

Pesticides at ALS

Technical publication

RIGHT SOLUTIONS RIGHT PARTNER



Content

ALS Environmental - Portrait of our company	4
Pesticides - General introduction	5
Fate of pesticides in the environment	6
Degradation of pesticides	8
Relevant versus nonrelevant metabolites	8
Legislation requirements - Limits of residues of pesticides and their metabolites	9
Surface water	9
Underground water	9
Drinking water	10
Basic classification of pesticides	11
A brief look on some classes of pesticides and related capabilities of ALS Environmental	13
Analytical methods for the determination of pesticides and their degradation products	23
LC/MS/MS or GC/MS/MS?	23
Determination of pesticides by LC/MS/MS	24
Determination of pesticides by GC/MS and GC/MS/MS	24
Determination of pesticides by GC/ECD	24
Pesticide laboratory facilities	25
Sample control	25
Instrumental laboratory	25
Quality system and Quality control	26
Validation parameters	26
Ensuring the quality of results	27
Identification	27
Quantification	27
Control samples	29
Interlaboratory testing systems	29
Reporting and services	30
Customer service	30
Confidentiality	30
Sample turnaround	30
LIMS, data management system	30
On-line web access	31
Data to your mobile phone	31
Certificate of analysis	31
References	34

ALS Environmental

Czech Republic

The ALS network includes 25 locations in 12 countries and still continues to grow. Main laboratories are located in Czech Republic, Scandinavia, United Kingdom & Ireland and Turkey.

While varying in size and capabilities, the network performs an extensive range of physical, chemical, microbiological, biological, radiological, ecotoxicological analysis to meet the needs of local and regional clients. Inter-office support and courier arrangements facilitate timely access to the full range of services and on-time delivery of results.

ALS Czech Republic has a number of laboratories and offices located across the Czech Republic, with three main laboratories in Prague, Pardubice and Česká Lípa. ALS Prague is home to the Europe headquarters for ALS Group's Environmental Division. The office includes accounting, human resources, information technology and marketing departments, part of the R&D group, as well as the strategic development team and the office of the General Manager for Europe. The Prague location operates as a full-service environmental laboratory, a food testing laboratory and an oil testing laboratory with a dominating presence in Central Europe, serving the industrial markets as well as consultants, state and municipal authorities. The state-of-the-art, almost 9000 square meter laboratory is GMP certified and ISO EN 17025 accredited. Through mutual recognition agreements between accreditation bodies, results produced in this high-capacity laboratory are recognised by all member states of European Union. The Prague laboratory provides testing services on soil, waste, sludge, sediment, wastewater, ground water, surface water, drinking water, air, emission and industrial samples, meeting all quality assurance levels from standard reporting to US EPA Level II data deliverables.

Do you wish to know more about pesticides?

You would like to organise a seminar or a workshop on this problematic, or you would appreciate to visit our laboratory and meet specialists in the field of pesticides analysis?

Call our Client Service at +420 226 226 228 or send an email to customer.support@alsglobal.com and we will find together a customised solution.



I. Pesticides - General introduction

Pesticides are substances intended for preventing, destroying, suppressing, repelling or controlling harmful pests, that is undesirable microorganisms, plants and animals during the production, storage, transport, distribution and processing of food and agricultural commodities.

The different environmental compartments receive a significant amount of contaminants that may act on other (non-target) agents and may initiate disruption of terrestrial or aquatic ecosystems. A negative consequence is the possibility of pest resistance to the effects of pesticides, especially if the product is misused.

There is a wide range of active ingredients of pesticides on the market. Worldwide, more than 1200 active substances are registered for pesticides production.

Pesticides can be classified into more than 100 classes - groups.

The active substances of pesticides are formulated into commercial products called plant protection products.

A commercial product is a physical mixture of one or more biologically active substances with different inert ingredients that help to achieve effective application, economical dosing and safe use.

Plant protection products can be found in two basic formulations, in liquid or solid, which can be used as solid or liquid baits, sprays, aerosols, powders, stains, coatings and impregnation media.

Example of classification

Carbamates

Triazines

Pyrethroids

Organophosphates

Organochlorines

Phenoxyalkane pesticides

Pesticides based on glyphosate



II. Fate of pesticides in the environment

The main sources of pollution of ecosystems involve the use of pesticides on agricultural fields, forest and in water management, public health and hygiene. These are mainly large-scale spraying of fields and forests, often also deliberate use on the water surfaces in order to protect them against carrier of disease or aquatic plants in irrigation systems. Other sources of direct pollution of watercourses are waste from the pesticides manufacturing, household waste, cleaning of agricultural machinery, etc. The indirect sources include erosive action of wind, soil flushing and rafting.

The ability to predict the behaviour of chemicals in biological and ecological systems largely depends on the knowledge of the physico-chemical properties of the compound.

One of these properties is called persistence of the pesticide in the environment.

Persistence expresses the half-life of the pesticide, the period during which the content of the substance in the environment drops to half.

Pesticides can be divided into 3 categories according to the criterion of half-life.

non-persistent pesticides - the half-life is less than 30 days	e.g. malathion, dicamba
moderate persistent pesticides - the half-life is 30 to 100 days	e.g. benomyl, diuron
highly persistent pesticides - the half-life is more than 100 days	e.g. prometon

Although pesticides are applied according to the principles of good agricultural practice (GAP), encroachment and contact with other non-targeted organisms or contamination of environmental compartments cannot be excluded.

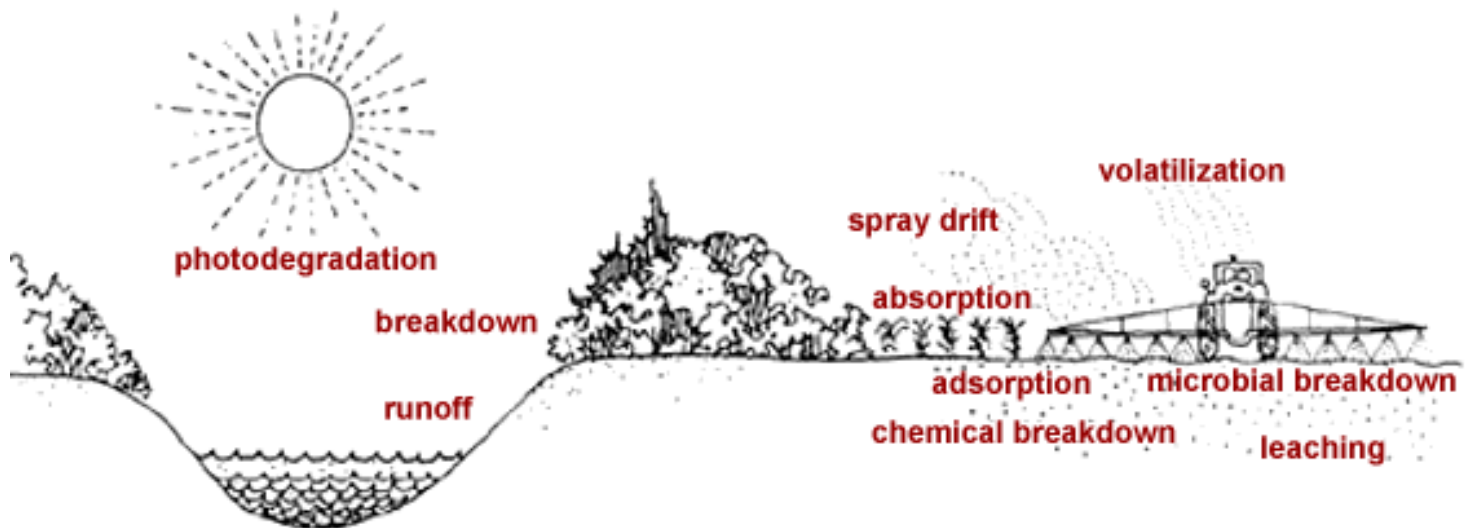
It is estimated that only 65% of the plant protection product used in spray form hits the leaf area, 25% of the product gets into the soil and 10% of the product is evaporated into the atmosphere. After atmosphere contamination, the pesticide molecules can bind to the solid particles suspended in the air. Sorbed to solid particles or in the form of vapour the pesticides are then transported to more or less remote locations.



The pesticides transfer between the environment compartments is often affected by many factors, such as temperature, rainfall, wind speed, soil type.

Through rain residues of pesticides may enter into soil and subsequently into groundwater or surface water and deposit into river sediments.

Pesticides are better adsorbed by clay or soil with high content of organic matter, and worst adsorbed by sand or sandy soil. The contrary happens with volatilisation, where pesticides volatilise most readily from sandy and wet soil.



source: www.agf.gov.bc/pesticides

Warm, windy weather with short rainfalls positively influence the vapour drift.

As an example of pesticides with high tendency to sorption can be mentioned triazine pesticides (atrazine, cyanazine), while the low tendency for sorption have phenyl urea pesticides (linuron, chlorbromuron).

The presence of pesticide residues in the environment is a significant risk factor; for this reason, maximum residue limits (MRLs) were set up for the content of pesticides in different commodities.

The residues present in the environment or in agricultural products can become precursors of other toxic compounds.

We can mention for example triazine pesticides, which can give rise to carcinogenic nitrosamines.

DEGRADATION OF PESTICIDES

Degradation of original compounds does not always eliminate the risks; on the contrary, the original compound can give rise to more toxic metabolites.

Degradation of pesticides in each environmental compartment (water, soil) is carried out by the action of physical (temperature, radiation), chemical (oxidation-reduction reactions, hydrolysis) and biological factors (microbial activity). Generally, low temperature, anaerobic conditions and the absence of organisms lead to a reduced degradation of pesticides.



RELEVANT VERSUS NONRELEVANT METABOLITES

The assessment of relevant and non-relevant metabolites of active substances of plant protection products is carried out according to the guidance document Sanco/221/2000-rev. 10 of 25th February 2003.

It is a procedure to determine whether the metabolite is relevant or irrelevant to the assessment criteria of biological activity, genotoxicity and toxicological hazards. This document also serves as a guideline for the inclusion of active substances to the list of approved active substances "Commission Implementing Regulation EU No. 540/2011 of 25th May 2011".

