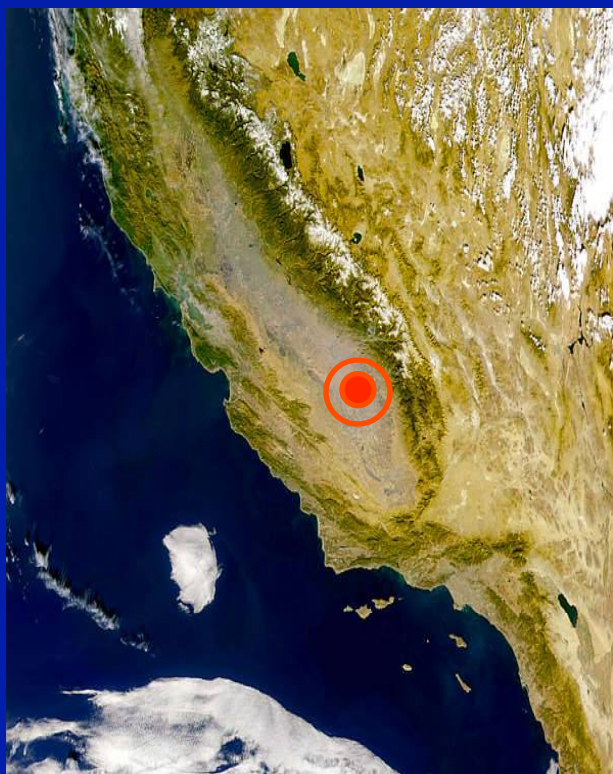


"Postharvest chemistry research at USDA-ARS: Breaking specialty crop trade barriers"

Crop Protection & Quality Unit

Spencer S. Walse

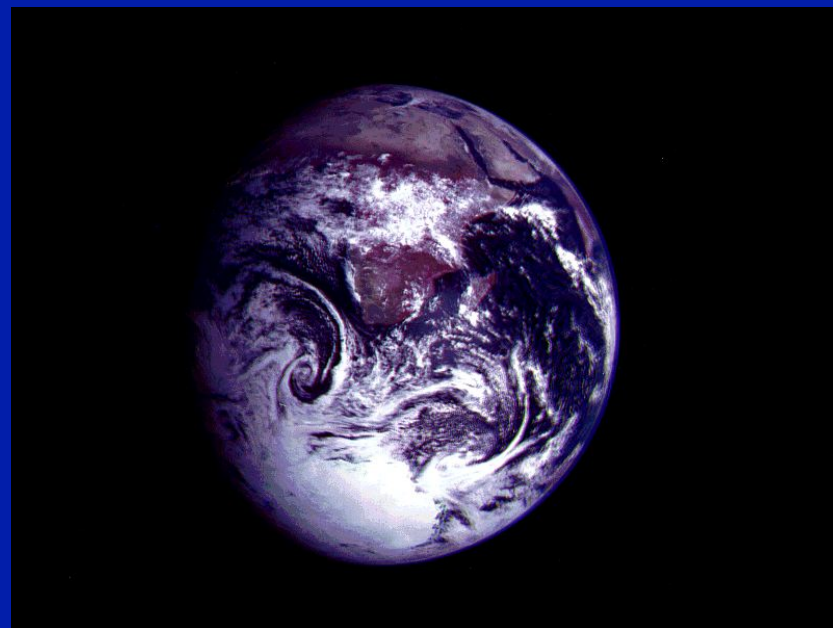
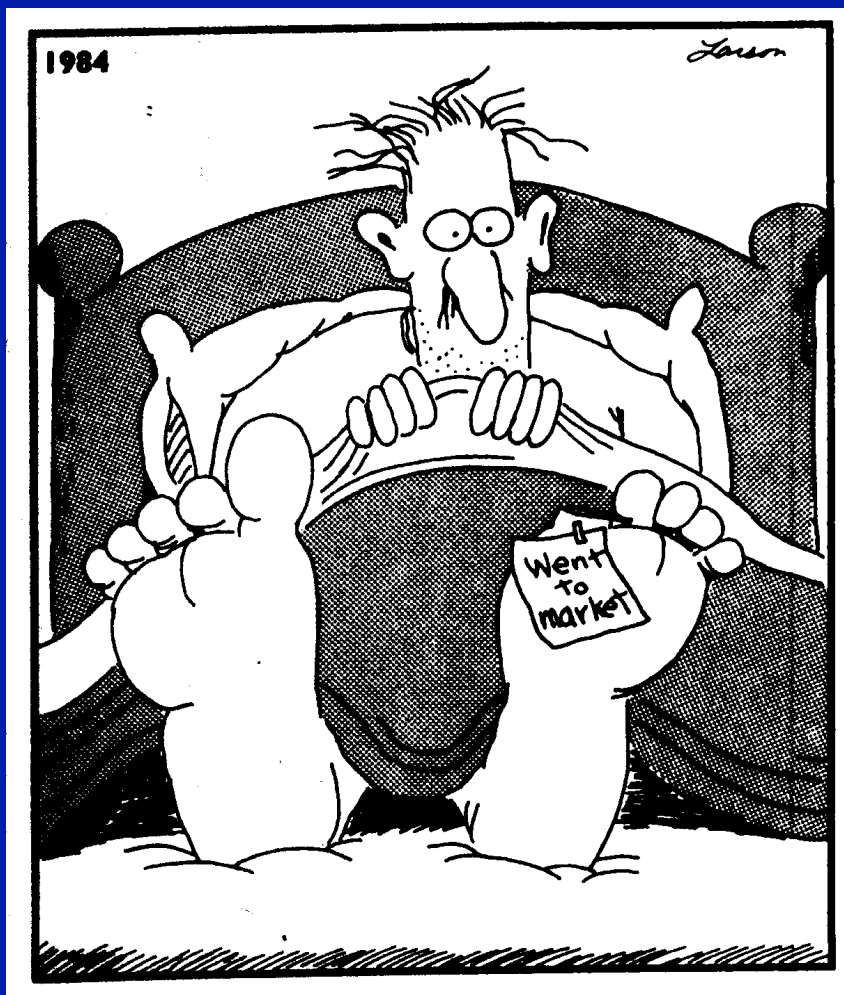


<http://fresno.ars.usda.gov>

<http://agchem.ucdavis.edu/> **UCDAVIS** UNIVERSITY OF CALIFORNIA

30,000 ft view – what do we want to do?

