The impact of pesticides used at the agricultural land of the Puck commune on the environment of the Puck Bay

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ABSTRACT

Background. The Puck commune is one of the largest agricultural regions in the Pomeranian Voivodship that due to the pollution of the coastal zone negatively affects the functioning of the Puck Bay, including health of its inhabitants, and causes decrease in tourism as well as in overall economic value of the region. The objective of the undertaken study was to assess the extent of risk to the environment posed by the pesticides used in agricultural production in the coastal area of the Puck commune.

Methods. The study focused on organochlorine insecticides (DDT and its metabolites: α, β, γ, δ-HCH, aldrin, dieldrin, endrin, isodrine), glyphosate and its metabolite AMPA, and 309 active substances used as pesticides. Analyses were carried out using GC-MS, GC-MS/MS and LC-MS/MS techniques. The undertaken novel approach included “tracking” of a large number of substances in multiple environmental matrices (surface water, groundwater, seawater, soil, sediment and fish), along with examination of their transport routes from the pesticides application locality to the Puck Bay.

Results. Glyphosate and its metabolite AMPA, anthraquinone, boscalid, chlorpyrifos-ethyl, dimethachlor, diflufenican, difenoconazole, epoxiconazole, fluopicolide and metazachlor were found in soil samples and surface water samples collected from drainage ditches surrounding the studied agricultural plots. In the samples of seawater and fish taken from the Puck Bay no studied pesticides were found.

INTRODUCTION

The Baltic Sea is a brackish, shallow, semi-enclosed shelf sea, with an inflow of the North Sea waters limited by three straits, i.e., Oresund, the Great Belt and the Little Belt. Its water density stratification and thermal stratification are both pronounced, which hinders mixing of well oxygenated surface waters with poorly oxygenated deep waters. Numerous rivers discharge into the Baltic Sea, which is the main reason for positive freshwater balance, where freshwater input exceeds evaporation (Lomniewski, Mańkowski & Zaleski, 1975; Cyberska, 1990; Gerlach, 1994; Andruliewicz et al., 2008). The aforementioned specific characteristics...
expose the Baltic Sea to strong anthropopressure resulting from extensive demographic and economic development of nine riparian countries (Andrulewicz et al., 2008).