According to the „Regulation of the European Parliament and Council Regulation (E) No. 1107/2009 of 21st October 2009 „can be registered on the list of active substances such substances, if is expected that plant protection products contain an active substance that has no harmful effects on groundwater.

The principle of the assessment is that a metabolite or a degradation product is considered as relevant if there is a reason to assume that it has comparable properties as an active substance from the point of view of targeted biological activity or if has any toxicological property, which is considered significant (genotoxicity, reproductive toxicity, carcinogenicity, toxicity or very high toxicity). According to Regulation No. 1107/2009, several studies have to be done prior to registration on the metabolism of active substances in different living conditions under which degradation of the products arise. For the risk assessment of active substances and their metabolites are very important the information about the metabolic process, its rate and its kinetics.

Metabolites are decomposition substances of plant protection products which are formed in the environment after application in biotic or abiotic processes.

Relevant metabolite is such metabolite, which can be expected to have comparable properties as an active ingredient of plant protection product in terms of target biological activity or has certain toxicological properties that are considered unacceptable. This metabolite is therefore considered as the parent active substance according to Directive 98/83/EC on the quality of water intended for human consumption, which sets a limit of 0.1 µg/l for each pesticide or its metabolites, with the exception of aldrin, dieldrin, heptachlor, heptachlor epoxide for which a limit is 0.03 µg/L. The limit for the sum of the quantitatively detected pesticides and their metabolites is 0.5 µg/l.

For irrelevant metabolites, that do not meet the criteria for relevant metabolites and occur at concentrations in the range of 0.75 µg/l to 10 µg/l, is required further risk assessment with regard to the potential toxicological effect on consumers of drinking water.

Each irrelevant metabolite is assessed individually.

III. Legislation requirements

Limits of residues of pesticides and their metabolites

To protect human health, the European Union (EU) released the Water Framework Directive (WFD) 2000/60/EC, which aims to gradually reduce emissions, discharges and losses of hazardous substances into the water across Europe and ensures its long-term and sustainable use. The Directive deals with surface waters, coastal waters and groundwater, and seeks to provide good chemical status of surface water and groundwater across Europe.

SURFACE WATER

In the case of surface water, the target concentration limits are defined by specific pollutants relevant for the EU, which are known as priority pollutants. Directive 2008/105/EC lays down environmental quality norms.

Environmental quality standards for priority substances

Focus on pesticide substances

Name of substance	AA-EQS Inland surface waters (µg/l)	MAC-EQS Inland surface waters (µg/l)	AA-EQS Other surface waters (µg/l)	MAC-EQS Other surface waters (µg/l)
Alachlor	0.3	0.7	0.3	0.7
Atrazine	0.6	2.0	0.6	2.0
Chlorfenvinfos	0.1	0.3	0.1	0.3
Chlorpyrifos-ethyl	0.03	0.1	0.03	0.1
Cyclodiene pesticides: • Aldrin • Dieldrin • Endrin • Isodrin	$\Sigma = 0.01$	Not applicable	$\Sigma = 0.005$	Not applicable
DDT total	0.025	Not applicable	0.025	Not applicable
p-p'- DDT	0.01	Not applicable	0.01	Not applicable
Diuron	0.2	1.8	0.2	1.8
Isoproturon	0.3	1.0	0.3	1.0

AA – annual average.

MAC – maximum allowable concentration.

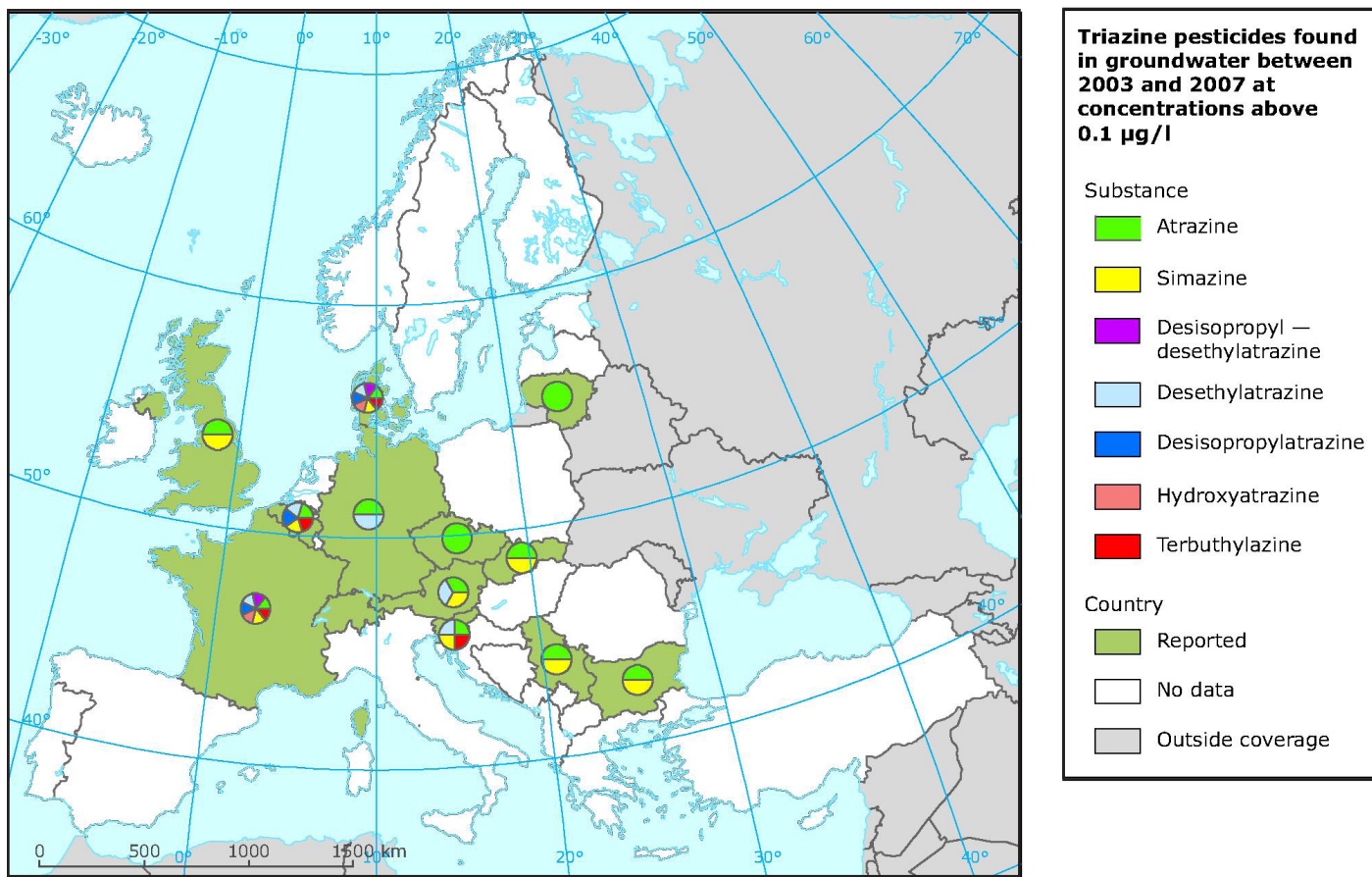
Inland surface waters encompass rivers and lakes and related artificial or heavily modified water bodies.

Where the MAC-EQS are marked as 'not applicable', the AA-EQS values are considered protective against short-term pollution peaks in continuous discharges since they are significantly lower than the values derived on the basis of acute toxicity.

GROUNDWATER

The WFD also requires good chemical status of groundwater. This requirement is supported by the Directive of the European Parliament and of the Council 2006/118/EC on the protection of groundwater against pollution and deterioration, which sets out the measures to assess, monitor and limit pollution of groundwater.

For individual pesticides or their metabolites is specified a limit of 0.1 µg/l
For the sum of specific pesticides and their metabolites, a limit of 0.5 µg/l.



source: Eionet-Water/European Environment Agency

This map indicates, where data were reported, which of the triazine group of pesticides have been found between 2003 and 2007 in groundwater, on at least one sampling occasion, at a concentration greater than 0.1 µg/l. The data does not reflect the frequency with which the threshold has been exceeded.

DRINKING WATER

The area of drinking and warm waters is regulated by Directive 98/83/EC on the quality of water intended for human consumption, which sets a limit of 0.1 µg/l for each pesticide or its metabolite, with the exception of aldrin, dieldrin, heptachlor, heptachlor epoxide which applies a limit of 0.03 µg/l. The limit for the sum of the set and quantitatively detected pesticides and their metabolites is 0.5 µg/L.

Legislative requirements constitute a guide to set up the limits of detection and quantification for the analytical methods at ALS Environmental.

IV. Basic classification of pesticides

Pesticides can be classified according to formulation, target, mode of action, and chemistry. Especially two last mentioned points of view are important to where and what pesticides or their residues could be present.