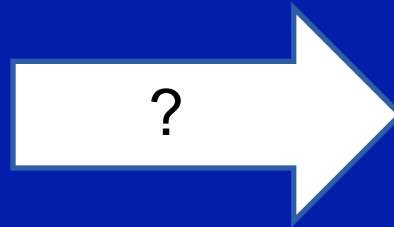
(Proactively) Address Consumer & Regulatory Demands.....



....for the Global Ag. Market

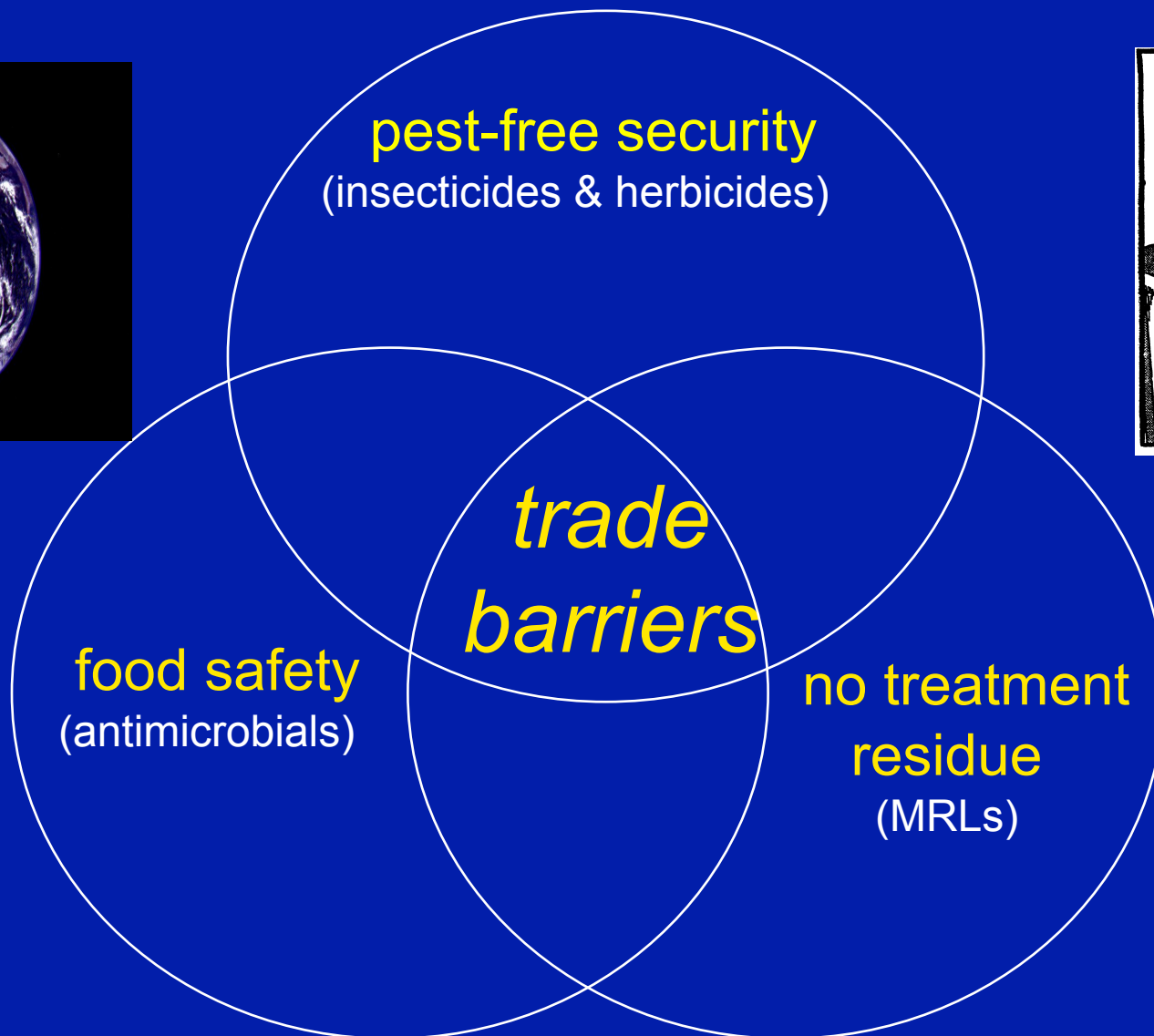
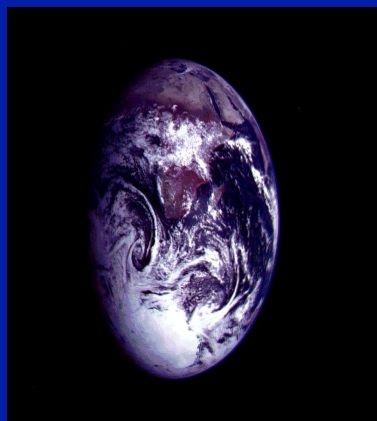
Consumer Ag. Demands (Phobias)

