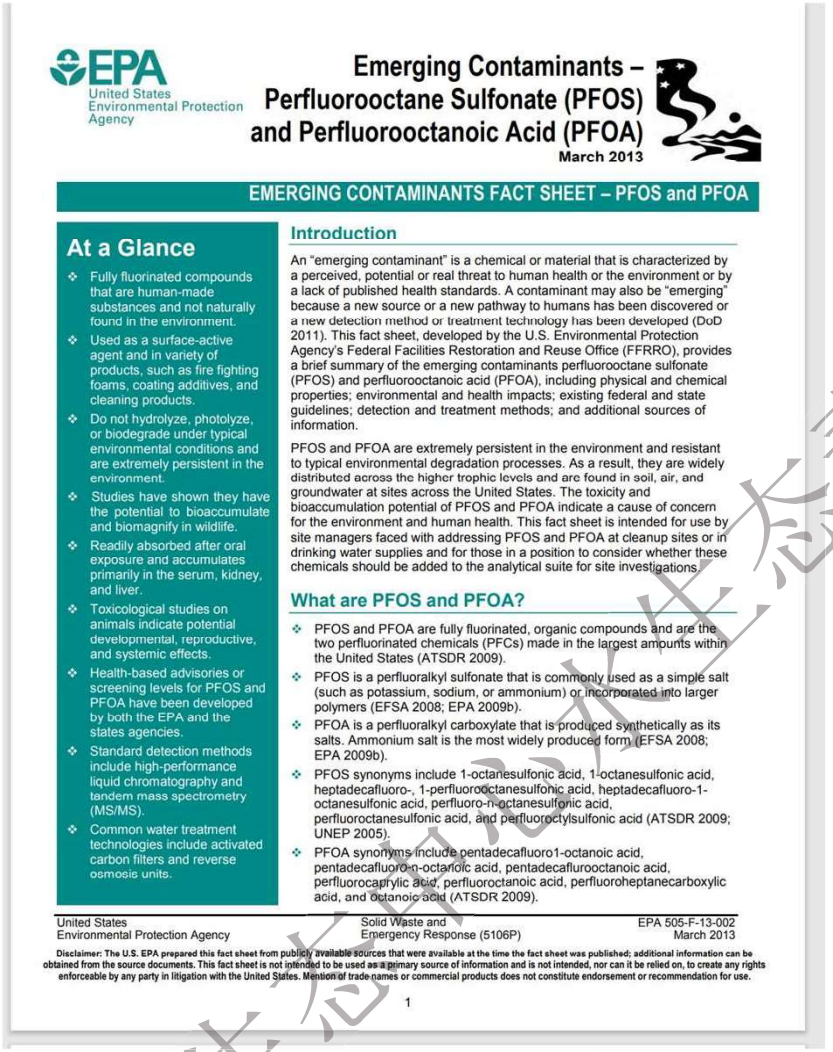
(a) perfluorooctane sulfonic acid and its derivatives, which are listed in Part A of Annex I to Regulation (EC) No 850/2004;

(b) the manufacture of a substance where this occurs as an unavoidable by-product of the manufacture of fluorochemicals with a carbon chain equal to or shorter than 6 atoms;

(c) a substance that is to be used, or is used as a transported isolated intermediate, provided that the conditions in points (a) to (f) of Article 18(4) of this Regulation are met;

(d) a substance, constituent of another substance or mixture that is to be used, or is used:

美国相关管理法规：EPA已经将其列入新关注污染物(2013)和技术情况说明书(2017)



EPA United States Environmental Protection Agency

Emerging Contaminants – Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoic Acid (PFOA)

March 2013

EMERGING CONTAMINANTS FACT SHEET – PFOS and PFOA

At a Glance

- Fully fluorinated compounds that are human-made substances and not naturally found in the environment.
- Used as a surface-active agent and in variety of products, such as fire fighting foams, coating additives, and cleaning products.
- Do not hydrolyze, photolyze, or biodegrade under typical environmental conditions and are extremely persistent in the environment.
- Studies have shown they have the potential to bioaccumulate and biomagnify in wildlife.
- Readily absorbed after oral exposure and accumulates primarily in the serum, kidney, and liver.
- Toxicological studies on animals indicate potential developmental, reproductive, and systemic effects.
- Health-based advisories or screening levels for PFOS and PFOA have been developed by both the EPA and the states agencies.
- Standard detection methods include high-performance liquid chromatography and tandem mass spectrometry (MS/MS).
- Common water treatment technologies include activated carbon filters and reverse osmosis units.