Pesticides can be classified:

- **By the effects of pesticides against harmful agents, according to biological activity (Tab.1)**
- **According to the chemical composition (Tab.2)**
- **By the way of their effect on the treated organism (Tab.3)**
- **According to the spectrum of action**

Type	Description
Algaecides	Restrict of algae growth in lakes, canals, swimming pools, water tanks etc.
Antifouling agents	Kill or repel organisms that attach to underwater surfaces, such as boat bottoms.
Antimicrobials /biocides	Kill microorganisms (such as bacteria and viruses).
Arboricides	Pesticides for pest trees and shrubs
Attractants	Attract pests (e.g. to lure an insect or rodent to a trap).
Avicides	Kill birds
Biopesticides	Types of pesticides derived from such natural materials as animals, plants, bacteria, and certain minerals.
Disinfectants and sanitizers	Kill or inactivate disease-producing microorganisms on inanimate objects.
Fungicides	Kill fungi including blights, mildews, moulds, and rusts.
Fumigants	Produce gas or vapour intended to destroy pests in buildings or soil.
Graminicides	Inhibit the growth of monocot grasses in dicotyledonous plants and tree species
Herbicides	Kill weeds and other plants that grow where they are not wanted.
Insecticides	Kill insects and other arthropods.
Miticides/ acaricides	Kill mites that feed on plants and animals.
Microbial pesticides	Microorganisms that kill, inhibit, or out compete pests, including insects or other microorganisms.
Molluscicides	Kill snails and slugs.
Nematicides	Kill nematodes (microscopic, worm-like organisms that feed on plant roots).
Ovicides	Kill eggs of insects and mites.
Pheromones	Biochemicals used to disrupt the mating behaviour of insects.
Piscicides	Kill fish
Repellents	Repel pests, including insects (such as mosquitoes) and birds.
Rodenticides	Control mice and other rodents.
Defoliants	Cause leaves or other foliage to drop from a plant, usually to facilitate harvest.
Desiccants	Promote drying of living tissues, such as unwanted plant tops.
Insect growth regulators	Disrupt the molting, maturity from pupal stage to adult, or other life processes of insects.
Plant growth regulators	Substances (excluding fertilizers or other plant nutrients) that alter the expected growth, flowering, or reproduction rate of plants.

Tab. 2. Classification according to chemical composition

Chemical classification	Example of compound
Organochlorine pesticides	aldrin, dieldrin, DDT, lindane
Organophosphates	chlorpyrifos, dimethoate, phorate
Carbamates	fenoxycarb, carbofuran, carbaryl
Pyrethroids	cypermethrin, bifenthrin, deltamethrin
Phenoxyalkanoic pesticides	2,4-D, MCPA, MCPB, MCPA, 4-CP
Urea pesticides	diuron, isoproturon, chloroturon
Diazine and triazine pesticides	atrazine, cyanazine, terbutylazine
Quaternary ammonium salts	diquat, paraquat
Metal based pesticides	phenyl mercury, tributyl tin
Glyphosate based pesticides	glyphosate, gluphosinate

Tab.3. Classification by the way of their effect on the treated organism

Contact pesticide	The active ingredient does not penetrate into the plant tissue and remains on the surface only at locations where it fell during application (DDT, diquat)
Systematic pesticide	Penetrate through the cuticle into the cells and vascular system. Pesticide application is better, but systematic preparations are prone to development of resistance (glyphosate, terbutylazin)
Combined preparation	Combination products containing both contact and systemic substances

Pesticides can be as well classified according to the spectrum of their action:

- **total**
- **broad**
- **selective**



V. A brief look on some classes of pesticides

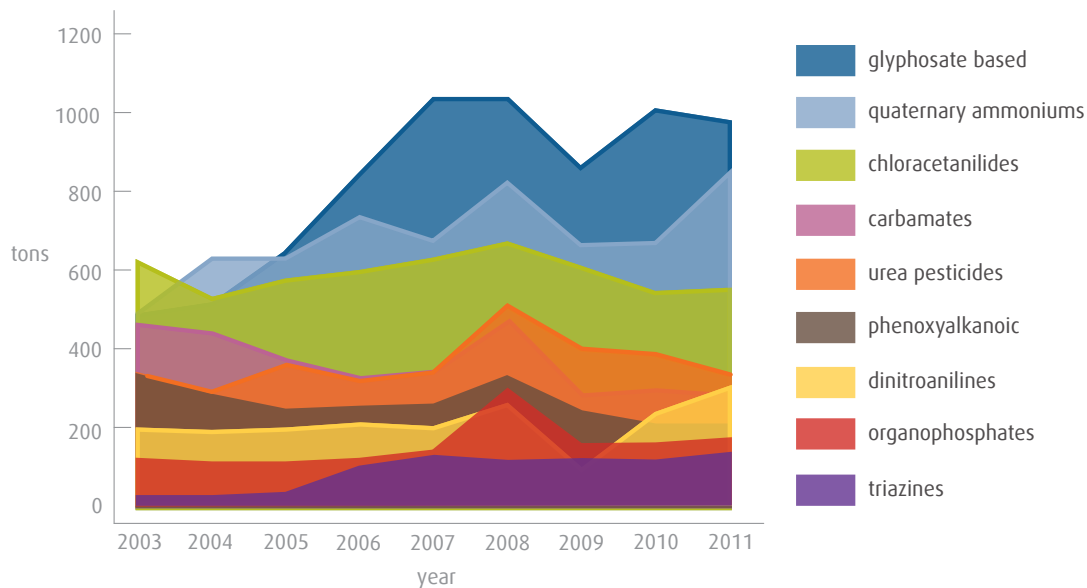
and related capabilities of ALS Environmental

Over the last few years the most commonly applied pesticides are so-called modern pesticides, which are characterized by lower lipophilicity and mainly limited stability and thus less time persistence in the environment.

Among these belong organophosphorus, urea, phenoxyalkanoic, triazine, chloracetanilide pesticides or glyphosate-based.

To illustrate this evolution, here is the example of the consumption of pesticides in Czech Republic and an overview of the main pesticides classes applied on agricultural lands in Europe.

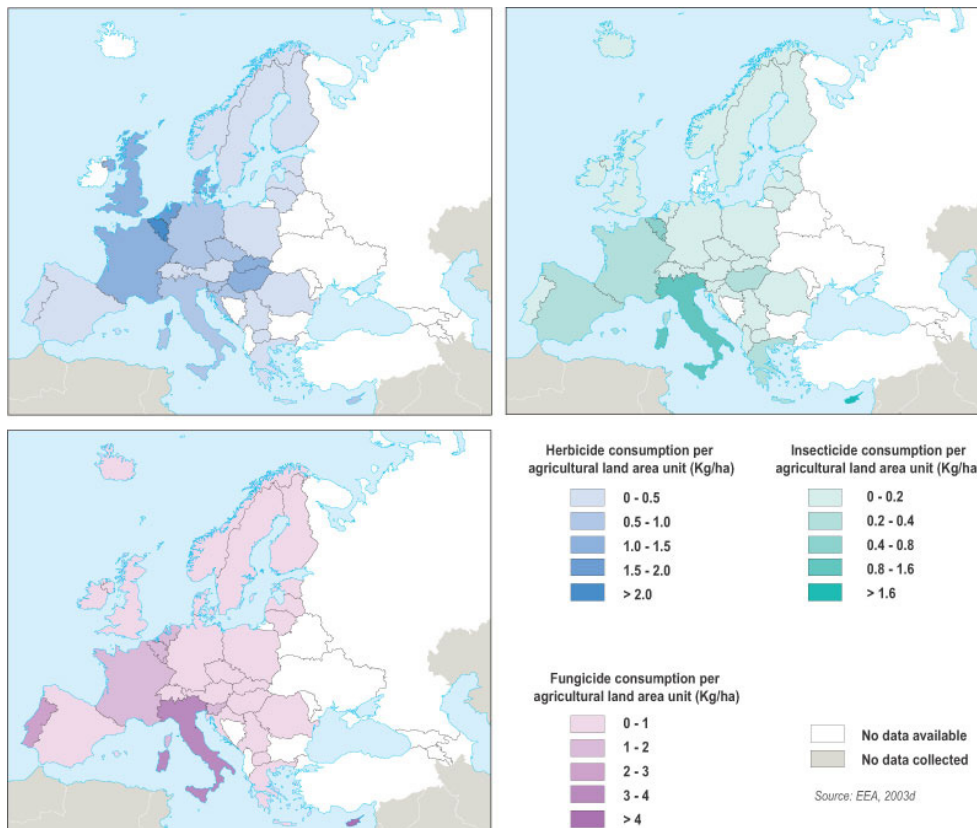
Consumption of active substances in CR according to classes



The consumption of most classes of pesticides is almost constant, a higher increase is evident in the case of glyphosate and quaternary ammonium salts.

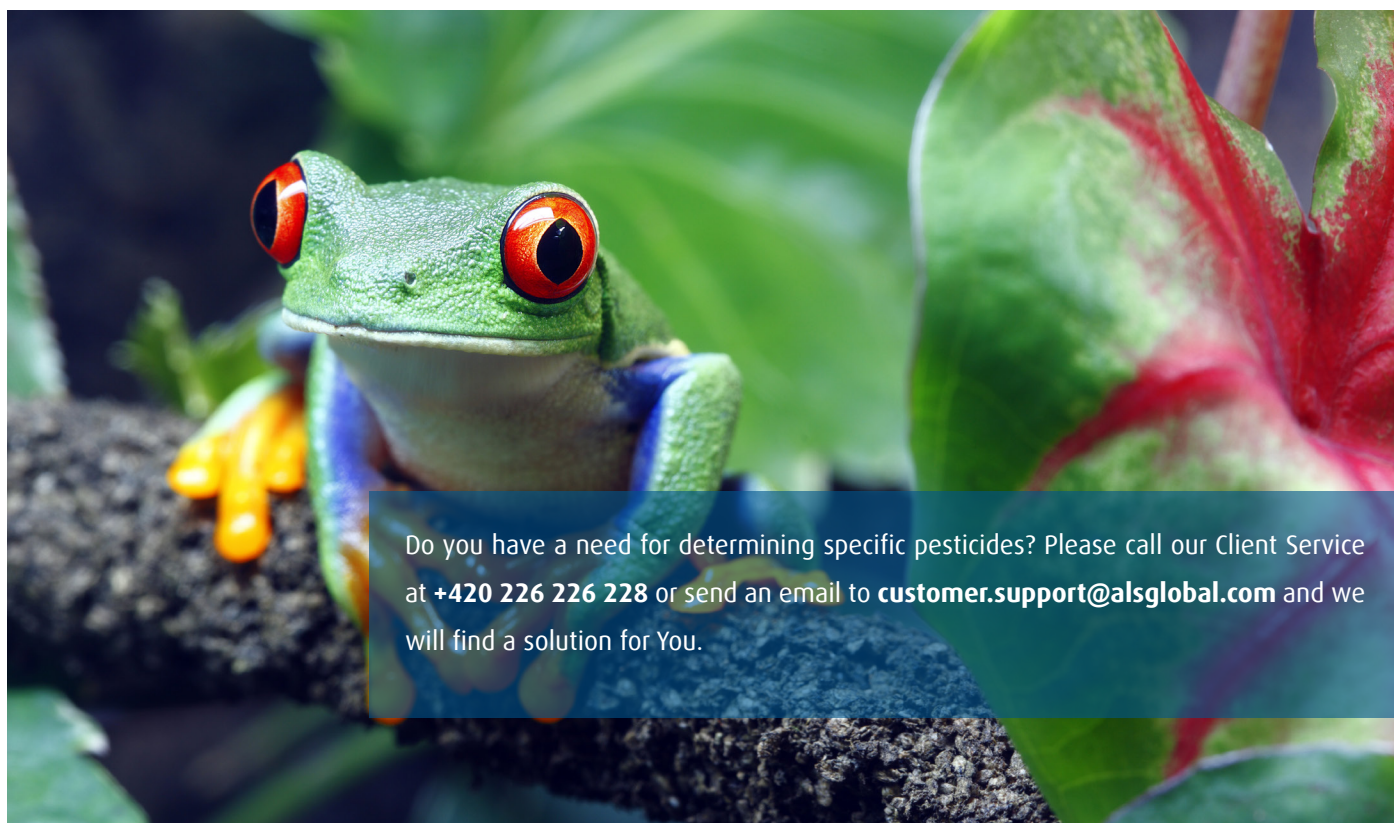
Triazine pesticides are replaced by chloracetanilide pesticides.