<http://phobialist.com/#l->



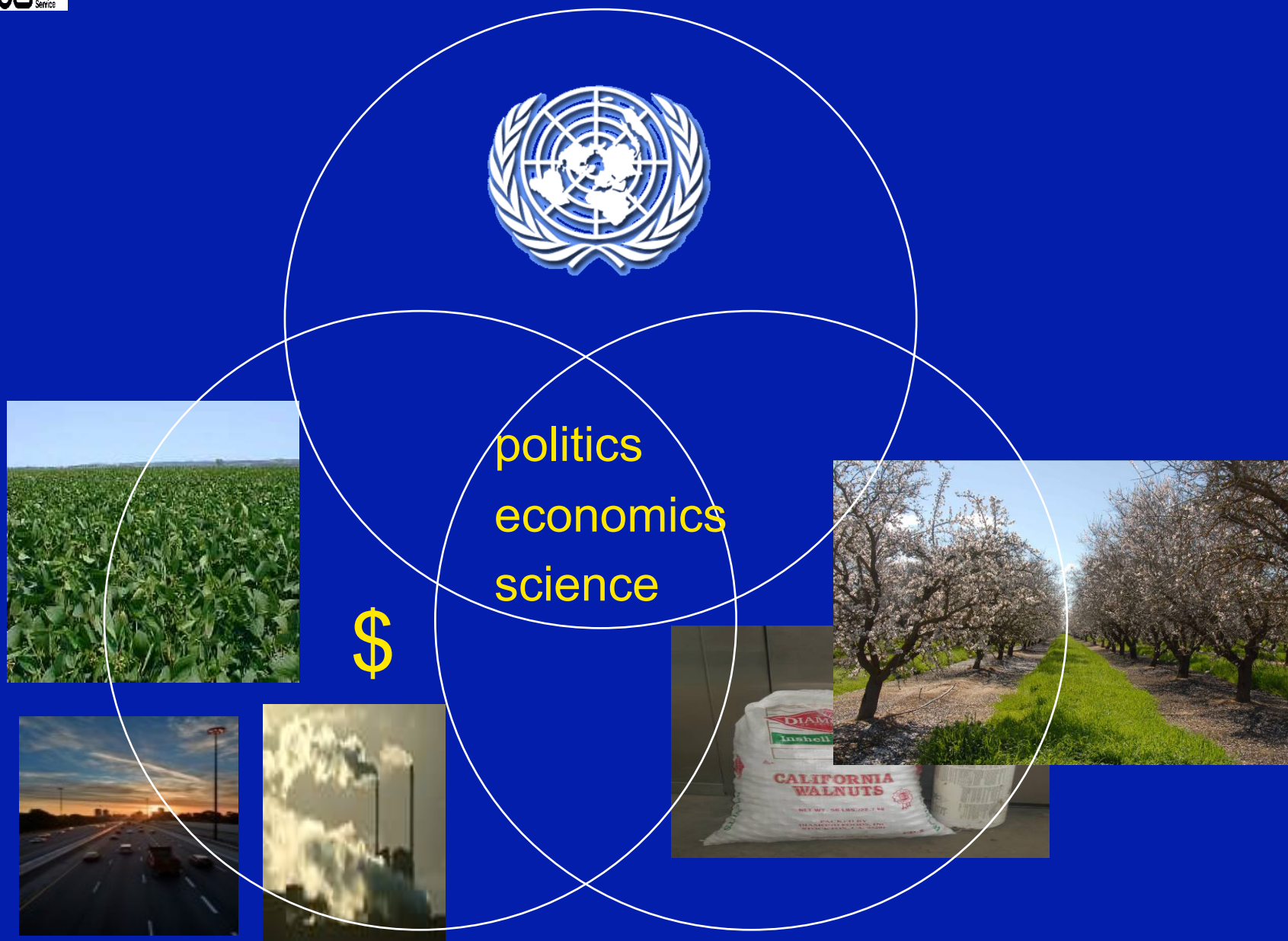
- Insectophobia – insects
- Iophobia- poison
- Radiophobia – radiation
- Microbiophobia - microbes (germs)
- Genophobia- **Fear of sex** (GMO)
- Chemophobia - chemicals
- Chrometophobia - \$\$ money
- Georgophobia - farms
- Gnosiophobia- knowledge

Consumer Ag. Demands



Agricultural Conundrum –
must use chemicals, but can't????

Trade barriers (fosetyl aluminum)





Overview

- fosetyl-AI
 - regulatory chronology
 - political paperwork
 - economic undertones
 - forward course
- scientific underpinnings
 - methodology
 - environmental chemistry
 - physiological relevance





California walnut recalls: fosetyl-Al

Dec, 2013

relana[®]
Mitglied im relana[®] Qualitätszirkel.



DAkKS
Deutsche
Akkreditierungsstelle
D-PL-14400-01-00

Durch die DAkKS nach ISO/IEC 17025
akkreditiertes Prüflaboratorium.
Die Akkreditierung gilt für die in der
Urkunde aufgeführten Prüfverfahren.

bilacon
Gesellschaft für Laboranalytik,
Lebensmittelhygiene
und Prozessmanagement mbH

Prüfumfang:	Fosetyl-Al und Phosphonsäure			
Untersuchungsverfahren:	PV-SA-085; Teil 4			
	PV-SA-085; Teil 4			
Parameter	Einheit	Ergebnis	HG	BG
Fosetyl-Aluminium	mg/kg	n.n.		0,01
Phosphonsäure	mg/kg	11,8		0,10
Fosetyl-Al (Summe aus Fosetyl und Phosphonsäure und deren Salzen, ausgedrückt als Fosetyl)	mg/kg	15,9	2,00	