Introduction

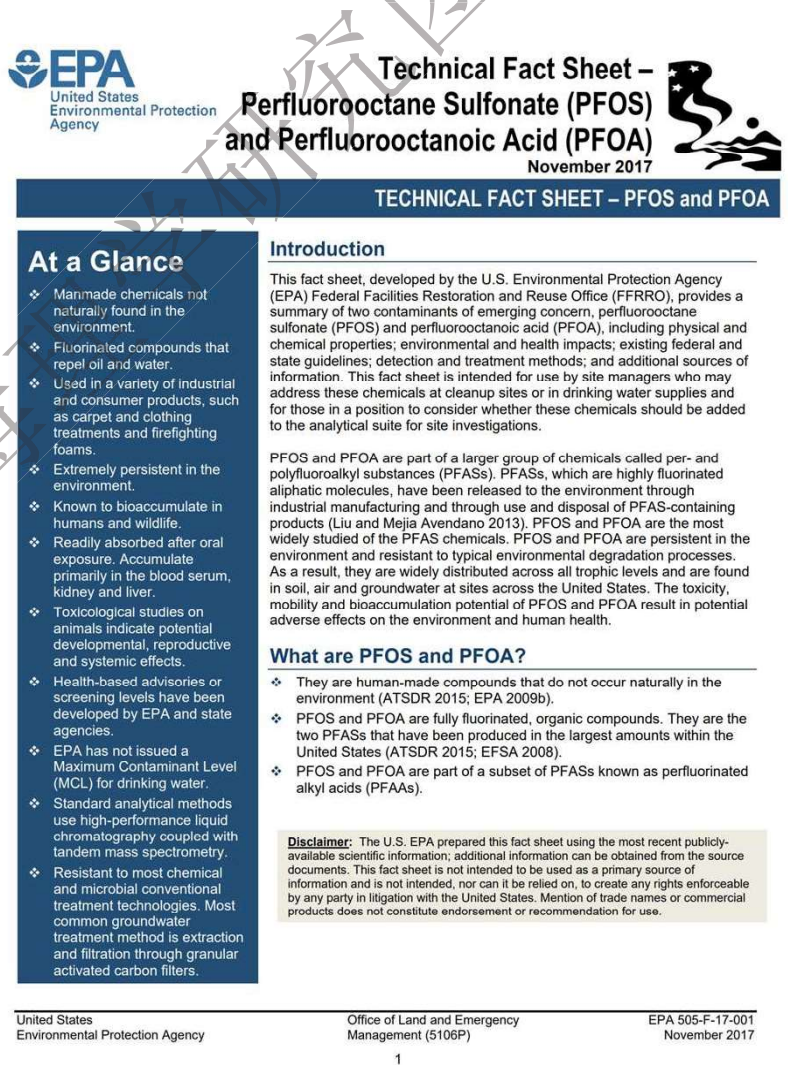
An "emerging contaminant" is a chemical or material that is characterized by a perceived, potential or real threat to human health or the environment or by a lack of published health standards. A contaminant may also be "emerging" because a new source or a new pathway to humans has been discovered or a new detection method or treatment technology has been developed (DoD 2011). This fact sheet, developed by the U.S. Environmental Protection Agency's Federal Facilities Restoration and Reuse Office (FFRRO), provides a brief summary of the emerging contaminants perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), including physical and chemical properties; environmental and health impacts; existing federal and state guidelines; detection and treatment methods; and additional sources of information.

PFOS and PFOA are extremely persistent in the environment and resistant to typical environmental degradation processes. As a result, they are widely distributed across the higher trophic levels and are found in soil, air, and groundwater at sites across the United States. The toxicity and bioaccumulation potential of PFOS and PFOA indicate a cause of concern for the environment and human health. This fact sheet is intended for use by site managers faced with addressing PFOS and PFOA at cleanup sites or in drinking water supplies and for those in a position to consider whether these chemicals should be added to the analytical suite for site investigations.

What are PFOS and PFOA?

- PFOS and PFOA are fully fluorinated, organic compounds and are the two perfluorinated chemicals (PFCs) made in the largest amounts within the United States (ATSDR 2009).
- PFOS is a perfluoralkyl sulfonate that is commonly used as a simple salt (such as potassium, sodium, or ammonium) or incorporated into larger polymers (EFSA 2008; EPA 2009b).
- PFOA is a perfluoralkyl carboxylate that is produced synthetically as its salts. Ammonium salt is the most widely produced form (EFSA 2008; EPA 2009b).
- PFOS synonyms include 1-octanesulfonic acid, 1-octanesulfonic acid, heptadecafluoro-, 1-perfluorooctanesulfonic acid, heptadecafluoro-1-octanesulfonic acid, perfluoro-n-octanesulfonic acid, perfluorooctanesulfonic acid, and perfluorooctylsulfonic acid (ATSDR 2009; UNEP 2005).
- PFOA synonyms include pentadecafluoro1-octanoic acid, pentadecafluoro-n-octanoic acid, pentadecafluorooctanoic acid, perfluorocaprylic acid, perfluorooctanoic acid, perfluoroheptanecarboxylic acid, and octanoic acid (ATSDR 2009).