The consumption of organochlorine pesticides for the entire period is zero.



source: http://www.grid.unep.ch/products/4_Maps/pesticideb.jpg

Not only these modern pesticides but also pesticides from the group of organochlorines are still the most frequently controlled compounds. ALS Environmental is mentioning in the next pages some of these groups together with analytical capabilities at the moment.



Do you have a need for determining specific pesticides? Please call our Client Service at +420 226 226 228 or send an email to customer.support@alsglobal.com and we will find a solution for You.

ORGANOCHLORINE PESTICIDES AND THEIR METABOLITES

1,2,3,4 – tetrachlorobenzene; 1,2,4,5 – tetrachlorobenzene; 1,2,3,5 – tetrachlorobenzene; aldrin; alpha – endosulfan; dieldrin; endrin; heptachlor; heptachlor epoxide; cis, trans-heptachlor epoxide; hexachlorobenzene; isodrin; methoxychlor; o, p'- DDD; o, p'- DDE; o, p'- DDT; p, p'- DDD; p, p'- DDE; p, p'- DDT; pentachlorobenzene; ...

Characterization and application

Organochlorine pesticides rank among the contact insecticides. These substances have a high bioaccumulation potential (affinity for fatty tissues of organisms). They are highly persistent in the environment and for this reason their application in most countries is prohibited. The oldest and best known of the organochlorine is the insecticide DDT, full name 1, 1, 1 - trichloro - 2,2- bis (4- chlorophenyl) ethane. DDT was used to control insect carriers of diseases such as typhoid and malaria in tropical countries, but also in Europe (lice, mosquitoes, etc.).

ORGANOCHLORINE PESTICIDES AT ALS

- Targeted analysis by GC/ECD
- 35 compounds
- 500 ml dark glass
- Accredited analysis
- TAT 7 days, express possible

Risks and limits

The negative effects of DDT on calcium metabolism were demonstrated, but also on hormonal system with the consequences of infertility or cancer.

In EU is determined allowable DDT limit in drinking water at 0.1 µg/l , while the World Health Organization (WHO) requires 1 µg/l, USA have a more tolerant limit set at 50 µg/l.

Degradation

DDT is rapidly degraded by sunlight, the half-life is two days. In the soil slowly decays with the help of microorganisms to DDE and DDD, with half-life of 2-15 years, depending on the nature of the soil. It is strongly bonded to soil particles and very little soluble in water, therefore, in the water only occurs sporadically.

ORGANOPHOSPHATE PESTICIDES AND THEIR METABOLITES

Acephate; azinphos-methyl; bensulid; chlorethoxyfos; chlorpyrifos; chlorpyrifos-methyl; diazinon; dichlorvos; dimethoate; disulfoton; ethoptop; fenamiphos; fenthion; phorate; phosalone; phosmet; malathion; methamidophos; methidathion; mevinphos; naled; oxydemeton-methyl; parathion-methyl; pirimifosmethyl; profenofos; terbufos; tetrachlorinfos; tribufos; trichlorfon; ...

Characterization and application

From the point of view of chemistry, organophosphate pesticides are esters of ortho- , thio- and pyro- phosphoric acids.

The class of organophosphate pesticides is characterised by its wide spectrum of application as fumigants, acaricides, but primarily as insecticides, killing moving individual pests (larvae, nymphs and adults), but is not effective on eggs.

Organophosphates act as contact pesticides and as orally ingestible poisons with time- limited residual effect.

The list of EPA includes organophosphates, which are highly acutely toxic to bees, wildlife, but also to humans.

ORGANOPHOSPHATE PESTICIDES AND THEIR METABOLITES AT ALS

- Targeted analysis on LC/MS/MS
- 60 compounds
- 40 ml glass vial
- Accredited analysis
- TAT 7 days, express possible

Risks

They are one of the most common causes of poisoning in the world. Organophosphorus pesticides enter the body by all routes, particularly by inhalation (30 minutes), stomach (one hour) but also through the skin (2 hours). Their toxicity is not limited to the only acute effect, they are known for chronic effects. They cause inhibition of a number of enzymes, especially the acetylcholinesterase on the nerve synapses; this inhibition is irreversible. Some organophosphates are not themselves toxic, but their major metabolites are (e.g. oxones). Examples of such metabolites are decomposition products of malathion (malaoxon) and of parathion (paraoxon).

Organophosphorus pesticides have low mobility in soil, sorb strongly to soil particles and their penetration to groundwater is therefore minimal, they occur mainly in surface waters. Because of their highly acute toxicity, they are often replaced by less toxic pyrethroids.

Degradation

The persistence of these substances is usually a few days or weeks, rarely months, for example chlorpyrifos figures a half-life of 2 to 4 months.

Organophosphates are easy subjected to photodegradation and thermodegradation, knowing that degradation rate depends also on the pH.

UREA PESTICIDES

Chlorotoluron; chlorsulfuron; diuron; fenuron; isoproturon; linuron; metoxuron; monuron; monolinuron; neburon; nicosulfuron; rimsulfuron; triasulfuron; tribenuron-methyl; ...

Characterization and application

Most of these compounds are now widely used as herbicides. They are mainly used as systematic herbicides. They act as inhibitors of photosynthesis in plants. The most commonly applied urea pesticides are isoproturon, chlorotoluron and fluorometuron. They are used for weed control in the cultivation of potatoes, cereals, corn, poppy seeds, sugar beet, but also for treatment of the seeds before planting. They act as pre-emergent herbicides after the incorporation into the soil but some are used as post-emergent. They are rather less soluble in water and better absorbed by soil.

UREA PESTICIDES AT ALS

- Targeted analysis on LC/MS/MS
- 35 compounds
- 40 ml glass vial
- Accredited analysis
- TAT 7 days, express possible

Risks

Some of these substances have toxic effects causing thyroid disorders, but can also be carcinogenic and teratogenic.

Isoproturon

It belongs to selective herbicides. Isoproturon is used in the agriculture of cereals, poppy seeds and marjoram. For humans, isoproturon is weakly toxic, but is included in the list of hazardous and extremely hazardous substances for aquatic environment. In soil, isoproturon absorbs relatively weakly and stays mobile to possibly move into groundwater. In the aquatic environment isoproturon degrades through slow hydrolysis with a half-life of about 30 days.

Chlorotoluron

It belongs to contact herbicides, mainly used to protect crops. In soil, chlortoluron is moderately mobile and after agricultural application is able to contaminate the surface water. Its half-life is given between 26 to 42 days.

DINTROANILINE PESTICIDES

Trifluralin; pendimethalin; oryzalin; prodiamine; ethalfluralin; benfluralin

Characterization and application

This is a group of selective pre-emergent herbicides. They prevent seed germination and are used for stopping development of weeds by inhibiting the growth of roots.

Trifluralin

Trifluralin is used in agriculture as a herbicide for the protection of plants (cotton, chamomile, peas, soybeans, sugar beet, winter cereals, sunflower and other vegetables).

Trifluralin is insoluble in water and soluble in fats.

In water, it strongly sorbs to sediments and suspended matters. From water is readily to evaporate into the atmosphere.

Trifluralin is a substance with high toxic potential for the aquatic environment.

It is a suspected human carcinogen and mutagen.

Trifluralin is characterized by a high bioaccumulation potential.

Easily decomposed by the direct light, it is also subject to biodegradation under aerobic and anaerobic conditions .

Half-life in the atmosphere was found during a sunny day about 25 to 60 minutes.

Half-life in sediments is estimated to be up to six months and depends on the weather conditions.

DINITROANILINE PESTICIDES AT ALS

- Targeted analysis on LC/MS/MS
- 2 compounds - Trifluralin, pendimethalin
- 40 ml glass vial
- Accredited analysis
- TAT 7 days, express possible

Pendimethalin

Selective herbicide used for weed control in field where corn, potato, rice, cotton, soybeans, tobacco, peanuts and sunflower are cultivated. It is used as a pre-emergent and post-emergent herbicide.

It is moderately toxic by ingestion, inhalation or skin absorption.

It presents high toxicity to fish and aquatic invertebrates. Currently are tested possible carcinogenic effects of pendimethalin.

Moderately persistent in soil, its half-life is about 90 days, but, under anaerobic conditions, more polar metabolites are formed with higher mobility, which may enter the groundwater and surface water.

CARBAMATES

Oxamyl; pirimicarb; carbofuran; methiocarb; fenoxycarb; mancozeb; ...

Characterization and application

Carbamates are derivatives or esters of carbamic acids.

There are about 25 kinds of carbamates such as: dithio-, benzimidazolyl-, dimethyl-, oxime-, phenyl-, methyl- carbamates.