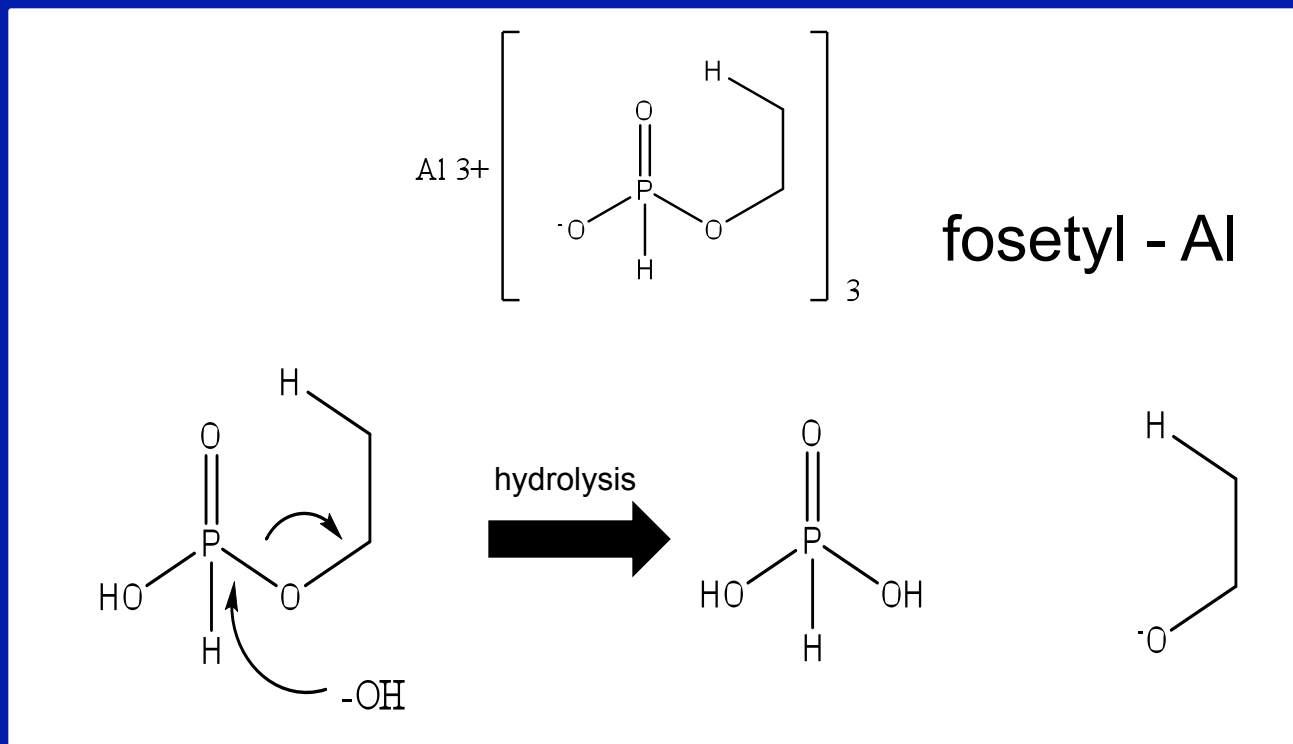
BG = Bestimmungsgrenze

HG = Höchstgehalt nach EU - Verordnung

n.n. = nicht nachweisbar entsprechend der Nachweisgrenze der Methode



fosetyl rapidly hydrolyzes

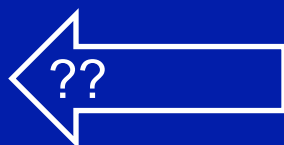


fosetyl (MW 110)

PO_3 (MW 82) phosphite,
phosphonate, phosphorous acid

$$110/82 = 1.34$$

MRL: 2ppm



1.5ppm



Those seeking tolerances.....



EFSA Journal 2009; 7(9):1313

REASONED OPINION

Modification of the existing MRL for fosetyl-Al in radishes¹

European Food Safety Authority²

European Food Safety Authority (EFSA), Parma, Italy

It is also noted that phosphorous acid in plants does not only result from the use of fosetyl-Al, but also other pesticides like potassium phosphonate, foliar P fertilizers and some organic products used for foliar fertilization can be a source of phosphorous acid which could mimic a treatment with fosetyl-Al. Therefore, in the framework of the MRL review under Article 12(2) of Regulation EC (No) 396/2005 the current residue definition and the MRLs established of should be reconsidered, taking into account other sources of phosphorous acid.



Why phosphite???

ABSTRACT

Ouimette, D. G., and Coffey, M. D. 1989. Phosphonate levels in avocado (*Persea americana*) seedlings and soil following treatment with fosetyl-Al or potassium phosphonate. Plant Disease 73:212-215.

The levels of ethyl phosphonate and phosphonate in avocado seedlings and soil were determined using high-performance ion chromatography at 1, 2, 4, 6, and 8 wk following foliar or soil applications of either 3 mg/ml of fosetyl-Al or 2.1 mg/ml of potassium phosphonate. After soil treatment with either potassium phosphonate or fosetyl-Al, phosphonate persisted in soil for 2 and 4 wk, respectively. With fosetyl-Al, low levels of ethyl phosphonate were present in soil, roots, and stems 1 wk after application, but none was detected thereafter. In contrast, no ethyl phosphonate residues were detected in either soil or avocado tissue 1 wk following foliar application of fosetyl-Al. Soil treatment with both potassium phosphonate and fosetyl-Al resulted in much higher phosphonate levels being present in all tissues compared with foliar treatment (up to 78 and 94 times more in the root samples following potassium phosphonate and fosetyl-Al treatment, respectively). Following both soil and foliar applications of the two fungicides, high phosphonate levels were maintained in avocado tissues for the 8-wk period of the experiments, suggesting that phosphonate is stable in plants. The phosphonate levels found in roots after either soil or foliar applications were sufficiently high to account for a direct antifungal effect in controlling avocado root rot caused by *Phytophthora cinnamomi*.

Ouimette, D. G., and Coffey, M. D. 1988. Quantitative analysis of organic phosphonates, phosphonate, and other inorganic anions in plants and soil by using high-performance ion chromatography. Phytopathology 78:1150-1155.



Questions were brewing



European Food Safety Authority

EFSA Journal 2012;10(11):2961

REASONED OPINION

Reasoned opinion on the review of the existing maximum residue levels (MRLs) for fosetyl according to Article 12 of Regulation (EC) No 396/2005¹

European Food Safety Authority^{2, 3}

European Food Safety Authority (EFSA), Parma, Italy

ABSTRACT

According to Article 12 of Regulation (EC) No 396/2005, the European Food Safety Authority (EFSA) has reviewed the Maximum Residue Levels (MRLs) currently established at European level for the pesticide active substance fosetyl. In order to assess the occurrence of fosetyl residues in plants, processed commodities, rotational crops and livestock, EFSA considered the conclusions derived in the framework of Directive 91/414/EEC as well as the import tolerance and European authorisations reported by Member States (incl. the supporting residues data). Based on the assessment of the available data, MRL proposals were derived and a consumer risk assessment was carried out. Although no apparent risk to consumers was identified, some information required by the regulatory framework was found to be missing. Hence, the consumer risk assessment is considered indicative only and some MRL proposals derived by EFSA still require further consideration by risk managers.



EPA exemption

Federal Register / Vol. 71, No. 163 / Wednesday, August 23, 2006 / Rules and Regulations 49373

§ 180.1210 Phosphorous acid; exemption from the requirement of a tolerance.

An exemption from the requirement of a tolerance is established for residues of phosphorous acid and its ammonium, sodium, and potassium salts in or on all food commodities when used as an agricultural fungicide and in or on potatoes when applied as a post-harvest treatment at 35,600 ppm or less phosphorous acid.

[FR Doc. E6-13954 Filed 8-22-06; 8:45 am]



EU Exemption?