United States Environmental Protection Agency | Solid Waste and Emergency Response (5106P) | EPA 505-F-13-002 March 2013



EPA United States Environmental Protection Agency

Technical Fact Sheet – Perfluorooctane Sulfonate (PFOS) and Perfluorooctanoic Acid (PFOA)

November 2017

TECHNICAL FACT SHEET – PFOS and PFOA

At a Glance

- Manmade chemicals not naturally found in the environment.
- Fluorinated compounds that repel oil and water.
- Used in a variety of industrial and consumer products, such as carpet and clothing treatments and firefighting foams.
- Extremely persistent in the environment.
- Known to bioaccumulate in humans and wildlife.
- Readily absorbed after oral exposure. Accumulate primarily in the blood serum, kidney and liver.
- Toxicological studies on animals indicate potential developmental, reproductive and systemic effects.
- Health-based advisories or screening levels have been developed by EPA and state agencies.
- EPA has not issued a Maximum Contaminant Level (MCL) for drinking water.
- Standard analytical methods use high-performance liquid chromatography coupled with tandem mass spectrometry.
- Resistant to most chemical and microbial conventional treatment technologies. Most common groundwater treatment method is extraction and filtration through granular activated carbon filters.

Introduction

This fact sheet, developed by the U.S. Environmental Protection Agency (EPA) Federal Facilities Restoration and Reuse Office (FFRRO), provides a summary of two contaminants of emerging concern, perfluorooctane sulfonate (PFOS) and perfluorooctanoic acid (PFOA), including physical and chemical properties; environmental and health impacts; existing federal and state guidelines; detection and treatment methods; and additional sources of information. This fact sheet is intended for use by site managers who may address these chemicals at cleanup sites or in drinking water supplies and for those in a position to consider whether these chemicals should be added to the analytical suite for site investigations.

PFOS and PFOA are part of a larger group of chemicals called per- and polyfluoroalkyl substances (PFASs). PFASs, which are highly fluorinated aliphatic molecules, have been released to the environment through industrial manufacturing and through use and disposal of PFAS-containing products (Liu and Mejia Avendano 2013). PFOS and PFOA are the most widely studied of the PFAS chemicals. PFOS and PFOA are persistent in the environment and resistant to typical environmental degradation processes. As a result, they are widely distributed across all trophic levels and are found in soil, air and groundwater at sites across the United States. The toxicity, mobility and bioaccumulation potential of PFOS and PFOA result in potential adverse effects on the environment and human health.

What are PFOS and PFOA?

- They are human-made compounds that do not occur naturally in the environment (ATSDR 2015; EPA 2009b).
- PFOS and PFOA are fully fluorinated, organic compounds. They are the two PFASs that have been produced in the largest amounts within the United States (ATSDR 2015; EFSA 2008).
- PFOS and PFOA are part of a subset of PFASs known as perfluorinated alkyl acids (PFAAs).

United States Environmental Protection Agency | Office of Land and Emergency Management (5106P) | EPA 505-F-17-001 November 2017

美国不同法规下PFOA管理的现状分析

Statutes/Regulations	Synonym	Synonym Quality	Effective Date	End Date	Active Status
2020 CDR TSCA 5(a) SNUR	Octanoic acid, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-	Unknown			Active
2020 CDR TSCA Inv Active	Octanoic acid, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-	Unknown			Active
CCL 4	Perfluorooctanoic acid (PFOA)	Unknown			
EPCRA 313	Perfluorooctanoic acid	Unknown			
TSCA 5(a) Final SNUR	Octanoic acid, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-	Unknown			
TSCA 5(a) Proposed SNUR	Octanoic acid, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-	Valid			
TSCA 12(b) Export	Octanoic acid, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-	Unknown			
TSCA Inv	Octanoic acid, 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluoro-	Valid			Active
UCMR3	Perfluorooctanoic acid	Valid	09/26/2013		Active