The Puck Bay is a unique part of the Baltic Sea, also called the “Little Sea”. The Bay is 364 km$^2$, with the maximum depth of 55 m (Chałupska Jama), but a significant part of it is very shallow. The Puck Bay borders the Hel Peninsula in the north, the Gulf of Gdansk in the east, and the North Kashubian coastline in the south-west. The Puck Bay is an attractive region and a perfect place for tourism, recreation, water sports and fishing. However, the Puck commune area is one of the largest agricultural regions in the Pomeranian Voivodship that due to the pollution in the coastal zone negatively affects functioning of the entire environment, including human health, and results in decrease in tourism and in overall economic value of the region. EU rules distinguish between active substances, such as glyphosate, and plant protection products. Plant protection products (PPP)—which are often referred to as pesticides (e.g., insecticides, fungicides, herbicides)—are mixtures containing one or several active substance(s) and other ingredients (so-called co-formulants) (European Commission, 2017a; European Commission, 2017b; Pérez-Lucas et al., 2018). Pesticides widely used in agriculture, horticulture and forestry, pose a significant threat to the environment (Karami-Mohajeri & Abdollahi, 2010; Rodney, Teed & Moore, 2013; Lari et al., 2014; Sidoli, Baran & Angulo-Jaramillo, 2016; Bento et al., 2017; Erban et al., 2018; Lupi et al., 2019; Shang et al., 2019). The use of pesticides in agriculture has help to improve yields by preventing crop losses. Pesticides include active ingredients that in spite of the beneficial actions on agricultural production could have other less positive impacts on the environment and habitats where they are used (Eurostat, 2016; Shang et al., 2019), e.g., they can contaminate food, air, soil and water (Grygiel et al., 2012; Żak, 2016; Bento et al., 2017). Pesticide toxicity results from the presence of biologically active ingredients, emulsifiers, excipients and fillers that may adversely affect environmental biocenosis (Nowak, Włodarczyk-Makula & Manzer, 2015). About 10,000 products of this type that differ in their purpose, composition and properties are known (Sadecka, 2003). Pesticides may undergo physical and/or chemical changes into the environment and also be transferred between different ecosystems as original compound or as product of degradation/metabolism. In the initial form or as a derivative, their metabolites have the ability to retention in soil, water, atmosphere, as well as human food and animal feed threatening wellbeing of all living organisms (Żelechowska, Biziuk & Wiergowski, 2001). Based on their function pesticides are divided into: fungicides, insecticides (protect plants against the harmful effects of insects) and herbicides. Pesticides are also classified based on their persistence in the environment and categorized as: unstable (spread out up to 12 weeks), moderately persistent (spread out in 1–18 months) and highly persistent (spread out within 2–3 years in 75–100%) (Nowak, Włodarczyk-Makula & Manzer, 2015). The last group includes organochlorine pesticides (DDT, HCH, aldrin and others), the use of which has already been banned, however, many years of research show that their residues still persist in the Baltic Sea both in inanimate matter (bottom sediments) and in the tissues of living plants and animals at all trophic levels (Backlund, Holmbom & Lepakoski, 1992; Singh & Agarwal, 1995; Wodarg & Graeve, 1996; Sapota, 2006a; Sapota, 2006b; Sapota & Wisniewska-Woitasik, 2007; Sapota et al., 2009; Staniszewska et al., 2011).