EUROPEAN COMMISSION
HEALTH AND FOOD SAFETY DIRECTORATE-GENERAL

Safety of the Food Chain

Pesticides and Biocides

SANCO/11188/2013
Rev. 2, 14 September 2015

Guidance document on criteria for the inclusion of active substances into Annex IV of
Regulation (EC) N° 396/2005.

2.	CRITERIA FOR INCLUSION OF AN ACTIVE SUBSTANCE IN ANNEX IV	3
2.1.	THE ACTIVE SUBSTANCE IS APPROVED AS A BASIC SUBSTANCE UNDER REGULATION (EC) No 1107/2009 (CRITERION 1)	3
2.2.	THE COMPOUND IS LISTED IN ANNEX I OF REGULATION (EC) No 396/2005 (CRITERION 2)	4
2.3.	THE COMPOUND HAS NO IDENTIFIED HAZARDOUS PROPERTIES (CRITERION 3)	4
2.3.1.	<i>Micro-organisms</i>	4
2.3.2.	<i>Chemicals and natural materials</i>	5
2.4.	THE CONSUMER EXPOSURE TO THE COMPOUND LINKED TO USE AS PPP IS CONSIDERED AS NEGLIGIBLE COMPARED TO OTHER USES IN THE FOOD CHAIN AND/OR NATURAL BACKGROUND	6
2.4.1.	<i>Natural exposure is higher than the one linked to the use as PPP (criterion 4)</i>	6
2.4.2.	<i>No consumer exposure is forecasted linked to the mode of application of the PPP (Criterion 5)</i>	7
2.5.	CASE-BY-CASE DECISIONS	8



the letter

Ref. Ares(2014)2846845 - 01/09/2014



EUROPEAN COMMISSION
HEALTH AND CONSUMERS DIRECTORATE-GENERAL

Directorate E - Safety of the Food Chain
E3 - Chemicals, contaminants, pesticides

Brussels,
SANCO/E3/VW/np

Letter to stakeholders:

Trade problems due to phosphonate residues in certain food products

In early 2014, the European Commission received information from Member States and food business operators showing the presence of phosphonates in or on certain products leading to higher residues than the maximum residue level (MRL) of 2 mg/kg laid down in Regulation (EC) No 396/2005¹ for those products, corresponding to the limit of determination. The MRLs for fosetyl apply to phosphonate residues because phosphorous acid and its salts are included in the residue definition for enforcement of fosetyl.

on the day following that of its publication. Application of the temporary MRLs will be limited until 31 December 2015.

It is the responsibility of food business operators to find solutions to ensure compliance with the MRLs at 2 mg/kg, which will be applicable again from 1 January 2016, in future growing seasons. Discussions are currently ongoing to clarify the most appropriate approach to regulate phosphonate-containing products, as phosphonates are approved as active substances in plant protection products in the EU, but also used in fertiliser products and as biostimulants. However, regardless of the legal status of products containing phosphonates, phosphonate residues fall within the scope of Regulation (EC) No 396/2005 and food placed on the market has to comply with the MRLs set in its Annexes. Stakeholder organisations have an important role to play in ensuring communication to different economic entities along the food chain, to prevent the occurrence of similar issues in the next growing seasons.



2015 Temporary MRL

pesticides.mrl@efsa.europa.eu

Type: Statement of EFSA

On request from: European Commission

Question number: EFSA-Q-2014-00358

Approved: 19 May 2014

Published: 20 May 2014

Affiliation: European Food Safety Authority (EFSA), Parma, Italy

Abstract

In accordance with Article 43 of Regulation (EC) No 396/2005, the European Commission requested EFSA to perform a dietary risk assessment of the proposed temporary MRLs for fosetyl-Al. These temporary MRLs should accommodate for residues found in different commodities which are according to food business operators most likely resulting from the use of foliar phosphorous fertilizers which could mimic the treatment with fosetyl-Al. The European Commission proposed to raise the existing MRLs as a proportionate risk management measure on a temporary basis to avoid market disruptions, provided that the proposed temporary MRLs do not pose a consumer health risk. EFSA concludes that the overall dietary exposure to fosetyl-Al (sum of fosetyl and phosphonic acid and their salts expressed as fosetyl) linked to the proposed temporary MRLs for the crops under assessment and the existing MRLs for other commodities covered by the EU MRL legislation is not expected to result in a consumer exposure exceeding the toxicological reference values for fosetyl. Considering that the exposure assessment was performed with a conservative approach which is likely to overestimate the real exposure, EFSA concludes that the proposed temporary MRLs are unlikely to pose a consumer health risk. Since the source of the occurrence of the residues in the crops under consideration is not clarified, the conclusions of the risk assessment are restricted to the identified residues of phosphonic acid. EFSA derived several recommendations to be considered by risk managers to identify the source of the contamination aiming to reduce the uncertainties of the risk assessment.



Pre 2016 season.....frantic

- Analytical investigation
- California Tree Nut Coalition
- USDA – FAS
- USTR
- Industry: importers & exporters



2019 Temporary MRL granted

EU-28

Date: 1/4/2016

GAIN Report Number: E16001

Post: Brussels USEU

New EU MRL for Fosetyl Takes Effect

Report Categories:

Fresh Fruit Tree Nuts

Trade Policy Monitoring

Approved By: Karisha Kuypers **Prepared By:**

Gerda Vandercammen

Report Highlights:

On January 1, 2016, the EU maximum residue limit (MRL) for fosetyl-al for several fruits and vegetables reverted back to the detection level set at 2 mg/kg. A yet-to-be published regulation will keep the fosetyl-al MRL for almonds, cashew nuts, hazelnuts, macadamias, pistachios, and walnuts at 75 mg/kg until March 1, 2019. However, imports of berries and other commodities that use fosetyl or other phosphonate crop inputs will likely be threatened by the return to the default MRL.



Those seeking tolerances.....

