Chemosphere 149 (2016) 24–33

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Evaluation of the effect of tetraethylammonium bromide and chloride on the growth and development of terrestrial plants

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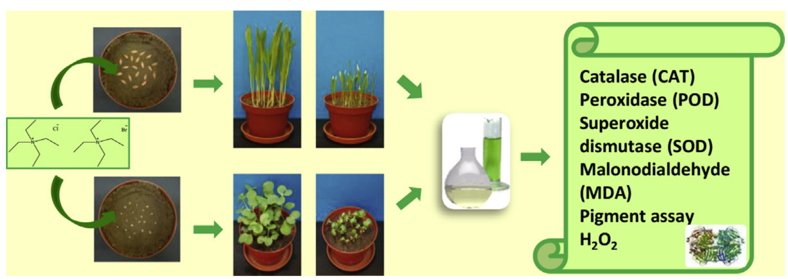
HIGHLIGHTS

- [TEA][Cl] is more toxic to spring barley and common radish than [TEA][Br].
- The lowest EC_{50} values determined from % inhibition of root length plants.
- The increased concentration of QAS in soil causes a decrease in content of plant pigments.
- The increased concentration of QAS in the soil increases the activity of POD.
- Common radish is a plant resistant of activity QAS.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 10 July 2015
Received in revised form
1 December 2015
Accepted 18 January 2016
Available online 2 February 2016

Handling Editor: Frederic Leusch

Keywords:
Quaternary ammonium salts
Phytotoxicity
Oxidative stress
Antioxidant enzyme activity
Photosynthetic pigments
Growth inhibition

ABSTRACT

Quaternary ammonium salts (QAS), which also include ionic liquids, constitute a vast group of chemical compounds that are increasingly common in the commercial use. This situation may lead to the contamination of the natural environment and may constitute a potential threat to all its elements, including terrestrial higher plants. This paper presents the effect of tetraethylammonium chloride [TEA][Cl] and tetraethylammonium bromide [TEA][Br] on the growth and development of spring barley and common radish. The applied QAS were characterized with phytotoxicity dependent on the concentration of compound and characteristics of the study plants. Spring barley turned out to be highly susceptible plant to the analyzed compounds, which was confirmed by % inhibition of length of plants, root length and fresh weight of plants and by calculated values for EC_{50}, NOEC as well as LOEC. On the contrary, a common radish revealed the resistance to QAS used in the study; although, phytotoxic symptoms were still observed when high concentrations of dry weight of soil were applied (1000, 3000 and 5000 mg/kg). The applied QAS caused oxidative stress symptoms, mainly in spring barley seedlings, which were manifested by decreased assimilation of pigments content, increased hydrogen peroxide (H_2O_2) and malondialdehyde (MDA) content in plant cells and with a changed activity of superoxide dismutase (SOD), catalase (CAT) and peroxidase (POD).

1. Introduction

Currently, plant production is one of the most important elements of modern agriculture, determining nourishment of

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http://dx.doi.org/10.1016/j.chemosphere.2016.01.072

constantly growing world's population, predicted to reach nine billion people by 2050. In order to provide enough food, agriculture must significantly increase global plant production. This can be achieved through conversion of land reserves located in areas characterized by water deficit, high salinity into arable lands, as well as the usage of species and varieties resistant to harsh climate conditions. Another important aspect of modern agriculture is intensification of plant production, using wide range of chemical compounds, such as fertilizers, pesticides and synthetic phytohormones (Chapman et al., 2012; Colla et al., 2012; Tavakkoli et al., 2012; Vermue et al., 2013).

All mentioned methods of intensification of plant production might result in an oxidative stress in susceptible plants, manifested by metabolism changes related to overproduction of reactive oxygen species (ROS) such as singlet oxygen ($^1O_2$), superoxide ($O^{\bullet -}{}_2$), ozone (O_3), hydrogen peroxide (H_2O_2) or hydroxide ($^\bullet OH$). The overproduction of ROS may lead to lipid peroxidation and permanent damage of cell membranes, nucleic acids and chloroplasts, and subsequent plant cell death and significant yield reduction (Herman et al., 1998; Morsy et al., 2007; Sánchez-Rodríguez et al., 2010; Jbir-Koubaa et al., 2015; Wang et al., 2015).

Abiotic oxidative plant stressors represent a wide range of chemical compounds, which are used in the production of mineral fertilizers or biocides, and then as a production waste may enter into the soil environment. This type of contamination can be retained in soil in the way of sorption and then can get into the cultivars causing negative metabolic changes. Quaternary ammonium salts (QAS) as well as ionic liquids (ILs) are chemical compounds very important for industry and agriculture. QAS are known for a long time; they are known for their supremely desirable frother-like, moisturizing, emulsifying, surfactant, anti-electrostatic, preserving, algicide, antifungal and bactericidal properties resulting in the worldwide QAS production of one million tons at the end of the twentieth century (Grabińska-Sota, 2004). The production and usage of such huge quantities of these compounds must represent potential danger to natural environment and humans, especially that toxicity of QAS to mammals and many aquatic organisms is known from the 1940s (Gruhzit et al., 1948; Kourounakis and Sylye, 1976; García et al., 2001).