It has been proven that the use of pesticides diminishes the agriculture losses, which is associated with economic growth. On the other hand, they may pose a serious threat to human health. It is true not only for individual active substances, but also for the components of preparations in which various chemical compounds “facilitate” practical use (Makles & Domański, 2008; STOA, 2019). Therefore, the new approach to agriculture and horticulture focuses on the introduction of new, resistant plant varieties, which significantly reduce the risk of diseases and pests and make the use of pesticides largely unnecessary (Calvert, 2019; Cary, 2019). However, the negative pressure of agriculture on the environment is still very strong. It means that recently the market of plant protection chemicals has been changing significantly and so it will in the near future, because further active substances are being withdrawn and pesticides with lower toxicity are introduced instead. The obligation to exercise control over the use of pesticides and plant protection products in agricultural production, including testing for residues of active substances of plant protection products, results both from national law, in particular the act on plant protection products (Journal of Laws of 2013, item 455 with later amendments), as well as from the European Union regulations (Miszczak, 2016; STOA, 2019). Directive 2009/128/EC establishing a framework for Community action for the sustainable use of pesticides (Official Journal of the European Union L 309, 24.11.2009, page 71) regulates at the level of the European Union the rules of trading and use of plant protection products, in order to reduce the risks to human health, animals and the natural environment posed by these preparations. In EU countries, the conditions for the registration approval of a given pesticide and its placing on the market are determination of the effectiveness of the preparation and assessment of the risks posed to humans and the environment. The only substances allowed for distribution are the ones for which tests have shown little effect on human health and the environment. If high risk is detected, actions are taken to reduce or to prohibit the use of the pesticide (Nowak, Włodarczyk-Makuła & Mamzer, 2015; Pérez-Lucas et al., 2018). In an action aiming to reduce pesticide environmental hazards, the European Union recommends a strategy for sustainable use of pesticides, through increased use and distribution controls, introduction of intensive training of farmers in maintaining proper dosing of pesticides, keeping records of spraying, types of substances used and type of crops, using certified spraying devices, or “pesticide” taxation of agrochemical companies, used to cover the costs of permit issuance, of inspections and testing as well as training (Makles & Domański, 2008; European Commission, 2017a). The objective of this study was to assess the extent of risk pesticides used in agricultural production in the coastal area of the Puck commune pose to the environment. For this purpose, the content of pesticides in arable lands as well as in water samples collected in selected watercourses and drainage ditches surrounding the investigated agricultural parcels in the area of the Puck commune, and also in samples of seawater, sediments and fish muscle were examined. When selecting agricultural land plots for research, the following criteria were taken into account: location of arable land in relation to watercourses, type of crops, application of specific pesticides and plant protection products. The information was derived from a questionnaire presented to farmers participating in the project titled “Modelling of the impact of the agricultural holdings and land-use structure on the quality of inland...
and coastal waters of the Baltic Sea set up on the example of the Municipality of Puck region—Integrated info-prediction Web Service WaterPUCK” (Dzierzbicka-Głowacka et al., 2019). The study covered organochlorine insecticides (DDT and its metabolites: α, β, ν, δ-HCH, aldrin, dieldrin, endrin, isodrin). At the same time, based on the information provided in the characteristic’s sheets of the declared plant protection products, a list of active substances with increased likelihood of leaving their residues in the environment and substances with a long half-life in the environment was established. 309 compounds classified as pesticides were included in this list. The novel approach undertaken in the study was “tracking” of a large number of substances in a number of environmental matrices, along with examination of their transport routes from their application place to the Puck Bay.