APPROVED: 20 November 2015

PUBLISHED: 11 December 2015

doi:10.2903/j.efsa.2015.4327

Modification of the existing maximum residue level for fosetyl in blackberry, celeriac and Florence fennel

European Food Safety Authority (EFSA)

Abstract

In accordance with Article 6 of Regulation (EC) No 396/2005, the evaluating Member State (EMS), Germany, received applications from Landwirtschaftliches Technologiezentrum Augustenberg and Landwirtschaftskammer NRW – Pflanzenschutzdienst to modify existing MRLs for the active substance fosetyl-Al in blackberry, celeriac and Florence fennel. Germany drafted evaluation reports in accordance with Article 8 of Regulation (EC) No 396/2005, which were submitted to the European Commission and forwarded to EFSA. According to EFSA data are sufficient to derive MRL proposals of 100 mg/kg for fosetyl in blackberries and of 8 mg/kg in celeriac. No change is recommended for fennel, since the supported use results in a lower MRL proposal than the MRL of 2 mg/kg currently into force under Regulation (EU) 991/2014. Based on the risk assessment results, EFSA concludes that the proposed use of fosetyl on blackberries, celeriac and Florence fennel will not result in a consumer exposure exceeding the toxicological reference value and therefore is unlikely to pose a consumer health risk.



EU Exemption?



EUROPEAN COMMISSION
HEALTH AND FOOD SAFETY DIRECTORATE-GENERAL

Safety of the Food Chain

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Help from USDA-FAS-TASC

- Establishing a fosetyl tolerance – IR4
- Understanding environmental chemistry of phosphite (and phosphate)



EU Exemption

Cartoon of “P” chemistry

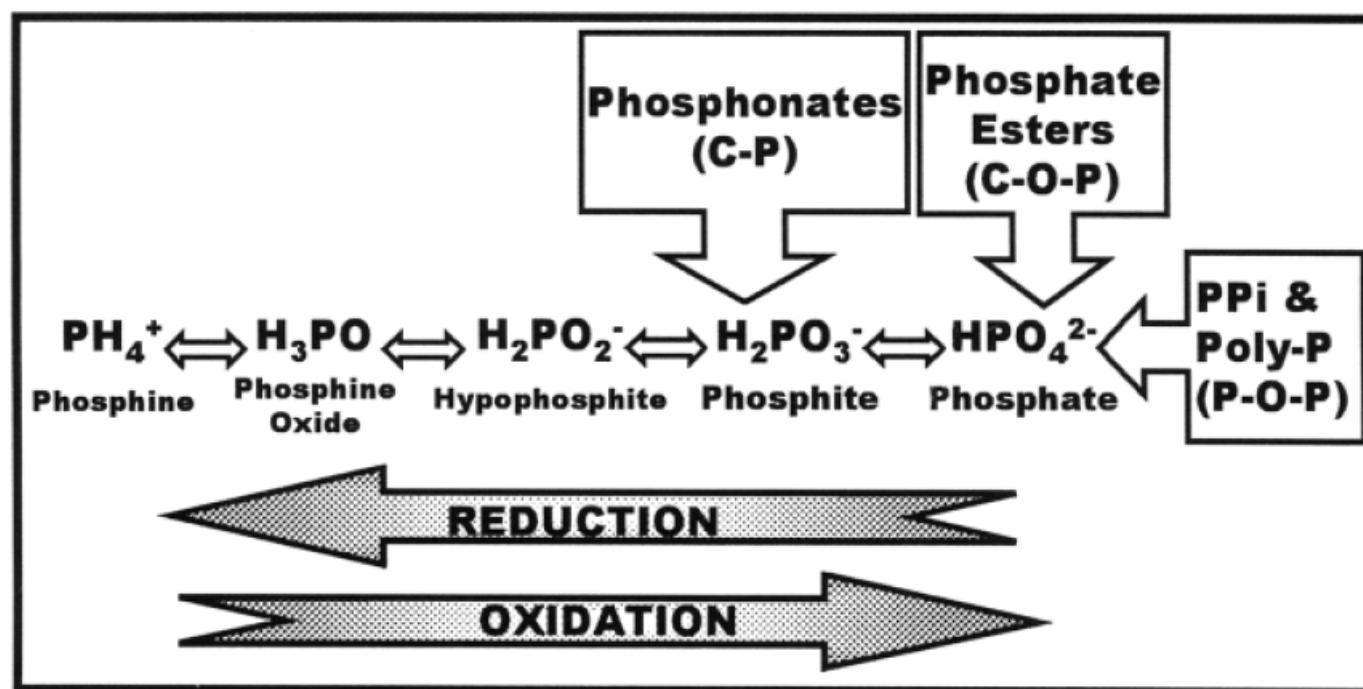
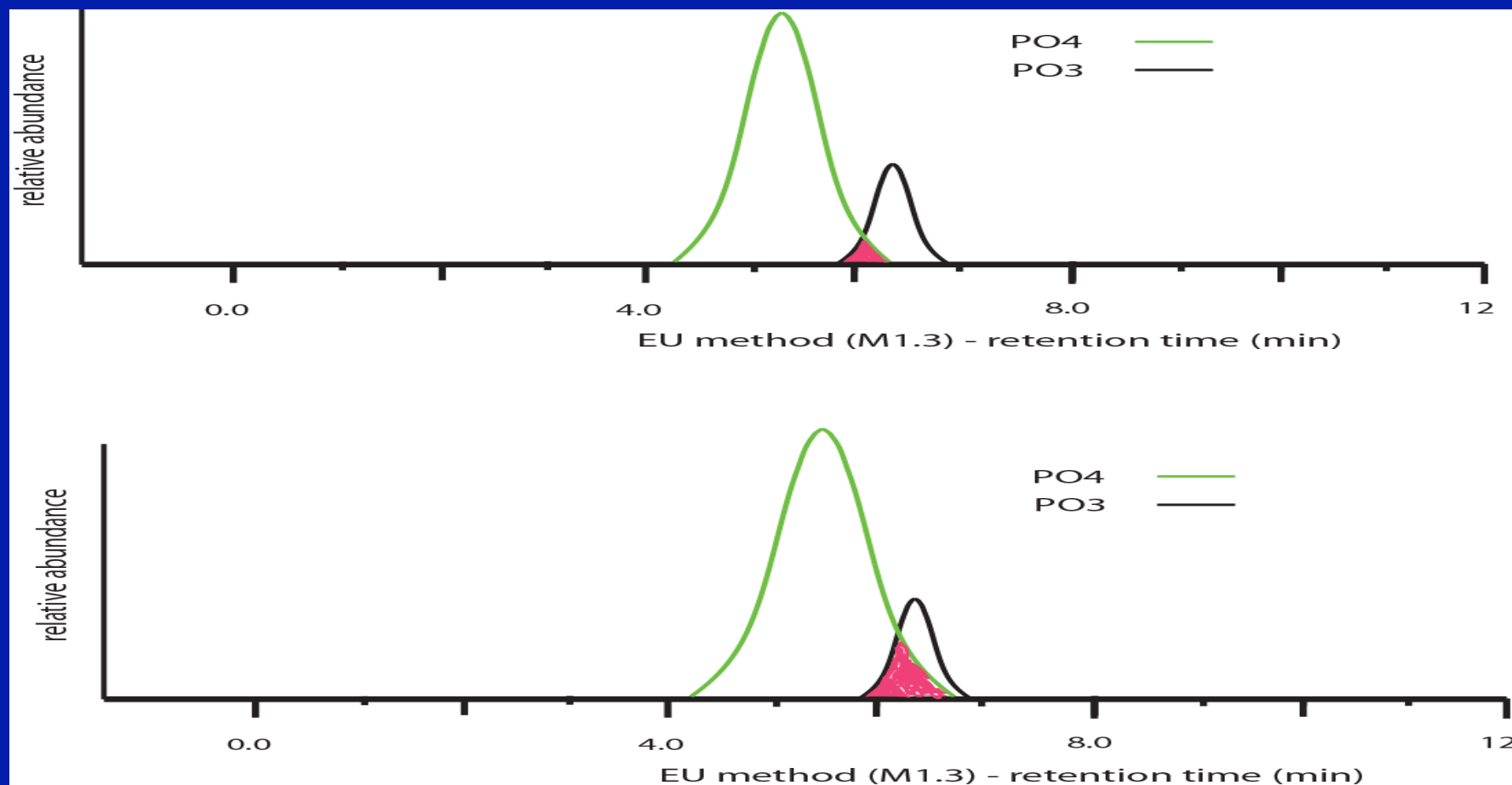