They are used as selective herbicides, insecticides, acaricides, nematocides, molluscicides or fungicides in fruits, vegetables, ornamental trees, hops cultures, or for seed treatment.

They are used as systematic and contact insecticides.

They act on insects as contact pesticides and as oral ingestible poison.

They can be applied to aphids, ants and wasps, soil nematodes, codling moth, ladybugs or other sucking insects.

Carbamates kill moving individuals (larvae, nymphs and adults) of pest; they are not effective on eggs.

CARBAMATES AT ALS

- Targeted analysis on LC/MS/MS
- 35 compounds
- 40 ml glass vial
- Accredited analysis
- TAT 7 days, express possible

Risks

They belong to highly toxic substances; carbamates are poisonous to warm-blooded vertebrates and humans.

The mechanism of action is similar to preparations based on organophosphates. Unlike organophosphates, the damage caused by carbamates to the central nerve system is reversible, if caught during the early phase of the poisoning. However, their toxicity to non-targeted organisms is higher than organophosphates, their effects occur and subside faster and symptoms last shorter.

Degradation

Carbamates evaporate under normal temperatures and decompose (hydrolysis) in the presence of alkaline substances (sodium hydroxide or soda).

As relatively persistent substances, their degradation half-life takes several days to several weeks.

The most hazardous carbamate seems to be methiocarb (phenyl methyl carbamate), currently used as acaricide, insecticide, molluscicide or repellent to protect the cultivation of potatoes, barley, beets and vegetables.

Although bioaccumulation potential yields relatively low (half-life in soil: 0.25 to 1.4 day), methiocarb is recognized, according to the WHO classification, as highly dangerous with high toxicity to both vertebrates and aquatic biota.

Mancozeb (dithiocarbamate) is used as a fungicide. Its use covers the protection of many fruits, nuts and field crops against a wide spectrum of fungal diseases. Mancozeb is a cholinesterase inhibitor and can affect the nervous system. Dangerous is its metabolite ethylene thiourea (ETU), which provokes thyroid disease and carcinogenic effects.

Carbamate pesticides have higher adsorption coefficient and low mobility in soil; when they are released into the water, they will adsorb to sediment.

Their half-life is estimated from several days to several weeks.

PYRETHROIDS

Cypermethrin , deltamethrin , permethrin , bifenthrin , cyhalothrin, ...

Characterization and application

Pyrethroids now constitute the majority of the market of synthetic insecticides and are a normal part of commercial products, such as household insecticides and repellents.

They are used as insecticides and repellents, acaricides or herbicides.

They do not act systemically or in-depth, they are rather lipophilic substances, which bind to the cuticle of plants and insects and resistant to rain wash off.

Pyrethroids kill adults and larvae, eggs of specific species, biting and stinging insects.

They sorb easily to soil particles and lose their effectiveness; they not flush into surface or ground waters.

PYRETHROIDS AT ALS

- Targeted analysis on GC/MS/MS
- 10 to 20 parameters in validation process

Risks

They are effective at low doses, significantly lower than organophosphates or carbamates, act faster and for a longer time than most organophosphates or carbamates. One treatment by pyrethroids can replace two treatments by organophosphates or carbamates.

Degradation

Pyrethroids are photostable, thermostable and rather insoluble in water.

In the environment, they rapidly decompose within 3 to 4 weeks maximum.

GLYPHOSATE-BASED PESTICIDES AND METABOLITE AMPA

Glyphosate, glyphosate-IPA, glufosinate, AMPA

Characterization and application

They are herbicides characterised by their broad spectrum, systematicity and non-selectivity. Their consumption is rapidly increasing.

They are used in agriculture, forestry, but also in households and urban areas.

They cause growth cessation of plants, which first show yellowing and browning of their surface with subsequent mortality.

Glyphosate-based pesticides easily adsorb onto soil particles:

- low probability of occurrence in groundwater
- frequent occurrence in surface waters

Risks

They exhibit teratogenic effects and synergistic toxic properties with other substances.

Degradation

Persistence is about two weeks, the degradation product of glyphosate is AMPA, a metabolite that has similar toxic effects but with a greater probability of occurrence in water.

GLYPHOSATE-BASED PESTICIDES AND METABOLITE AT ALS

- Targeted analysis on LC/MS/MS
- 4 compounds
- 150 ml plastic container
- Accredited analysis
- TAT 7 days, express possible

TRIAZINE PESTICIDES AND THEIR METABOLITES

Atrazine; cyanazine; simazine; propazin; prometryn; pymethroline; terbutylazin; ...

Characterization and application

Triazine pesticides are gradually replaced by chloracetanilide pesticides.

They operate primarily as herbicides (atrazine, cyanazine, simazine), then as zoocides (pymethroline) or fungicides (some triazine derivatives).

They are used to control broad-leaved and grassy weeds in crops such as corn, sorghum and sugar beets. They influence photosynthesis of plants, causing yellowing, stopping their growth, and finally causing the total collapse of the weed.

Concerning the insecticide pymetroline, the mechanism of action is based on blocking the food intake (aphids, whiteflies).

Risks

Due to contamination of groundwater by atrazine, simazine and their metabolites, the Commission Decision 2004/248/EC and 2004/247/EC decided on their non-inclusion in the list of active substances.

The Commission Regulation 2076/2002/EC decided not to include cyanazine, prometryn and propazin to the list of active substances.

The Commission Decision 2008/934/EC decided on the removal of terbutylazin from the list of active substances.

TRIAZINE PESTICIDES AND METABOLITES AT ALS

- Targeted analysis by LC/MS/MS
- About 35 compounds including metabolites
- 40 ml glass vial
- Accredited analysis
- TAT 7 days, express possible

The major problem of triazines is their low biodegradability and their long-term persistence in the aquatic environment for both parent compounds and their metabolites.

Triazine pesticides show possible human carcinogenicity; they also may be precursors for the formation of nitrosamines. Atrazine is xenoestrogens, resulting in feminisation of mammals.

Degradation

The persistence time is longer than two years. The parent compounds persist in groundwater under the form of metabolites such as desethyl-, desisopropyl-, hydroxy- and desethyl-desisopropyl- triazines.

CHLORACETANILIDE PESTICIDES AND THEIR METABOLITES

Metazachlor; metolachlor; alachlor; propachlor; acetochlor; dimethachlor; ...

Characterization and application

Chloracetanilide pesticides belong to systematic, selective herbicides. They kill monocots and dicotyledonous weeds and are used in the cultivation of maize, corn, potatoes, cucumbers, beets and stone fruits.

Risks

Acetochlor and metolachlor are highly toxic, alachlor is a suspected carcinogen.

CHLORACETANILIDE PESTICIDES AT ALS

- Targeted analysis on LC/MS/MS
- 6 compounds and 10 metabolites
- 40 ml glass vial
- Accredited analysis
- TAT 7 days, express possible

Degradation

Chloracetanilide herbicides are known to degrade more rapidly in soil than triazine herbicides, they are also often found in surface water.

They decompose at light; decay is influenced by pH, however decomposition is enhanced by bacteria.

Half-time in the environment is approximately 2 to 12 weeks.

They are unstable; they decompose rapidly to give rise to metabolites, carboxylic derivatives (OA) and sulfonic acid acids (ESA), which are very stable in the environment.

Alachlor

Alachlor is on the list of substances that are likely to affect the endocrine (hormonal) system; were found influences on reproduction and formation of evolution defects. This pesticide is considered to be a possible carcinogen.

Alachlor remains in the soil for two to four weeks, depending on soil type and climate.

Acetochlor

Acetochlor is used for the elimination of annual grasses and weeds.

Acetochlor is absorbed by germinating plants, but may also be adsorbed through the roots. It is applied on fields with cabbage, citrus, coffee beans, cotton, peas, corn, cucumbers, potatoes, peanuts, beets, soybeans, sugar cane, sunflowers and grapes, very often used for grain.

Due to its solubility and mobility, it readily penetrates into surface and waste waters, mostly by runoff from fields.

Acetochlor belongs to the group of herbicides with limited use, and is classified as toxicity I (highly toxic). Products containing acetochlor must be labeled „Danger“. According to the U.S. EPA, acetochlor is considered to be as a probable human carcinogen. Acetochlor is mostly degraded by microbes; its half-life is approximately 3 months.

Metolachlor

This is a pre-emergent herbicide, usually applied to soil before crops grow up. It is used to eliminate weeds in corn, soybeans, peanuts, potatoes and wool fields.

It has a very high potential to contaminate groundwater and surface water, as it is relatively mobile and persistent in soil. Its half-life will vary depending on environmental condition, that is between 15 to 132 days. Degradation of metolachlor is affected by temperature, moisture, microbial activity, soil type, nitrification, oxygen concentration and sunlight.

Both anaerobic and aerobic bacteria can degrade this pesticide. Degradation by bacteria with aerobic metabolism takes about 16 days. Anaerobic degradation takes a little longer.

PHENOXYALKANOIC ACIDS

2,4-D; 2,4-DP; 2,4,5-T; MCPA; MCPB; MCPP; ...

Characterization and application

They are used as herbicides; they are effective in particular on dicotyledonous weeds, thistle, chamomile, burdock, dandelion, sorrel and goosefoot.

They are applied for the treatment of cereals, pastures, but also for example, for treating roadsides.

They have primarily systematic and broad spectrum effects.

They cause metabolic disorders, growth retardation of overground parts and underground parts of the plant, which cause its death.

The most common symptoms are distortion of the plant (twisting of leaves, stalks).

These substances are present in the environment in the form of anions, usually absorbed by soil because they are very little soluble in water.

PHENOXYALKANOIC ACIDS AT ALS

- Targeted analysis on LC/MS/MS
- 15 compounds
- 40 ml glass vial
- Accredited analysis
- TAT 7 days, express possible

Risks

2,4-D, 2,4-DP, 2,4,5-T and MCPA are suspected carcinogens.

According to WHO, they belong to substances of toxicity classes II. and III.

Degradation

In the environment, they persist a week to a month; their degradation depends on the pH of the environment; they decompose at light and more rapidly in the presence of oxygen.