**MATERIALS & METHODS**

**Sampling**

Analyses of the content of pesticides in watercourses and arable lands were carried out in the area of the agricultural Puck commune, located in the north-eastern region of the Pomeranian Voivodeship, on the west coast of the Puck Bay, which is part of the Baltic Sea. Agricultural land in the Puck commune constitutes 57.3% of the total area of the region, the vast majority of which is characterized by high crops potential. The area landscape is largely undulating, with land slopes of up to approx. 9% (5.14°). Such terrain characteristics are conducive to leaching of the applied plant protection products from soils as a result of surface runoff. Sampling was carried out with the consent of the Puck commune and farmers who took part in the project. Figure 1 shows the points and areas for sampling.

The study covered three agricultural land plots belonging to two farms participating in the WaterPUCK project which were marked as G1 and G2. One of the plots number Dz 1, belonged to the G1 farm, and two plots, number Dz 2 and Dz 3, to the G2 farm. Selection of farms was made taking into account location of arable land relative to watercourses and the size of the average consumption of active substances of plant protection products declared in the questionnaire in relation to the arable land area. On the studied plots occurred mainly brown soils (Pietrzak et al., 2020). In terms of the agronomic category the soils belonged to medium soils, slightly acidic.

Soil samples for chemical analyses were collected in 2018 during the intensive application of pesticides (in March, April and June) and after the use of it (in July and August). According to standard PN-R-04031:1977, 60 general samples (averaged) from the soil surface layer (0–30 cm) were collected. For one general sample, up to 20 single samples were taken uniformly from the surface of the entire field.

Water samples were collected once a month from February to September 2018 from:
- drainage ditches surrounding each parcel (56 surface water samples)
- watercourses receiving water from the drainage ditches investigated and then flowing to the Puck Bay, i.e., the Bladzikowski Stream; the channel connecting the Bladzikowski Stream with the Gizdebka River; the Gizdebka River (21 surface water samples)
- seawater from the Puck Bay (two points in the mouths of the studied watercourses) (16 sample of surface water)
and:
- four piezometers: No. 8, 31, 56 and 61 (4 samples of groundwater taken in August 2018).

Bottom sediment samples were taken with van Veen grab in the same points as seawater samples (16 samples of surface layer).

Research fishing was carried out using the “MEC-8” fishing unit and the Maritime Institute boat “BOSMINA II”. The spatial range included fishing squares R-5, R-6, S-5, S-6 (Fig. 2) within the boundaries of the Puck Bay. A total of 60 catch using the NORDIC multi-panel gillnet set were carried out from May to the end of October. Two species of fish, cod (Gadus morhua) and flounder (Platichthys flesus), were selected for the study. 25 specimens of each species were taken for testing of the pesticides content.