- 已经进入2020 CDR 5(a)目录(TSCA显著性新用途工具)和TSCA评估物质工作计划；
- 在安全饮用水法规中的UCMR-3清单和CCL-4清单物质，已经发布饮用水健康标准；
- 美国许多州已经有不同法规下关于PFOA/S及其盐和类别物质的管理规定。

水质标准：美国安全饮用水法规下的PFOA/S饮用水基准(2018年3月公布)

Chemicals	CASRN Number	Standards			Status HA Document	Health Advisories						Cancer Descriptor
		Status Reg.	MCLG (mg/L)	MCL (mg/L)		10-kg Child One-day (mg/L)	10-kg Child Ten-day (mg/L)	RfD (mg/kg/day)	DWEL (mg/L)	Life-time (mg/L)	mg/L at 10^{-4} Cancer Risk	
Metolachlor	51218-45-2	-	-	-	F '88	2	2	***0.1***	3.5	0.7	-	***C***
Metribuzin	21087-64-9	-	-	-	F '88	5	5	***0.01***	0.35	0.07	-	***D***
Monochloroacetic acid	79-11-8	F	0.07	0.06[1]	-	0.2	0.2	0.01	0.35	0.07	-	I
Monochlorobenzene	108-90-7	F	0.1	0.1	F '87	4	4	**0.02**	0.7	0.1	-	D
Naphthalene	91-20-3	-	-	-	F '90	0.5	0.5	**0.02**	0.7	0.1	-	**I**
Nitrocellulose[2]	9004-70-0	-	-	-	F '88	-	-	-	-	-	-	-
Nitroguanidine	556-88-7	-	-	-	F '90	10	10	0.1	3.5	0.7	-	D
Nitrophenol p-	100-02-7	-	-	-	F '92	0.8	0.8	0.008	0.3	0.06	-	D
N-nitrosodimethylamine		-	-	-	-	-	-	-	-	-	**0.00007**	**B2**
Oxamyl (Vydate)	23135-22-0	F	0.2	0.2	F '05	0.01	0.01	0.001	0.035		-	N
Paraquat	1910-42-5	-	-	-	F '88	0.1	0.1	***0.0045***	0.2	0.03	-	***E***
Pentachlorophenol	87-86-5	F	zero	0.001	F '87	1	0.3	**0.005**	0.2	0.04	**0.009**	**L**
PFOA	335-67-1	-	-	-	F '16	-	-	2×10^{-5}	3.7×10^{-4}	7×10^{-5}	5×10^{-2}	S
PFOS	1763-23-1	-	-	-	F '16	-	-	2×10^{-5}	3.7×10^{-4}	7×10^{-5}	-	S
Phenanthrene (PAH)	85-01-8	-	-	-	-	-	-	-	-	-	-	D
Phenol	108-95-2	-	-	-	D '92	6	6	**0.3**	11	2	-	D
Picloram	1918-02-1	F	0.5	0.5	F '88	20	20	***0.02***	0.7	-	-	D
Polychlorinated biphenyls (PCBs)	1336-36-3	F	zero	0.0005	D '93	-	-	-	-	-	0.01	B2
Prometon	1610-18-0	-	-	-	F '88	0.2	0.2	***0.05***	2	0.4	-	***N***
Pronamide	23950-58-5	-	-	-	F '88	0.8	0.8	***0.08***	3	-	***0.1***	***B2***
Propachlor	1918-16-7	-	-	-	F '88	0.5	0.5	***0.05***	2	-	0.1	***L***
Propazine	139-40-2	-	-	-	F '88	-	-	***0.02***	0.7	0.01	-	***N***
Propham	122-42-9	-	-	-	F '88	5	5	0.02	0.6	0.1	-	D
Pyrene (PAH)	129-00-0	-	-	-	-	-	-	0.03	-	-	-	D
RDX[3]	121-82-4	-	-	-	F '88	0.1	0.1	0.003	0.1	0.002	0.03	C
Simazine	122-34-9	F	0.004	0.004	F '88	-	-	***0.02***	0.7	-	-	***N***
Styrene	100-42-5	F	0.1	0.1	F '87	20	2	0.2	7	0.1	-	C
2,4,5-T (Trichlorophenoxy-acetic acid)	93-76-5	-	-	-	F '88	0.8	0.8	0.01	0.35	0.07	-	D

不同环境质量标准之间的关系：

- 对难以通过简单混凝沉淀工艺去除的污染物，饮水质标准按照1：1直接转换成水源标准；
- 对以供水为服务功能的水源，按照水质许可(WQBEL)方式对相关污染源追加排污许可。

