Submission of Information to the Stockholm Convention Secretariat: Sulfluramid Uses, Environmental Releases, Alternatives

By PAN International

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1. Sulfluramid use

Sulfluramid production and environmental dispersal has been increasing since PFOS was listed under the Stockholm Convention with sulfluramid as an acceptable use for two species of leaf-cutting ants, *Atta* spp. and *Acromyrmex* spp.

A recent paper by the government of Brazil,[1] describes the control of leaf-cutting ants as "essential for Brazilian agribusiness", referring to these two species of ants as "the main pest of forest plantations, agriculture and livestock" – mentioning in particular eucalyptus and pine plantations, grass for livestock, sugar cane, grains, and fruit, but provides no argument for the control of leaf-cutting ants in urban houses. Information provided by Brazil to the POPRC[2] for the addendum to its Risk Management Evaluation also refers only to economic losses due to the impacts of leaf-cutting ants on trees, sugar cane, soybean and maize, whilst the original Risk Management Evaluation[3] referred only to Brazilian agriculture.

No argument has been made for the use of sulfluramid in urban areas or for use on other species of ants or insects, and yet it continues in Brazil in contravention of the Stockholm Convention.

Use appears to be very poorly controlled in Brazil, both in terms of exports to countries that have not registered acceptable uses under the Stockholm Convention, and in terms of uses that are not regarded by the Brazilian government as essential or are not listed as acceptable purposes under the Stockholm Convention.

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[1] De Brito JS, Forti LC, de Oliveira MA et al. 2016. Use of alternatives to PFOS, its salts and PFOSF for the control of leaf-cutting ants *Atta* and *Acromyrmex*. *Int J Res Environ Studies* 3:11-92.
[2] UNEP/POPS/POPRC.4/15/Add.6.
[3] UNEP/POPS/POPRC.3/20/Add.5.

1.1 According to the review by Gilljam et al (2016):[4]

- Sulfluramid was introduced to Brazil in 1993.
- From 2004-2006, production in Brazil was estimated as 30 tonnes per year, with imports of ≤1 tonne/yr from China.
- Production and use of sulfluramid in Brazil jumped dramatically between 2009 and 2010: production increased from 22.67 tonnes/yr in 2008, to 51.31 tonnes/yr in 2010, and it continued to escalate at least until 2013.
- By 2013, Brazilian sulfluramid manufacturing had increased to 59.66 tonnes per year, with over 1 tonne imported, and internal use of 57.98 tonnes.
- The number of manufacturers increased from 5 nationally-owned companies in 2007 to 7 companies in 2012.
- During this time <1.3 tonnes per year were imported, while exports increased from ∼0.3 tonnes in 2004/yr to 2 tonnes/yr in 2014.
- From 2004 to 2015, most exported sulfluramid went to Argentina (7.2 tonnes), Colombia (2.07 tonnes), Costa Rica (1.13 tonnes), Ecuador (2.16 tonnes), and Venezuela (2.4 tonnes).
- Other countries importing sulfluramid from Brazil in 2014-2015 were Bolivia, Guatemala, Honduras, Panama, Paraguay, Suriname, Uruguay, and USA.
- Between 2004 and 2013, sales of sulfluramid in Brazil increased from ∼23 to 58 tonnes/yr, during which time nearly 87% of cumulative sales were in 5 states: Minas Gerais (33.6 tonnes), Mato Grosso do Sul (25.6 tonnes), São Paulo (22 tonnes), Bahia (11.7 tonnes), and Espiŕito Santo (8 tonnes).
- 2 tonnes of sulfluramid were used in Bahia in 2013. These quantities are likely to be underestimated because of data missing for certain years.
- Sulfluramid is manufactured in a variety of formulations containing 0.01−1% w/w granular baits and 93−98% w/w (technical product).