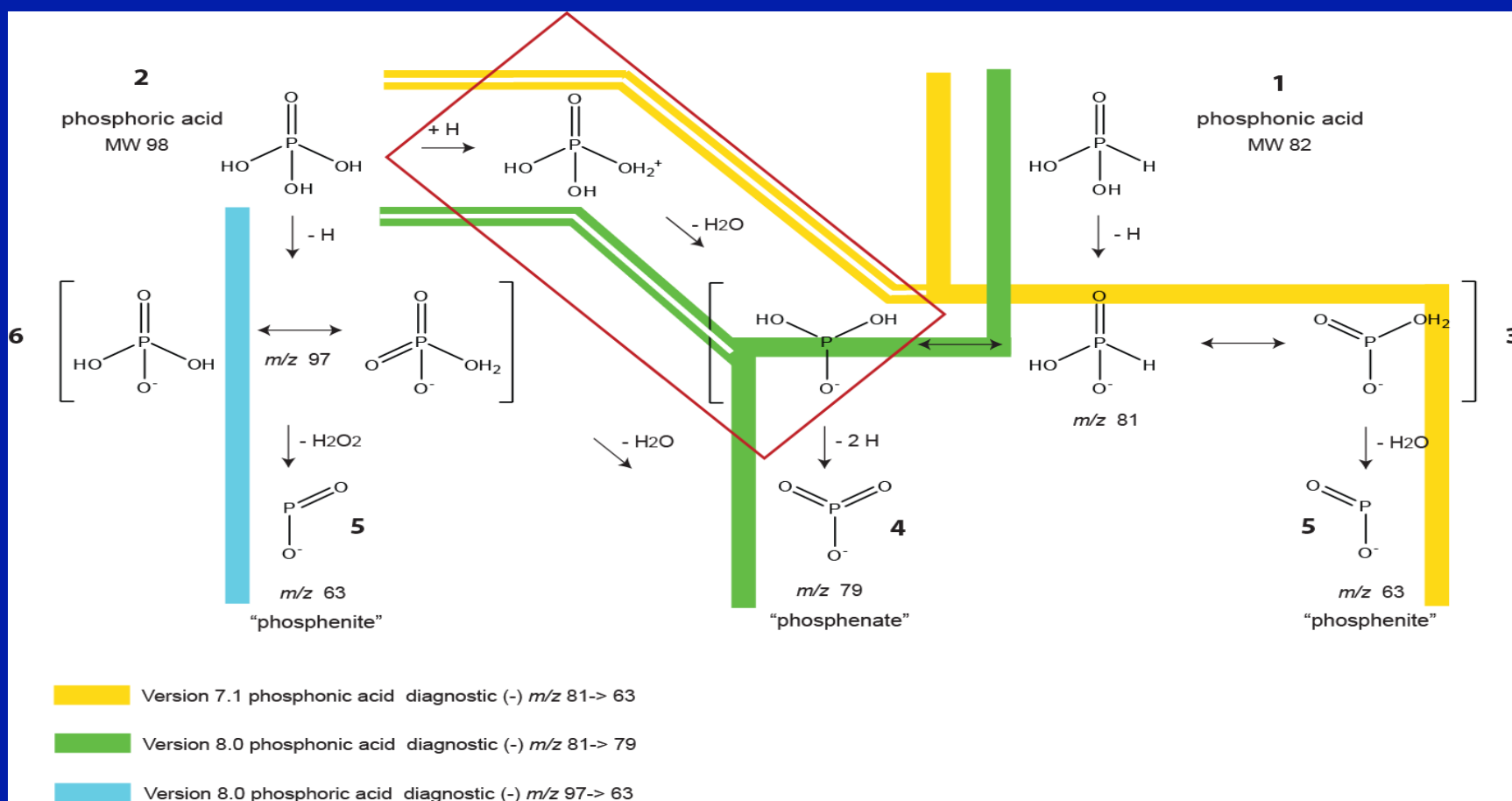
Figure 1. Natural P cycle that is believed to exist in various soil dwelling microbes. Adapted from Ohtake et al. (2).