QUATERNARY AMMONIUM SALTS

Paraquat; diquat; chlormequat

Paraquat

It is a type of non-selective herbicide to destroy all groups of plants.

It is mainly used in the cultivation of soybeans, corn and rice.

Paraquat is a highly toxic and persistent chemical, which penetrates into the human body through contaminated food (treated food) and also by inhalation of contaminated air.

Paraquat in higher doses causes damage to lungs, liver, heart and kidneys.

Long-term exposure to paraquat may impair reproduction and may cause the development of skin cancer.

The European Court canceled the authorization for paraquat issued by the European Commission, so paraquat is effectively banned in the European Union.

Paraquat was the third most common pesticides in the world and yearly it is still sold about 20 000 tons, mainly in the developing countries.

QUATERNARY AMMONIUM SALTS AT ALS

- Targeted analysis on LC/MS/MS
- 3 compounds
- 40 ml glass vial
- Accredited analysis
- TAT 7 days, express possible
-

Chlormequat

The most widely used herbicide in Czech Republic, its annual consumption is up to 800 tons.

It is mainly used in the cultivation of cereals, oilseeds and legumes.

Chlormequat acts as a plant growth regulator in the form of the salt, chlormequat chloride.

This substance is included in the list of extremely hazardous substances.



VI. Analytical methods

for the determination of pesticides and their degradation products

To analyse the large numbers of samples whose pesticide treatment history is usually unknown, there is evident reason to use analytical methods capable of simultaneously determining a large number of pesticide residues. These multiresidue methods can determine simultaneously pesticide substances that differ in their mode of action, usage and chemical classification. The most commonly used multiresidue methods can also detect many metabolites, impurities, and alteration products of pesticides.

ALS Environmental offers to its customers either LC/MS/MS or GC/MS-based multiresidue methods or different sets of targeted methods.

The main user benefits of multiresidue method offered by ALS Environmental are as follows.

- Can identify and determine approximately 400 pesticides.
- Gives nearly complete outline information about pesticide residues and even about non-regulated pesticides present in assayed material.
- Results of analyses could be available within relative short response despite large number of pesticides is monitored.
- It is the optimal solution for extensive screening purposes when many circumstances can influence potential presence of pesticide or pesticide residues.
- It is the best solution to achieve optimal ratio between costs and amount of pesticides monitored.
- The main user benefits of targeted methods offered by ALS Environmental are as follows.
- It is the optimal solution for targeted monitoring of selected compounds, especially in cases where some compounds have been previously detected and/or those are subjects of attention.
- They can be better applied when some other substances than pesticides can cause that the results obtained by multiresidue method are difficultly readable and thus interpreted.
- They are the best solution to achieve optimal costs when only selected pesticides or group of pesticide substances should be monitored.

To determine the presence and the amount of pesticides in water are most commonly used methods based on direct injection, liquid-liquid extraction and solid phase extraction (SPE) with subsequent analysis by chromatographic methods (gas or liquid chromatography) using different detectors (UV, ECD and more recently MS).

LC/MS/MS OR GC/MS/MS?

While gas chromatography (GC) is limited to materials that are sufficiently thermally stable, polar or ionic substance have to be derivatised prior to determination.

Liquid chromatography (LC) has from this perspective greater application, but only with UV detection was less sensitive and selective than GC, until liquid chromatography with mass spectrometry allows sufficient increase in sensitivity and selectivity of the measurements.

During a MS/MS detection is observed the intensity of breakup of ion precursor to ion product after the supply of collision energy (MRM multiple reaction monitoring). For each analyte are determined two MRM transitions. Such result is considered to be positive when the ratio between transitions of the analyte in the sample corresponds to the ratio of transitions in the standard.

DETERMINATION OF PESTICIDES BY LC/MS/MS

In our laboratory is used LC/MS/MS technique, especially by direct injection of the sample, where the sample is not concentrated nor purified; it only involves the addition of labeled extraction standards, the removal of mechanic impurities by centrifugation followed by a filtration of the sample and the final pH adjustment.

In ALS, determination of the pesticide is carried out by liquid chromatograph coupled with mass spectrometer, where analytes are ionized especially by electrospray, and where for isolation of positively or negatively charged ions according to m/z ratio a triple quadrupole is employed.

For each analyte are measured two multiple reaction monitoring (MRM) transitions. One MRM is used for quantification and the other MRM for analyte confirmation.

Quantification is carried out with the help of an external standard and corrected to the yield of isotopically labeled internal standards, eventually to the recovery of the fortified matrix.

DETERMINATION OF PESTICIDES BY GC/MS AND GC/MS/MS

The determination is based on standard EPA 525.3 and EPA 8270.

The method is based on the extraction of analytes to organic solvent, extraction is more time consuming and solvent consumption is higher compared with the LC/MS/MS technique.

The extract is analysed by gas chromatography with MS detection either using single quadrupole (GC/MS) or triple quadrupole (GC/MS/MS).

Confirmation of positive results can be made either by measuring two MRM transitions within one injection or using other chromatographic methods so that the method meet the requirements of the analytical methods, according to Commission Decision 2002/657/EC.

Quantification is carried out using an internal standard.

DETERMINATION OF PESTICIDES BY GC/ECD

The determination is based on DIN EN ISO 6468, EPA 8081b and DIN 38407 part 2.

Analytes are extracted from the sample with an organic solvent. The proportion of the organic extract is separated from the sample and concentrated. Concentration ratio of extract is subjected to purification in which interfering substances are eliminated.

Purified and concentrated extract is then analysed by gas chromatography with electron capture detection (GC/ECD).

Quantification is performed by external standard with subsequent correction for recovery of internal standard.



VII. Pesticide laboratory facilities

SAMPLE CONTROL

ALS Environmental maintains a sample control department designed to meet samples stability and hygiene safety standards. A segregated sample login area has been dedicated to receipt and unpacking samples. Sample security, temperature maintenance and document tracking are conducted according to ALS's standard operating procedures.

INSTRUMENTAL LABORATORY

For the determination of pesticides by mutiresidual methods or by targeted methods, ALS Environmental owns the following instruments:

- 1 liquid chromatograph Agilent 1100 series with MS detector API 4000, AB Sciex
- 1 liquid chromatograph UPLC I- class with MS detector XEVO TQ- S, Waters
- 1 liquid chromatograph 1200 series with MS detector 6120 SQ from Agilent
- 2 gas chromatographs with MS detector type QqQ (GC/MS/MS)
- 18 gas chromatographs with MS detector (GC/MS), Agilent
- 17 gas chromatographs with ECD/FID detectors, Agilent
- 7 liquid chromatographs with UV-VIS, DAD, FL detectors, mostly Waters

Environmental control systems are designed to maintain constant temperature, decrease dust amount, reduce floor vibrations, and minimize electricity field interferences with electricity power back-up system.



VIII. Quality system and Quality control

ALS Environmental laboratory is accredited according to international standard ISO/IEC 17025. Accreditation is granted after detailed assessment of the competence of the organization and its staff against technical and management system criteria defined in ISO/IEC 17025. The intent of this accreditation is to provide the client with the highest quality data by proving each laboratory's capabilities through laboratory audits, check samples, and interlaboratory studies. The accreditation process is also an integral part of our philosophy of continuous Improvement. This assessment is periodically conducted by the Czech Accreditation Institute (CAI) (www.cia.cz).



The Czech Accreditation Institute maintains Mutual Recognition Agreement/Arrangements with other international certification agencies that have recognized ALS' quality through accreditation and/or certification.

The annex of the Certificate of Accreditation contains the list of all accredited tests for specific matrices, including the full range of pesticides.

VALIDATION PARAMETERS

To ensure that the analytical method is suitable for obtaining reliable data, the method must be fully validated. Validation is performed according to ISO/IEC 17025 "confirmation by examination and provision of objective evidence of, that certain requirements are met for the intended application." The validation protocol then describes methods and procedures of validation tests. The protocol includes validation parameters and their calculation. The selection of validation parameters always depends on the purpose of the method, so that it fulfils the customer needs.

Validation parameters include:

- Selectivity
- Linearity and working range of the method
- The limit of detection (LOD)
- The limit of quantification (LOQ)
- Precision
- Accuracy
- Robustness
- Stability
- Uncertainty of results