New York lawmakers vote to ban PFASs in food packaging

28 July 2020

Bill excludes consideration of alternatives included in Washington, Maine laws

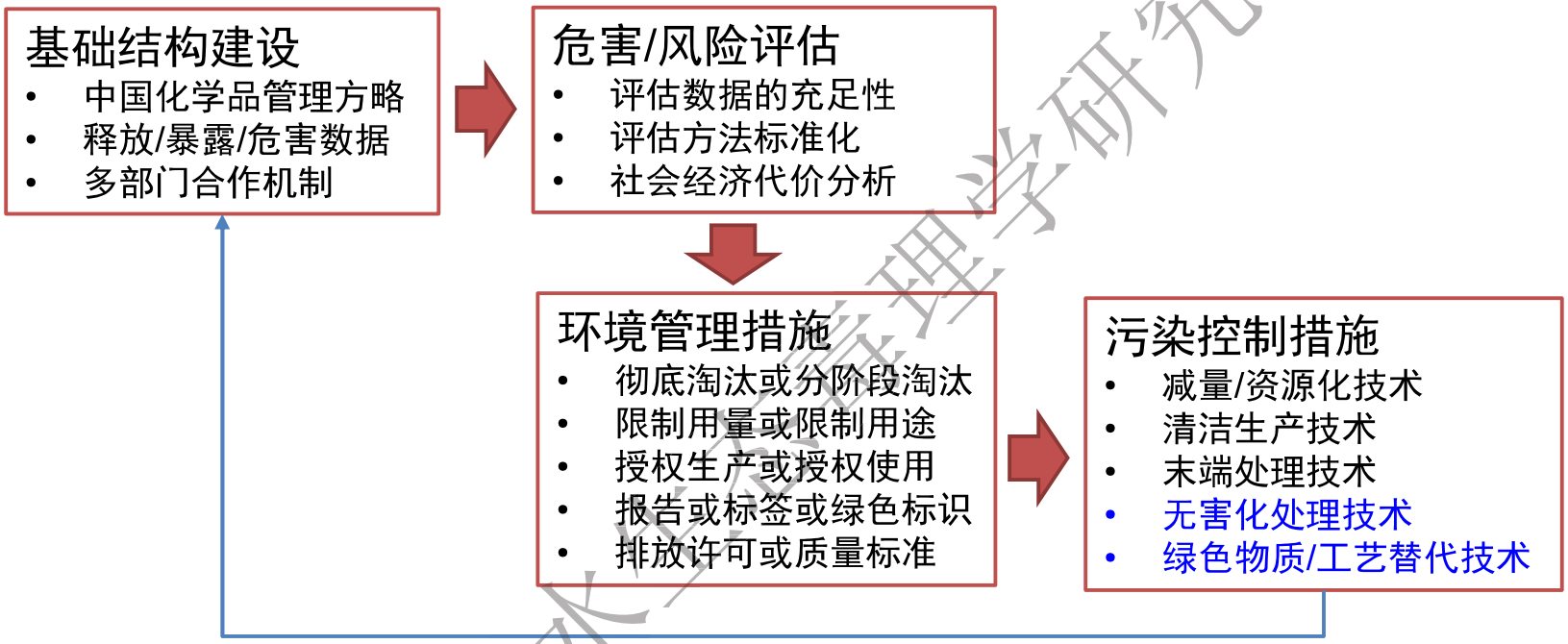
Food contact | PFAS | Chemical restrictions | Food & drink | US states

The New York legislature has approved a measure to ban per- and polyfluoroalkyl substances (PFASs) from food packaging.

If signed into law by Governor Andrew Cuomo, the legislation would make the state the first in the nation to prohibit the full substance class from food packaging without consideration of whether there are suitable substitute products available.

全氟和多氟烷基化合物(PFASs)类别的人造和商业在用化学品总数估计在4730种，建议的管理方式是采用类别化工具(Scoping Plan, NASEM-2019)、根据SNUR规则或全面淘汰。

新关注污染物环境管理的政策工具和风控技术措施建议(仅代表个人意见)



- 化学品管理目的：健康地球、健康人类、促进中国化学工业创新和全球竞争力
- 采用(健全)化学品风险管理和全过程控制路线，创新管理思路
- 强化化学品管理法规顶层设计和立法，签署和执行国际公约要慎重
- 兼顾社会舆论和决策科学性，风险控制节奏与社会经济发展协调或妥协
- 根据风控可靠性和社会经济代价选择风险管理工具，灵活应用多种措施组合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环境检测
水质模拟
流域管理
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大数据中心
智慧决策应用