PO4 & PO3 chromatographic interference



the greater the PO4 and/or PO3 in a sample,
the greater potential for interference
method, matrix, and instrument specific

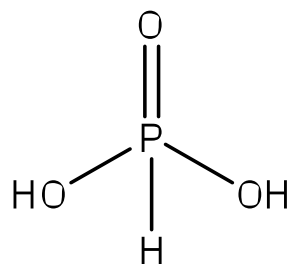
PO₄ & PO₃ spectrometric interference



LC(-)ESI MS/MS results provide evidence to support the conclusion that phosphoric acid (2) can interfere with the quantification of phosphonic acid (1) when analyzed with the negative ion (-) MS² transitions cited in QuPPE-Method Versions 8.0 and 7.1.

positive mode = spectrometric resolution

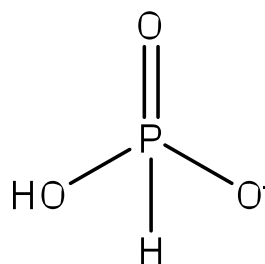
PO3



-H

[M]

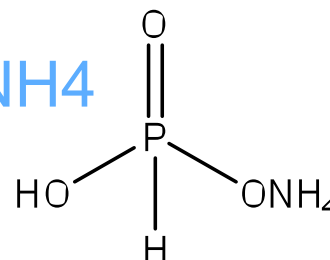
m/z 82



[M-H]-

m/z 81

+NH4



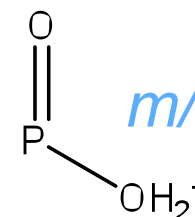
[M-H+NH4]⁺

m/z 100

m/z 47.2



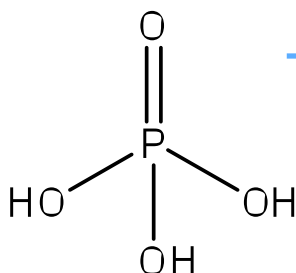
[M-H2O-H2O-NH4]⁺



m/z 65.2

[M-H2O-NH4]⁺

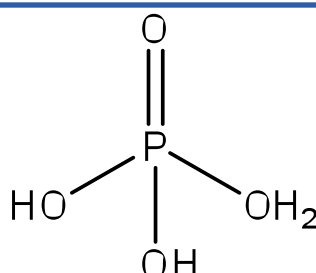
PO4



+H

[M]

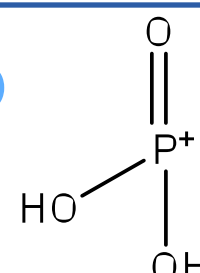
m/z 98



-H2O

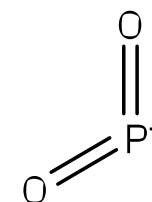
[M+H]⁺

m/z 99



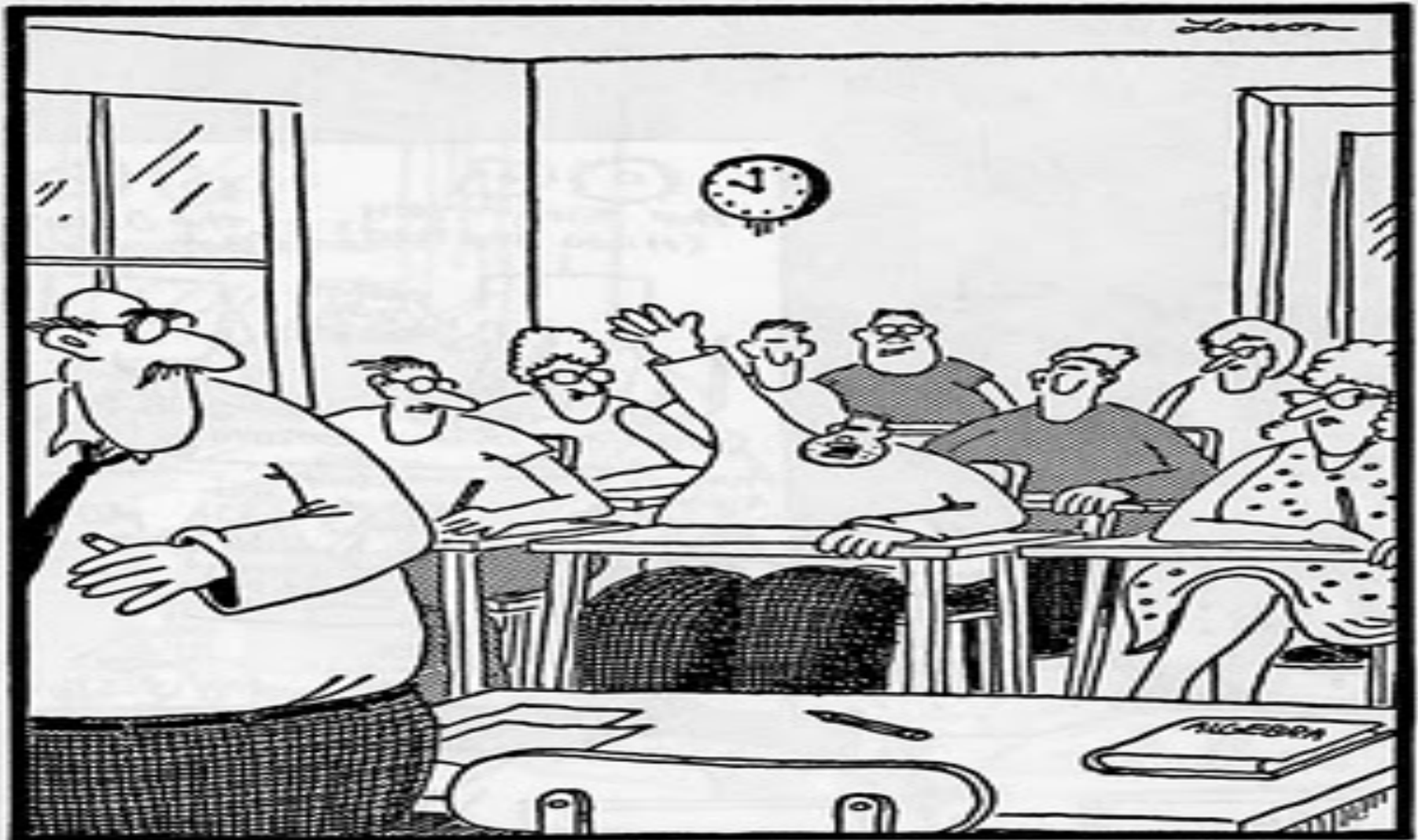
[M+H-H2O]⁺

m/z 81.1



m/z 63.1

Thank you!



"Mr. Osborne, may I be excused? My brain is full."