ENSURING THE QUALITY OF RESULTS

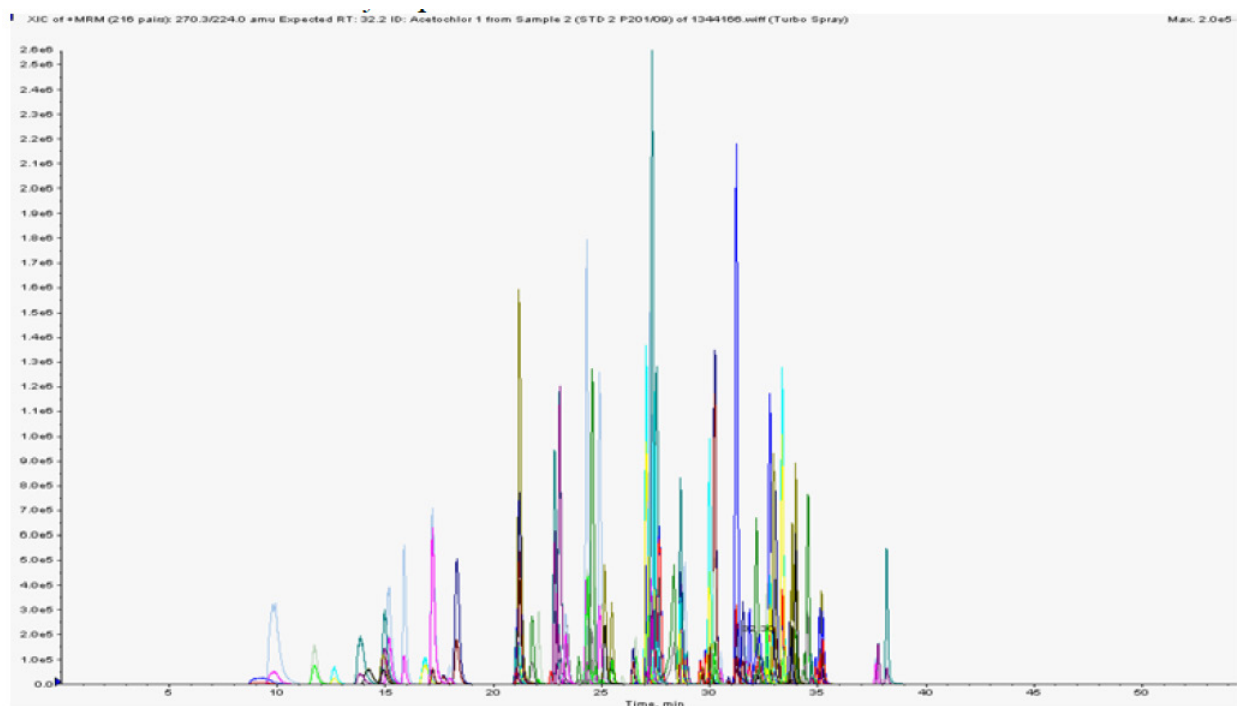
Identification

- Retention time (or relative retention time) of the analyte in the sample must be within the specified range
- Correspond to the retention time (relative retention time) of the calibration standard
- Minimum acceptable retention time for the analyte under examination is twice the retention time corresponding to the void volume of the column
- Measurement of selectivity is determined by using MS detection , two MRM transitions are monitored and also their ratio must be the same for each analyte in both the standard and the sample, this method satisfies the requirements on the performance of analytical methods and the interpretation of the results according to Commission Decision 2002/657/EC

Quantification

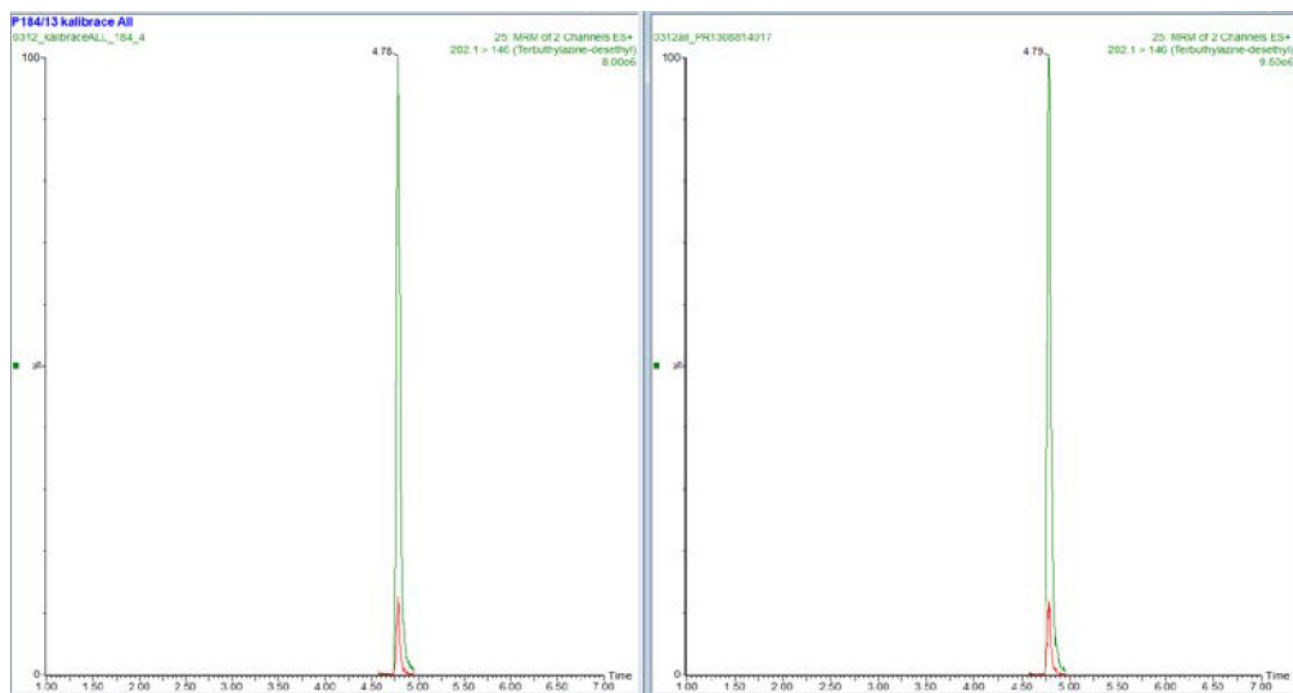
- Prior to each sample analysis is performed calibration
- Quantification is performed by the external standard method and yield corrected on the recovery of extraction standards
- If concentrations of analytes in samples exceed the upper limit of the concentration range, samples are diluted and their analysis repeated
- Control samples are monitored during the analysis





Multiresidual analysis of pesticides by LC/MS/MS

Here is an example of chromatogram, when a few hundreds of pesticides are monitored. The sample was injected on LC/MS/MS instrument, which is able to separate and quantify numerous pesticides and their metabolites during one single analysis.



Here is the comparison of chromatograms of terbutylazine-desethyl for the **standard** at the concentration level of 0.05 µg/l (left) and for a **real sample** with positive signal above the same concentration (right).

Thanks to LC/MS/MS are measured two MRM transitions, one more intense (MRM 1) is used as a quantitation (green), less intense as confirmation (red), which allow direct identification and confirmation of the amount of the controlled substance without the need to carry out further independent analysis, so as the method complies with the Commission Decision 2002/657/EC. A positive result is considered such when the ratio between transitions corresponds to the ratio of transitions in the standard.

Control Samples

In the frame of analytical measurements, ALS Environmental uses a wide variety of control procedures for a systematic quality monitoring process. They are represented mainly by regular measurement of control samples (certified reference materials, duplicates, fortified samples and blanks) and by the participation in national and international interlaboratory comparison tests.

As elements of operative quality management are applied analyses of method blanks, laboratory duplicates and fortified blank methods, respectively fortified matrices.

Method Blanks

- Prepared in the same manner as the sample
- Verifies the purity of glass, chemicals, solvents, equipment and the environment during the manipulation with the samples

Instrument Blanks

- To check a contamination of the instrument
- A clean solvent is injected into the instrument

Fortified Blank

- Processed like a real sample, from extraction to data processing
- Provided as a periodic control procedure to precise uncertainty
- To routinely check analysis using control charts from previous data
- Can be realised after the analysis of a very contaminated sample

Laboratory Duplicate

- Checks the accuracy of the measured data for the matrix analyzed
- Processed through all steps of the analytical procedure
- To routinely check analysis using control charts from previous data

The frequencies of these control samples are shown in the following table

Frequency of control samples

Laboratory duplicate (% from the total number of samples)	Method blank (% from the total number of samples)	Fortified blank/fortified matrix (% from the total number of samples)
5 % minimum 1x each measurement day	5 % minimum 1x each measurement day	5 % minimum 1x each measurement day

Interlaboratory testing systems

A regular independent assessment of the technical performance of a laboratory is recognized as an important means of assuring the validity of analytical measurements, and as part of an overall quality strategy.

Each year, ALS's ultra-trace laboratory for pesticides analysis takes part in interlaboratory testing systems/programs, which are managed by different organizations. These tests ensure our laboratory to monitor our tests over time. Longer-term trends can therefore be identified, and any necessary corrective action considered. Interlaboratory comparisons can be also designed for purposes other than the self-assessment of the laboratory's performance, i.e. validation of methods, characterization of Reference Material and Proficiency Tests.

Participation in appropriate International or European Union's interlaboratory testing systems/programs, covering the scope of our laboratories' accreditation, in a useful and cost-effective manner, constitutes a tangible proof for our clients that ALS Environmental is producing valuable and reliable test results.

Here are examples of interlaboratory testing programs to which ALS Environmental participated:

- IFA - 2009, 2013 - Austria - www.ifatest.eu
- FAPAS - 2009, 2010, 2013 - United kingdom - www.fapas.com
- LGC standards - 2010 - United Kingdom - www.lgcpt.com
- SZPI Brno - 2009 - Czech Republic - www.szpi.gov.cz
- CSLab - 2011, 2013 - Czech Republic - www.cslab.cz
- ASlab - 2009, 2011, 2013 - Czech Republic - www.aslab.cz

IX. Reporting and services

CUSTOMER SERVICE

We have committed ourselves to a strong customer focus: Our Customer Service is aiming to facilitate communication and transparency between ALS Environmental and its clients.

This Service is composed of an experienced and multidiscipline team to answer your requirements, which offers you a personalized service with clear and efficient communication at all times.

The team is trained to ensure that shipping conditions, containers, and preservatives are consistent with requirements for the needed analyses.

Call our Client Service at +420 226 226 228 or send an email at customer.support@alsglobal.com and we will find a solution to your challenge.

The Customer Service coordinates all activities between the laboratories for a designated client. It finally ensures the release of the test reports, analytical results protocols and related documentation, and follows the project with the client.

CONFIDENTIALITY

During the course of the business, we protect data or information considered confidential or proprietary by our clients.

This confidential information includes all analytical raw data, test results, origin of samples, business relationship with client, any procedure, process and specification that they conduct, investigate or create, information about their business and plans, our own laboratory procedures, technology, plans, and clients.

All such information is kept confidential and discussed only with designated technical contacts, consultants for the particular project. The information will not be disclosed to anyone, even within the client's company not designated as a contact, without permission from the client.

SAMPLE TURNAROUND

Our routine turnaround delivery time for pesticides analysis is 7 working days. Rush turnaround time services are available, even for projects of exceptional size.

LIMS, DATA MANAGEMENT SYSTEM

Working closely with our clients, our information systems staff develops electronic data deliverables that interface directly with our clients' data management systems. The end result is seamless reporting which reduces costs associated with data entry and improves the quality and timeliness of information transfer.