Analyses
All samples: soils, sediments, surface and ground waters and fish muscle have been tested for the presence of organochlorine insecticides (aldrin, dieldrin, endrin, isodrine, sum of DDT, hexachlorocyclohexane (HCH): alpha, beta, gamma and delta); herbicide glyphosate and its metabolite AMPA (aminomethylphosphonic acid); and 309 active substances of plant
protection products (Table 1). Both active substances, which according to the regulations are tested in environmental samples, as well as those currently examined only as residues in food were analysed. The lower limits of quantification of individual compounds were below the environmental quality standards (EQS) set out in the Regulation of the Minister of the Environment of July 21, 2016 on the method of classification of the surface water bodies and environmental quality standards for priority substances (Journal of Laws 2016 poz.1187), as well as below the Maximum Residues Level of an active substance in food (MRL) defined in the EC Regulation No. 396/2005 of the European Parliament and of the Council of 23 February 2005 on maximum residue levels of pesticides in food and feed of plant and animal origin and on their surface.
| No. | The active substance               | No. | The active substance               | No. | The active substance               | No. | The active substance               |
|-----|-----------------------------------|-----|-----------------------------------|-----|-----------------------------------|-----|-----------------------------------|
| 1   | 2,4,5-T-Methylester               | 78  | 4,4-Dibromobenzophenone           | 155 | Fluopicolide                      | 232 | Pentachloraniline                 |
| 2   | 2,4-D-Methylester                 | 79  | Dicapthon                         | 156 | Fluorodifen                       | 233 | Pentachlorobenzene                |
| 3   | Acetochlor                        | 80  | Dichlobenil                       | 157 | Fluotrimazole                     | 234 | Pentachlorothioanisole            |
| 4   | Aclonifen                         | 81  | Dichlofenthion                    | 158 | Fluchinconazole                   | 235 | Permethrin                        |
| 5   | Acrinathrin                       | 82  | Dichlofluinid                     | 159 | Flurenol-buthyl                   | 236 | Pertan                            |
| 6   | Alachlor                          | 83  | Dichloran                         | 160 | Flurochloridone                   | 237 | Phenkapton                        |
| 7   | Aldrin+Dieldrin                   | 84  | Dichlorvos                        | 161 | Flurtamone                        | 238 | Phenothrin                        |
| 8   | Allethrin                         | 85  | Diclofop-methyl                   | 162 | Flusilazole                       | 239 | Phenothoate                       |
| 9   | Amidithion                        | 86  | Dicofol (sum)                     | 163 | Fopet                             | 240 | Phosalone                         |
| 10  | Anthraquinone                     | 87  | Dicofol,o-p-                      | 164 | Fonofos                           | 241 | Phosfolane                        |
| 11  | Atrazine                          | 88  | Dicofol,p,p-                      | 165 | Formotion                         | 242 | Phosmet                           |
| 12  | Azaconazole                       | 89  | Dicrotophos                       | 166 | Genite                            | 243 | Picolinafen                       |
| 13  | Azinophos ethyl                   | 90  | Dienoehlor                        | 167 | Halfenprox                        | 244 | Picoxytobrin                     |
| 14  | Azinophos methyl                  | 91  | Difenconazole                     | 168 | Haloxyfop-Ethoxyethyl             | 245 | Piperophos                        |
| 15  | Azoxyostrobin                     | 92  | Diffufenicnan                     | 169 | Haloxyfop-methyl                  | 246 | Pirnymilos methyl                 |
| 16  | Benfluralin                       | 93  | Dimefox                           | 170 | HCH (sum of isomers - without lindane) | 247 | Pirnymilos ethyl                 |
| 17  | Benoxacor                         | 94  | Dimethachlor                      | 171 | Epsilon-HCH                       | 248 | Pifenate                          |
| 18  | Benzoylprop-ethyl                 | 95  | Dimethipine                       | 172 | Lindane                           | 249 | Prallethrin                       |
| 19  | Biofenox                          | 96  | Dimethoate                        | 173 | Heptachlor                        | 250 | Procymidone                       |
| 20  | Binapacryl                        | 97  | Dimethomorph                      | 174 | Heptachlor (sum)                  | 251 | Profenfos                         |
| 21  | Bifenthrin                        | 98  | Diniconazole                      | 175 | Heptachlor-trans-epoxide          | 252 | Propfuralin                       |
| 22  | Bitertanol                        | 99  | Dinitramine                       | 176 | Heptachlor-cis-epoxide            | 253 | Propachlor                        |
| 23  | Boscalid                          | 100 | Dinobuton                         | 177 | Heptenophos                       | 254 | Propanil                          |
| 24  | Bromofenvinphos                   | 101 | Disulfofon                        | 178 | Heksaconazole                     | 255 | Propazine                         |
| 25  | Bromocyclen                       | 102 | Disulfofon-sulfone                | 179 | Indianofan                        | 256 | Propetamphos                      |
| 26  | Bromophos methyl                  | 103 | Ditalimfos                        | 180 | Indoxacarb                        | 257 | Propiconazole                     |
| 27  | Bromophos ethyl                   | 104 | Edifenphos                        | 181 | Jodofenfos                        | 258 | Propyzamide                       |
| 28  | Bromopropylate                    | 105 | Endosulfan (sum of isomers)       | 182 | Ioxynil-Octanoate                 | 259 | Prothiofos                        |
| 29  | Buprofezin                        | 106 | alpha-Endosulfan                  | 183 | Iprobenfos                        | 260 | Prothoat                          |
| 30  | Butachlor                         | 107 | Endosulfan sulphate               | 184 | Iprodion                          | 261 | Pyraclofos                        |
| 31  | Butamifos                         | 108 | beta-Endosulfan                   | 185 | Isazophos                         | 262 | Pyraflufen-ethyl                  |
| 32  | Butralin                          | 109 | Ketoendrin-delta                  | 186 | Isobenzan                         | 263 | Pyrazophos                        |
| 33  | Cadusafos                         | 110 | EPN                               | 187 | Isocarbofos                       | 264 | Pyrethrin                         |
| 34  | Captafol                          | 111 | Epoxiconazole                     | 188 | Izofenfos                         | 265 | Pirydaben                         |
| 35  | Captan                            | 112 | Etaconazole                       | 189 | Isofenphos-Methyl                 | 266 | Pyridaphenthion                   |
| 36  | Carbophenothion                   | 113 | Ethalfluralin                     | 190 | Isomethiozin                      | 267 | Pyrifentox                        |
| 37  | Carbophenothion-methyl            | 114 | Ethion                            | 191 | Isopropalin                       | 268 | Pirimithate                       |
| 38  | Carfentrazone-ethyl               | 115 | Ethiprol                          | 192 | Isoxadifen-ethyl                  | 269 | Chinalofos                        |