1.2 According to information provided by MAPA (Brazilian Ministry of Agriculture) in February 2018, and relevant from 2013:[5]

- Since 2013, 5 companies are producing sulfluramid baits for use in agriculture: Adama do Brasil S / A; Atta Kill Indústria e Comércio de Defensivos Agrícolas Ltda; Bio Soja Industrias Químicas e Biológicas Ltda; Dinagro Agropecuária Ltda and Unibrás Agro Química Ltda.
- The following quantities were produced:

  2013 – 28.68 tonnes
  2014 – 30.64 tonnes
  2015 – 29.54 tonnes
  2016 – 35.51 tonnes
  2017 – 35.01 tonnes

[4] Gilljam Jl, Leonel J, Cousins IT, Benskin JP. 2016. Is ongoing sulfluramid use in South America a significant source of perfluorooctanesulfonate (PFOS)? Production inventories, environmental fate, and local occurrence. *Environ Sci Technol* 50:653-9.

[5] This information is provided in English translation in the attached document titled RESPOSTAS INGLÊS.

- Information on sales and use for other than leaf-cutting ants was not available from MAPA.
- Brazil does not import sulfluramid.
- Since 2009, Brazil has exported sulfluramid to Argentina, Bolivia, Colombia, Costa Rica, Ecuador, El Salvador, Guatemala, Honduras, Nicaragua, Panama, Paraguay, Peru, Suriname and Uruguay.
- Two companies export sulfluramid: Atta kill Industry and Commerce of Defensivos Agrícolas Ltda, and Adama Brasil S / A, in the following quantities:

  2013: 1518,87 kg
  2014: 1943,25 kg
  2015: 1473 kg
  2016: 2110,23 kg
  2017: 1903,56 kg

1.4 Gilljam et al 2016b[6]

This follow-up paper to acknowledges the differences in estimates of sulfluramid production between Gilljam et al 2016 and the Government of Brazil, specifically in terms of the information in their National Implementation Plan, 2015; but this is also relevant to the above information from MAPA. There appears to be uncertainty as to the actual amount of sulfluramid produced because of a lack of clarity about the amount of imported PFOS and how much of that is converted to sulfluramid.

1.5 Non-complying domestic use of sulfluramid

Gilljam et al (2016b) also reported 69 additional sulfluramid products produced by 31 companies for household use, and that agricultural companies also have sulfluramid products registered for domestic use – including pastes to control termites, pastes to control cockroaches, and paste and granulated baits to control household ants. All these uses do not comply with the Stockholm Convention. According to Gilljam et al (2016b), as of January 8th, 2015, the Brazilian Health Surveillance Agency (Anvisa) set a period of 1 year for companies to sell their stocks and remove products from the Brazilian market (Anvisa Resolution, RE No. 41).

However, sulfluramid is still widely available, including being sold over internet, to the general public at cheap prices, for uses other than those of economic importance involving leaf-cutting ants, including for cockroaches and household ants that are called sweet ants or urban ants. These products are for sale to the general public without any warnings about danger to the environment or persistence. Technical information provided by the Paraná state government states that DINAGRO-S (0.3% sulfluramid) is for three *Atta* spp. only (*Atta capiguara* or saúva parda*, Atta sexdens rubropilosa or* saúva limão, *Atta laevigatta or* saúva cabeça de vidro), and that the product is classified as dangerous

[6] Gilljam JL, Leonel J, Cousins IT, Benskin JP. 2016. Additions and correction to Is ongoing sulfluramid use in South America a significant source of Perfluorooctanesulfonate (PFOS)? Production inventories, environmental fate, and local occurrence. *Environ Sci Technol* 50(2):653-9.

for environment, highly persistent and has high bioaccumulation.[7] Yet a manufacturer UNIBRAS AGRO QUIMICA states that its product ATTA MEX-S is of low toxicity for humans and the environment.[8]

The following products were still advertised for purchase over Internet and/or available in stores in Brazil on February 14th 2018:

- Atratex – contains sulfluramid (0.3%); advertised for sweet ants.[9] Product was purchased from a garden and pet store in Curitiba, the capital city of the state of Paraná, on February 14th 2018. The reverse side of the label recommends it for domestic ants; states how to used (Distribute the content of ATRATEX in various points using the dispenser. Apply in dry places most frequented by the ants); manufactured by SINGRA QUIMICA LTDA, Piracicaba, São Paulo State; manufacturing date: February 2017 (see attached photos).
- Formikell Gel: contains sulfluramid (0.1%); all types of ants including sweet ants in houses and gardens.[10]
- Formisca: contains sulfluramid; for use against ants in homes and gardens.[11]
- Formibel: contains sulfluramid (0.2%); sold in supermarkets for use against sugar ants.[12]
- Rainha Verde S: contain sulfluramid (0.01%); for amateur use in gardens and near houses.[13]
- Blatacel S: contains sulfluramid (1%); for use on cockroaches (*Blatella germanica* and *Periplaneta americana*); registered with ANVISA (No Registro no M.S./ANVISA: 3.1704.0048.001-1).[14]
- Formicida 7 Belo Gel: according to the website this product contains sulfluramid (0.2%); for ants in homes (sweet ants);[15] however on another part of the website it says the active is indoxacarb.

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[7] http://www.adapar.pr.gov.br/arquivos/File/defis/DFI/Bulas/Inseticidas/FORMICIDA_DINAGRO_-_S.pdf

[8] http://www.unibras.com.br/tecnico-detalhe/controle-das-formigas-cortadeiras/

[9] (i) https://agrovendas.loja2.com.br/5305210-Atratex-Mata-Formigas-Doceiras
(ii) https://agrovendas.loja2.com.br/category/1221354-Formicidas
(iii) http://www.boutinagrocomercial.com.br/resultadopesquisa?pag=1&departamento=&buscarpor=formiga&smart=0

[10] (i) https://www.americanas.com.br/produto/10527957/formikell-gel-mata-formiga-10gr?tamanho=Nao%20se%20aplica
(ii) http://kelldrin.com.br/wp-content/uploads/2016/06/kelldrin-2016.pdf
(iii) https://www.unir.br/noticias_arquivos/23602_fispq_formikell.pdf

[11] https://produto.mercadolivre.com.br/MLB-905570528-isca-mata-formiga-500gr-formicida-granulado-_JM

[12] http://www.casafiesta.com.br/produto/inseticida-em-gel-formibel-mata-formigas-doceiras-10g-68213

[13] (i) http://www.tecnocellagro.com.br/linha-domestica/rainhaverdes.html
(ii) http://www.tecnocellagro.com.br/linha-domestica/images/produtos/single/rainhaverdes/ficha-tecnica-rainha_verde.pdf

[14] http://www.tecnocellagro.com.br/linha-domestica/images/produtos/single/blatacel/ficha-tecnica-blatacel.pdf

- Ferra Baratas: contains sulfluramid; for cockroaches.[16]
- FORISK GEL: contains sulfluramid; for "urban ants";[17] also sold in a pet shop for home and garden use.[18]
- BARAMID GEL: contains sulfluramid; also sold in a pet shop, for cockroaches.[19]

2. Sulfluramid in the environment

2.1 According to the review by Gilljam et al (2016):

- All catchments from the 5 states Minas Gerais, Mato Grosso do Sul, São Paulo, Bahia, and Espiŕito Santo where the majority of sulfluramid is used, drain into the Atlantic Ocean.
- PFASs were detected in all samples of surface water taken in Bahia, at concentrations ranging from 287 to 4879 pg/L ΣPFASs. Whilst sulfluramid itself was not detected, PFOS was detected in all samples (63-1061pg/L). FOSA was found in four out of seven samples and was present in the highest levels (≤14−3362 pg/L).
- The high FOSA/PFOS ratio observed (up to 14:1) is unprecedented in the scientific literature; and is suggestive of degradation of sulfluramid. The ΣPFAS profile of some samples, those that did not contain elevated FOSA are indicative of an industrial source.
- Depending on the extent of conversion of sulfluramid to PFOS, cumulative Brazilian sulfluramid production and import from 2004 to 2015 may contribute between 167 and 487 tonnes of PFOS/FOSA to the environment.
- Modelling, using the Level III Fugacity-based Multimedia Environmental Model (Version 2.80), which simulates the steady state distribution of a chemical in a closed environment, predicts that the only significant removal process of sulfluramid is predicted to be transformation in soil to form FOSA, FOSAA, and PFOS, with PFOS readily transported in the soil pore water and to enter surface waters. As the application of sulfluramid is to the soil to control leaf-cutter ants, emissions were assumed to occur exclusively to soil. While the emission rate is often arbitrary in evaluative modelling, the authors chose a "realistic emission rate" of 0.35 tonnes/yr or 0.04 kg/h.
- Cumulative import and production of sulfluramid in Brazil from 2004 to 2015 are estimated to equate to approximately 147.3 tonnes of anionic FOSA and 19.5 tonnes of anionic PFOS (166.8 tonnes total), but this is thought to be an underestimation. If complete conversion of sulfluramid to PFOS is assumed, then