Our information system features:

- ORACLE® based laboratory information management system (LIMS)
- Microsoft Windows® applications (i.e., Word®, Excel®)
- Wide area network (WAN) augmented with local area networks (LANs)
- Wide range of electronic data deliverables
- Electronic transfer of data via the Internet

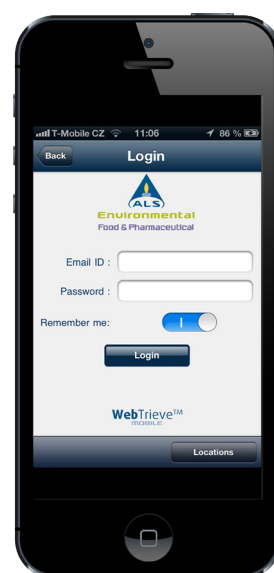
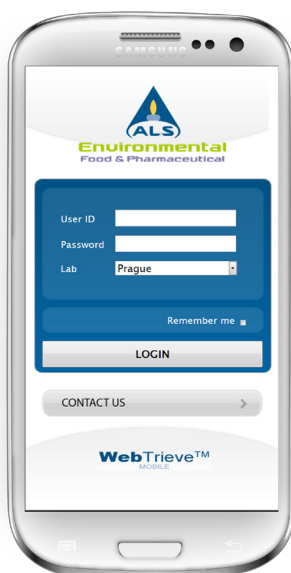
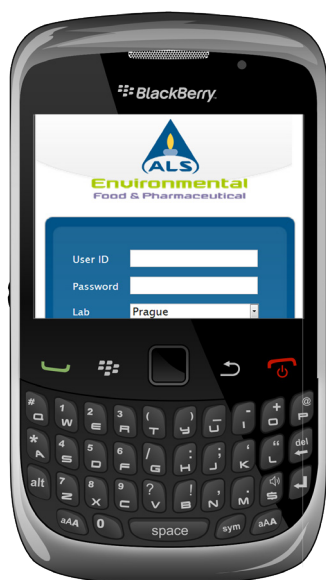
ON-LINE WEB ACCESS

ALS Environmental offers an advanced, on-line web access service called WebTrieve™. The most unique feature is its simplicity, providing user friendly navigation to access results, compare against regulatory levels, and download data into spreadsheets for electronic data deliverable functions, and email directly from the website. In addition, clients can view the progress of their samples through the laboratory, from anywhere in the world, by way of an online, encrypted account. WebTrieve™ is fast and convenient saving clients' time and money. Simply put, WebTrieve™ delivers performance.

If you do not already use Webtrieve, please visit: <https://envirowebtrieve.alsenviro.com>

DATA TO YOUR MOBILE PHONE

ALS Environmental delivers exceptional service to your mobile device. You can check the status of your work orders, retrieve sample handling information, and find contact information for any laboratory in Europe by using the ALS Enviro iPhone Application or by accessing mobile.alsenviro.com (Blackberry and Android users).



Try the advantages of this new application!

Require it at +420 226 226 228 or send an email at customer.support@alsglobal.com.

CERTIFICATE OF ANALYSIS

Laboratory data is much more than the concentration of a compound in a sample. ALS Environmental data report provides all the information needed for a client to track the sample from collection to results, assess the validity of the results obtained, and assure them the sample was analyzed using appropriate good laboratory practices. An example of COA is shown on the next pages.

CERTIFICATE OF ANALYSIS

Work Order	: PR1354063	Issue Date	: 19-NOV-2013
Amendment	: 1		
Client	: ALS Czech Republic, s.r.o.	Laboratory	: ALS Czech Republic, s.r.o.
Contact	: OLIVIER LECOT	Contact	: Client Service
Address	: Na Harfe 336/9 Praha Ceska republika 190 00	Address	: Na Harfe 336/9 Prague 9 - Vysocany Czech Republic 190 00
E-mail	: Olivier.lecot@alsglobal.com	E-mail	: customer.support@alsglobal.com
Telephone	: ----	Telephone	: +420 226 226 228
Facsimile	: ----	Facsimile	: +420 284 081 635
Project	: Testovací zakazka	Page	: 1 of 2
Order number	: ----	Date Samples	: 12-NOV-2013
		Received	
C-O-C number	: ----	Quote number	: PR2008ALSCR-CZ0020
Site	: ----	Date of test	: 12-NOV-2013 - 12-NOV-2013
Sampled by	: ----	QC Level	: ALS CR Standard Quality Control Schedule

General Comments

This report shall not be reproduced except in full, without prior written approval from the laboratory.
The laboratory declares that the test results relate only to the listed samples.

Responsible for accuracy

Signatories

Zdenek Jirak



Position

Environmental Business Unit
Manager

Testing Laboratory
Accredited by CAI



L 1163

ALS Czech Republic, s.r.o.

Na Harfe 336/9 Prague 9 - Vysocany Czech Republic 190 00



Analytical Results

Sub-Matrix: **WATER**

Client sample ID

Laboratory sample ID

Client sampling date / time

				TEST		----		----	
				PR1354063001		----		----	
				12-NOV-2013 00:00		----		----	
Parameter	Method	LOR	Unit	Result	MU	----	----	----	----
Pesticides									
2,4,5-T	W-PESLMSA1	0.050	µg/L	<0.050	---	----	---	----	---
2,4,5-TP	W-PESLMSA1	0.050	µg/L	<0.050	---	----	---	----	---
2,4-D	W-PESLMSA1	0.050	µg/L	<0.050	---	----	---	----	---
2,4-DB	W-PESLMSA1	0.050	µg/L	<0.050	---	----	---	----	---
2,4-DP (isomers)	W-PESLMSA1	0.050	µg/L	<0.050	---	----	---	----	---
4-CPP	W-PESLMSA1	0.050	µg/L	<0.050	---	----	---	----	---
Acifluorfen	W-PESLMSA1	0.050	µg/L	<0.050	---	----	---	----	---
Bentazone	W-PESLMSA1	0.050	µg/L	<0.050	---	----	---	----	---
Bromoxynil	W-PESLMSA1	0.050	µg/L	<0.050	---	----	---	----	---
Dicamba	W-PESLMSA1	0.050	µg/L	<0.050	---	----	---	----	---
Diclofop	W-PESLMSA1	0.050	µg/L	<0.050	---	----	---	----	---
Dinoseb	W-PESLMSA1	0.050	µg/L	<0.050	---	----	---	----	---
Dinoterb	W-PESLMSA1	0.050	µg/L	<0.050	---	----	---	----	---
DNOC	W-PESLMSA1	0.050	µg/L	<0.050	---	----	---	----	---
Fluroxypyr	W-PESLMSA1	0.050	µg/L	<0.050	---	----	---	----	---
Ioxynil	W-PESLMSA1	0.050	µg/L	<0.050	---	----	---	----	---
MCPA	W-PESLMSA1	0.050	µg/L	<0.050	---	----	---	----	---
MCPB	W-PESLMSA1	0.050	µg/L	<0.050	---	----	---	----	---
MCPP (isomers)	W-PESLMSA1	0.050	µg/L	<0.050	---	----	---	----	---
Propoxycarbazone-sodium	W-PESLMSA1	0.050	µg/L	<0.050	---	----	---	----	---
Triclopyr	W-PESLMSA1	0.050	µg/L	<0.050	---	----	---	----	---
Quaternary Ammonium Pesticides									
Chlormequat	W-PESLMS03	0.050	µg/L	<0.050	---	----	---	----	---
Diquat	W-PESLMS03	0.050	µg/L	<0.050	---	----	---	----	---
Paraquat	W-PESLMS03	0.050	µg/L	<0.050	---	----	---	----	---

If the client does not specify the date and time of sample collection, the laboratory will specify the date on sample delivery in parentheses, instead. If the time of sample collection is specified as 0:00 it means that the client did specify the date but not the time. Measurement uncertainty is expressed as expanded measurement uncertainty with coverage factor $k = 2$, representing 95% confidence level.

Key: LOR = Limit of reporting; MU = Measurement Uncertainty

The end of result part of the certificate of analysis

Brief Method Summaries

Analytical Methods	Method Descriptions
Location of test performance: Na Harfe 336/9 Prague 9 - Vysocany Czech Republic 190 00	
W-PESLMS03	CZ_SOP_D06_03_183.A (Application note of Applied Biosystems 114AP43-01) Determination of pesticides, pesticide metabolites and drug residues by liquid chromatography method with MS detection. We applied flexible accreditation type 2 to chlormequat. The method was conferred flexible accreditation type 2 and is mentioned on Annex of Certificate of Accreditation No. 345/2013 dated 18th June 2013. 12082013
W-PESLMSA1	CZ_SOP_D06_03_182.A (Application note Applied Biosystems 114AP59-01) Determination of acidic herbicides and drug residues by liquid chromatography method with MS detection and calculation of acidic herbicides and drug residues sums from measured values

A ** symbol preceding any method indicates non-accredited test. In the case when a procedure belonging to an accredited method was used for non-accredited matrix, would apply that the reported results are non-accredited. Please refer to General Comment section on front page for information.

The calculation methods of summation parameters are available on request in the client service.

X. References

ALS Environmental participates to different national conferences and meetings where the pesticides problematic is introduced or focused on, for example Pesticides clients days 2009 in Portugal, Isranalytca 2012 in Israel, Water and sanitation 2013 in Czech Republic or Balneotechnical days 2013, during which our specialists on pesticides animated a discussion on the topic.



ALS Environmental informs as well professionals in the field of water treatment, water processing and other branches related to water management by the means of specific leaflets.

ALS Environmental has a long experience in the analysis of pesticides for various projects, ranging from very clear water intended for human consumption to very contaminated samples from pesticides production plan remediation. Here are a few examples:

- Groundwater monitoring – Background levels, Czech Republic
- Groundwater monitoring – Background levels, Turkey
- Surface water monitoring – WFD legislation levels, Portugal
- Remediation of a pesticide plant (chlorobenzene chemistry) – High levels and monitoring of the remediation technology efficiency, Czech Republic
- Remediation of pesticide plant (chlorophenoxy acids) – High levels, Sweden



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