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| No. | The active substance        | No. | The active substance        | No. | The active substance        | No. | The active substance        |
|-----|----------------------------|-----|----------------------------|-----|----------------------------|-----|----------------------------|
| 39  | Chinomethionat             | 116 | Ethofumesate               | 193 | Kresoxim-metylu            | 270 | Qinoxyfen                  |
| 40  | Chlorbenzyl                | 117 | Ethophosphos               | 194 | Lactofen                   | 271 | Quinozene                  |
| 41  | Chlordane (total)          | 118 | Etridiazole                | 195 | Leptophos                  | 272 | Quinozene (sum)           |
| 42  | Chlordan, cis-             | 119 | Etrifos                    | 196 | Lufenuron                  | 273 | Chisalofope ethyl          |
| 43  | Chlordan, oxi-gamma/trans- | 120 | Famophos                   | 197 | Malaoxon                   | 274 | Resmethrin                 |
| 44  | Chlordan, gamma/trans-     | 121 | Famoazadone                | 198 | Malathion                  | 275 | S421 Octachlordipropylet  |
| 45  | Chlordecon                 | 122 | Fenamidone                 | 199 | Mekarbam                   | 276 | Spiromesifen               |
| 46  | Chlorehydroxyflos          | 123 | Fenamiphos (sum of isomers) | 200 | Mephosfolan                | 277 | Sulprofos                  |
| 47  | Chlorfenapyr               | 124 | Fenarimol                  | 201 | Merphos                    | 278 | Sulprofos                  |
| 48  | Chlorfenprop-methyl        | 125 | Fenbuconazole              | 202 | Metazachlor                | 279 | Swep                       |
| 49  | Chlorfenon                 | 126 | Fenchlorazole              | 203 | Metakrifos                 | 280 | Tau-Fluvalinate            |
| 50  | Chlorfenvinphos            | 127 | Fenchlorofos               | 204 | Methidation                | 281 | Tebupirimfos               |
| 51  | Chloridazon                | 128 | Fenfluthrine               | 205 | Metoxychlor                | 282 | Tecnazene                  |
| 52  | Chlorimphos                | 129 | Fenhexamid                 | 206 | Metolachlor                | 283 | Tefluthrin                 |
| 53  | Chlorobenzilate            | 130 | Fenprothion                | 207 | Mefrafenone                | 284 | Temephos                   |
| 54  | Chloroneb                  | 131 | Fenoxaprop-ethyl           | 208 | Metribuzin                 | 285 | Terbufos                   |
| 55  | Chloropropylate            | 132 | Fenpropiconil              | 209 | Mevinfos                   | 286 | Tetrachlorvinphos          |
| 56  | Chlorothalonil             | 133 | Fenpropathrin              | 210 | Mirex                      | 287 | Tetraconazole              |
| 57  | Chlorpyrifos ethyl         | 134 | Fenpropimorph              | 211 | Molinate                   | 288 | Tetradifon                 |
| 58  | Chlorpyrifos methyl        | 135 | Fenson                     | 212 | Myclobutanol               | 289 | Tetramethrin               |
| 59  | Chlorothalidimethyl        | 136 | Fensulfothion              | 213 | Niralin                    | 290 | Tetrasul                   |
| 60  | Chlorotion                 | 137 | Fervalerate (sum of isomers) | 214 | Nitrapyrin                 | 291 | Tolklofos methyl           |
| 61  | Chlortrifos                | 138 | Fenvalerate                | 215 | Nitrofen                   | 292 | Tollylfluanid              |
| 62  | Chlozoilate                | 139 | Fenvalerate (RS-/SR-Isomer)| 216 | Nitrothal-isopropyl        | 293 | Toxahpane Parlar 26       |
| 63  | Cinidion-ethyl             | 140 | Fipronil                   | 217 | Norflurazon                | 294 | Toxahpane Parlar 50       |
| 64  | Clodinafop-propargyl       | 141 | Fipronil, desulfynil-      | 218 | Nuarimol                   | 295 | Toxahpane Parlar 62       |
| 65  | Cumafos                    | 142 | Fipranil + Sulfonmetab. MB46136 (sum) | 219 | Ometoate                   | 296 | Transfluthrin              |
| 66  | Crotuxyphos                | 143 | Fipronil sulphide          | 220 | Oxadiazon                  | 297 | Triadimefon                |
| 67  | Cyjanofenphos              | 144 | Fipronil sulphone          | 221 | Oxydemeton-methyl          | 298 | Triadimethol              |
| 68  | Cyanophos                  | 145 | Flamprop-isopropyl         | 222 | Oksyfluorotelin            | 299 | Triadimeno/Triadimefon (sum) |
| 69  | Cyfluthrin                 | 146 | Flamprop-methyl            | 223 | Paclobutrazole             | 300 | Triallate                  |
| 70  | lambda-Cyhalothrin         | 147 | Flonicamid                 | 224 | Paraaxon-ethyl             | 301 | Triamiphos                |
| 71  | Cypermethrin               | 148 | Fluazifop-buthyl           | 225 | Paraaxon-methyl            | 302 | Triazophos                |
| 72  | Cyphenothrin               | 149 | Fluazinam                  | 226 | Parathion                  | 303 | Tribuphos                 |
| 73  | Cyproconazole              | 150 | Fluchloralin               | 227 | Parathion methyl           | 304 | Trichloronate             |
| 74  | Delamethrin                | 151 | Flucythydrinate            | 228 | Parathion methyl/Paraaxon methyl (sum) | 305 | Tridiphane                |
| 75  | Dialifos                   | 152 | Flufenoxuron               | 229 | Penconazole                | 306 | Trifloxystrobin           |