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[15] http://www.serverquimica.com.br/produtos/formicida-7-belo/gel

[16] (i) https://www.cobasi.com.br/inseticida-ferra-barata-nobel-10g-3544353/p?idsku=544353&utmi_cp=melhorpreco&gclid=CjwKCAiA5OrTBRBlEiwAXXhT6MWQz5OFBSGsbmB-8rf5rnmMPa3lqjW2SEhptiC6VcTgs5-e4AbTGhoCw9EQAvD_BwE
(ii) https://www.lojatudo.com.br/casa-cozinha-jardim/inseticida-sulfluramida-ferra-barata-nobel-10g.html

[17] http://www.fazfertil.com.br/produtos/forisk-inseticida-gel

[18] https://www.redepetminas.com.br/casa-e-jardim/inseticidas-e-agrotoxicos/for-isk-gel-10-gr/

[19] https://www.redepetminas.com.br/casa-e-jardim/inseticidas-e-agrotoxicos/baramid-gel-10-grs/

Brazilian sulfluramid could contribute up to 487 tonnes of PFOS in the environment.

2.2 Uptake by crops

An experiment carried out in a soil/carrot mesocosm over 81 days, to assess uptake, leaching, and biodegradation of sulfluramid (N-ethyl perfluorooctane sulfonamide (EtFOSA) and its transformation products, demonstrated that the use of sulfluramid baits can lead to residues of PFOS in crops, and in the surrounding environment, in considerably higher yields than previously thought. The more hydrophilic transformation products, such as PFOS, were found mainly in the leaves, and the more hydrophobic products (e.g. FOSA, FOSAA and EtFOSA) in the peel and core of the carrots. A sulfluramid technical standard yielded 34% PFOS, while the commercial bait formulation Grão Forte bait formulation containing 0.0024 % EtFOSA yielded up to 277 %, the higher yield thought to be associated with one or more unidentified PFOS-precursors in the commercial bait. A longer exposure time is expected to produce even higher yields of PFOS.[20]

3. Alternatives

3.1 Bioisca

Bioisca is a biological alternative to sulfluramid, developed in Brazil and based on an extract of the leguminous plant *Tephrosia candida* (white hoarypea). It is a granulated bait approved in Brazil for use by organic farmers against the ant species *Atta sexdens rubropilosa* (saúva-limão) and *Atta laevigata* (saúva cabeçade-vidro).[21] It is highly attractive to ants, which carry it into their nests. It has a fungicidal action that eliminates the fungus that leaf-cutting ants cultivate to break down hard-to-digest plant material. The product was approved by ANVISA in 2010, registered by the Ministry of Agriculture in 2011, and in 2015 certified as an organic product by Biodynamic. Application rate is recommended at 10 gms/m^2. Efficacy of the product has been validated in various regions of Brazil.

3.2 Pathogenic fungi Escovopsis sp.

A 12-year study by Meirlles et al (2015) of sites in Brazil (22 sites), Panama (four sites), the Caribbean island of Guadeloupe (one site), Argentina (one site) and Mexico (one site) has identified 61 strains of *Escovopsis* parasitic fungi infecting the fungal gardens of leaf-

[20] Zablate I, Bizkarguenaga E, Nunoo DB, Schultes L, Leonel J, Prieto A, Zuloaga O, Benskin JP. 2018. Biodegradation and uptake of the pesticide sulfluramid in a soil/carrot mesocosm. *Enivron Sci Technol* Epub Feb 8th].