QAS include ILs that are the most promising alternative to organic solvents. The attractiveness of ionic salts comes from a large number of their desirable features which can be successfully used in a variety of various industrial processes. The features include low vapor pressure, incombustibility and non-volatility, high thermal and chemical stability, excellent ionic conduction and good catalytic properties (Cvjetko Bubalo et al., 2014b; Bruzzone et al., 2011; Das and Roy, 2014; Zhang et al., 2010).

The above-mentioned properties of ionic liquids determine the wide use of these chemicals in the processes of catalysis, practical chemistry, extraction and separation processes. They are also used in the pharmaceutical, industry and in nanotechnology and electrochemistry. They also find their application in capacitors and as electrolytes in batteries. However, the increasing commercial interest in ionic liquids leads to a rapid growth in their production and practical use, which may result in leakage of these substances into the environment. It concerns especially soil media, which ionic liquids might enter as production wastes, waste water discharges, and waste dump effluents. After passing to soils, these compounds may affect the development of soil organisms and the growth, development and quality of terrestrial plants (Biczak et al., 2010, 2014b; 2015; Bruzzone et al., 2011; Peric et al., 2013).

There is lack of adequate data regarding QAS effect on the growth and development of terrestrial plants. This study partially completes these missing data. Here, we report the effect of two quaternary ammonium salts with chloride and bromide anions on the growth and development of terrestrial plants. Both these compounds have very similar physicochemical properties and are used in large quantities for synthesis of different materials, biologically active compounds and surfactants. The stress level in plants exposed to these QAS present in soil was also assessed. The assessment and comparison of the degree of QAS influence on monocotyledons and dicotyledons will provide good indicator for future crop selection. This knowledge is especially valuable regarding plants that grow on soil contaminated with these salts and the way they can handle the oxidative stress and provide expected yield with good quality at the same time. Also, it is interesting to investigate the phytotoxicity and physiological changes in plants by the QAS. The collected toxicity results will also enable us to estimate the risk assessment of environmental contamination upon the possible use of these substances, taking particularly into consideration that there are still few studies on this subject in the available literature.

2. Materials and methods

2.1. Chemicals

The tetraethylammonium chloride [TEA][Cl] ($\geq$98% purity) and tetraethylammonium bromide [TEA][Br] (98% purity) used in the study was purchased from Sigma–Aldrich Chemical Co. The structure of the tested QAS illustrates the general formula: $(C_2H_5)_4N^+ X^-$, where X^- respectively shall mean ion Cl^- and Br^-.

2.2. Growth conditions and treatment

A pot experiment for the determination phytotoxicity of the tetraethylammonium chloride and tetraethylammonium bromide was carried out in the vegetation hall of the Department of Biochemistry and Ecotoxicology at Jan Długosz University in Częstochowa based on the OECD/OCDE 208/2006 Guide.

A monocotyledonous plant – the spring barley (*Hordeum vulgare*) and a dicotyledonous plant – the common radish (*Raphanus sativus* L. subvar. *radicula* Pers.) were used in the experiment. Identical seeds of the plants, originating from the same source, were sown into 90 mm-diameter plastic plant pot was filled with the reference soil and a soil thoroughly mixed with the examined QAS. The treatment concentration of QAS were set to 0, 1, 10, 50, 100, 400, 700, 1000, 3000 and 5000 mg per 1 kg of soil d.w. The soil used in the experiment was light loam with a dissolved matter contain of approx. 10%, an organic carbon of 0.9% and pH equal to 6.0. Throughout the testing period (14 days), constant substrate moisture content at the level required for the plants (70% field water capacity), a constant temperature 20 $\pm$ 2 °C and a constant illumination of 7000 lux were maintained in the system of 16 h/day and 8 h/night.

The evaluation of the phytotoxicity of the quaternary ammonium salts determined and compared the sprouts, the fresh and dry mass content and the value of LOEC (*lowest observed effect concentration*) and NOEC (*no observed effect concentration*). For the determination of dry and fresh plant mass, on the basis of which we determined NOEC and LOEC and for the determination of fresh mass yield, only plant sprouts were used. The length of plants and root length were measured as described by Wang et al. (2009). The length of plants can be defined as the length the tip of the longest leaf to the base of culms, and root length can be defined as the length from the tip of the longest root to the root–shoot junction. Inhibition ratio was calculated as (length in control group – length in treatment group) x 100%/length control group. Results were expressed as yield fresh weight inhibition, length of plants and root length inhibition in comparison on control and corresponding EC_{50}