[21] http://www.adapar.pr.gov.br/arquivos/File/defis/DFI/Bulas/Outros/bioisca.pdf; https://www.agrolink.com.br/agrolinkfito/produto/bioisca_8631.html

cutting ant species, that show promise as potential biological control agents of leaf-cutting ants although more research is needed to confirm this potential.[22]

3.4 Pathogenic fungi Syncephalastrum sp

The pathogenic fungus *Syncephalastrum* sp. shows considerable potential as a biological control for leaf-cutting ants. In a controlled experiment, various strains of *Syncephalastrum* sp., isolated from fungus gardens of colonies of *Atta sexdens rubropilosa* reared in a laboratory and which had been treated with sulfluramid, were introduced to sub-colonies containing workers and fungus garden sampled from a mature *A. sexdens rubropilosa* colony (14 years old) maintained at the Centre for the Study of Social Insects.[23]

The sub-colonies inoculated with *Syncephalastrum* sp. spores developed an infection, and although this was recognised by worker ants, which then removed contaminated fragments from the fungus garden, they were unable to remove sufficient of it.

All *Syncephalastrum* sp. strains inhibited the mycelial growth of *Leucoagaricus. gongylophorus* when compared with the control. *L. gongylophorus* is a mutualistic fungus that leaf-cutter ants maintain to obtain food: *L. gongylophorus* converts plant polysaccharides into glucose, which is consumed by leaf-cutter ants.

Sub-colonies treated with spores of the *Syncephalastrum* sp. strain LESF 127 exhibited a significant decline in foraging activities compared with the control from the 3rd day, and were interrupted on the 11th day. Ant mortality increased significantly relative to the control on the fifth day, and all workers died in the 13th day. Sub-colony deterioration had already begun on day 1, and sub-colony death occurred on day 13. In response to *Syncephalastrum* sp. infection, worker ants ceased foraging and leaf-fragment incorporation activities, and removed a large amount of fungus garden fragments, leading to garden decay. Thus, it appears that fungus garden deterioration is a complex outcome resulting from pathogen-mediated damage in association with host-mediated damage

Sub-colonies treated with the spores of both *Syncephalastrum* sp. and *Metarhizium anisopliae* had significantly lower foraging activity, compared with the control, from the 3rd day, and these activities were completely interrupted by the 9th day. Ant mortality increased significantly from the 3rd day, with total mortality on the 11th day. Sub-colonies deteriorated significantly relative to the control from the 1st day, and the death of the fungus garden occurred on the 8th day.

3.3 Biodiversity

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[22] Meirelles LA, Solomon SE, Bacci M, Wright AM, Mueller UG, Rodrigues A. 2015. Shared Escovopsis parasites between leaf-cutting and non-leaf-cutting ants in the higher attine fungus-growing ant symbiosis. *Royal Society Open Science* 2:150257.

[23] Barcoto MO, Pedrosa F, Bueno OC, Rodrigues A. 2017. Pathogenic nature of *Syncephalastrum* in *Atta sexdens rubropilosa* fungus gardens. *Pest Manag Sci* 73: 999-1009.

On-farm biodiversity dramatically reduces the damage caused by leaf-cutting ants. In a study of coffee farms in Costa Rica, the provision of complex shade reduced leaf lost from 40% experienced in coffee monocultures to <1%. The ant species *Atta cephalotes* L. significantly preferred the leaves of the predominant shade tree *Erythrina poeppigiana* to those of coffee plants.[24]

Hence, an integrated approach involving improvements in on-farm diversity in conjunction with biological controls such as the pathogenic fungi described above have the capacity to reduce damage by leaf-cutter ants below the economic threshold, such that sulfluramid and other chemical interventions would no longer no longer necessary.

4. Benefits of leaf-cutting ants

Leaf-cutting ants have developed anti-fungal bacteria, which they store on their bodies, to preserve their food-digesting fungi. Scientists have identified these bacteria as a promising new source of antibiotics for human use.[25]

[24] Varón EH, Eigenbrode SD, Bosque-Pérez NA, Hilje L. 2007. Effect of farm diversity on harvesting of coffee leaves by the leaf-cutting ant *Atta cephalotes*. *Agricultural and Forest Entomology* 9:47–55.
[25] https://hms.harvard.edu/news/ants-and-antifungals