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| No. | The active substance | No. | The active substance | No. | The active substance | No. | The active substance |
|-----|----------------------|-----|----------------------|-----|----------------------|-----|----------------------|
| 76  | Di-allate            | 153 | Flumethrine          | 230 | Pendimethalin        | 307 | Trifluralin          |
| 77  | Diazinon             | 154 | Flumetralin          | 231 | Pentachloranisol     | 308 | Vamidothion          |
|     |                      |     |                      |     |                      | 309 | Vinclozolin          |

**Water samples**

The determination of chloroorganic pesticides residue in water samples had been performed following PN-EN 16693: 2015-12 standard *Water quality—Determination of selected chloroorganic pesticides (OCP) in whole water samples—Solid phase extraction method (SPE) using extraction discs and gas chromatography with mass spectrometry (GC-MS)*. To 1 dm$^3$ of water sample was adding internal standard (e.g., chrysene D12, Accu Standard). The entire sample volume was transferred through speed disc filled by C18 (SPE, J.T. Backer) and then washed by dichloromethane acetone (Merck for GC-MS SupraSolv) 1:1 (v/v). The sample was reconstituted to 1 cm$^3$ and measured by GC-MS. LOQ depending on pesticide was 0.005–0.01 µg dm$^{-3}$.

The examination of the content of 309 active substances classified as pesticides, glyphosate and AMPA in water samples had been performed in accordance with the methodology contained in SOP-LA-GC-015-06. The 309 active substances were liquid/liquid extracted from 30 cm$^3$ of water sample using mixture of n-hexane/toluene/ethyl acetate (Merck for GC-MS SupraSolv). The organic solvents were evaporated to dryness. Dry residue were resolved in 300 mm$^3$ of ethyl acetate and measured using GC-MS/MS. LOQ depending on pesticide ranged from 0.02 to 0.10 µg dm$^{-3}$.

The glyphosate and AMPA in water samples was analysed after sample homogenization and pre-column derivatization on line with 9-fluorenylmethyl chloroformate (FMOC, Sigma-Aldrich) (pH 9), and chromatographic column separation. Finale analyses had been performed on LC-MS/MS. LOQ was 0.02 µg dm$^{-3}$.

**Soil and sediment samples**

The determination of chloroorganic pesticides content in soil and sediment samples had been performed according own research procedure PB-45 “Determination of organochlorine pesticides in soil samples”, edition No. 2. Pesticides were extracted from 10 g of dry soil or sediment sample with 50 cm$^3$ n-hexane/acetone (Merck for GC-MS SupraSolv) 1:1 (v/v) in ASE (Accelerated Solvent Extraction). After cleaning with sulphuric acid (Merck, Suprapur) on the column filled by silica gel (J.T. Baker) and evaporating to 1 cm$^3$, chloroorganic pesticides were measured using GC-MS. LOQ for each pesticide was 0.02 mg kg$^{-1}$.

The examination of the content of 309 active substances classified as pesticides was carried out in accordance with the methodology described in SOP-LA-GC-033-04 and D. Becker 1.4.2019. The active substances were extracted from 5 g of dry soil or sediment sample with water, acetone, n-hexane (Merck for GC-MS SupraSolv) and sodium chloride (Sigma-Aldrich). After shaking (0.5 h) and centrifuging, 1 cm$^3$ of supernatant was transferred into vial and measured using GC-MS/MS. LOQ depending on pesticide ranged from 0.015 to 0.12 mg kg$^{-1}$.
The content of glyphosate and AMPA had been performed following SOP-LA-LCMS-039-04 and D. Becker 1.4.2019. The 2 g of dry soil or sediment sample was extracted with 10 cm³ KOH (Supelco). After neutralising and centrifuging the samples, 1 cm³ of the supernatant was transferred to a plastic tube. Isotopic marked internal standard was adding and then derivatization step was carried out with FMOC-Cl (Sigma-Aldrich) and acidation to improve retention and LC-MS/MS detection. LOQ was 0.05 mg ·kg⁻¹.

**Fish**

The determination of chloroorganic pesticides content in muscle tissue of fish had been performed according own research procedure PB-46 “Determination of organochlorine pesticides in biota samples”, edition No. 2.

Pesticides were extracted from 2 g of dry (lyophilised) tissue with 20 cm³ n-hexane/acetone/dichloromethane (Merck for GC-MS SupraSolv)1:1:2 (v/v/v) in ASE (Accelerated Solvent Extraction). After that, an extract was cleaning on the column filled by silica gel (J.T. Baker) with sulphuric acid (Merck, Suprapur). The sample was reconstituted to 1 cm³ and measured by GC-MS. LOQ was 0.01 mg kg⁻¹.

The determination of content of 309 active substances classified as pesticides in muscle tissue of fish had been carried out in accordance with the method delineated in own procedure SFFET-10. Pesticides were extracted from 2.5 g of wet tissue with MTBE (methyl t-butyl ether) (Sigma-Aldrich, Supelco) in Soxhlet/Microwave. Then the sample was separated using gel permeation chromatography (GPC) (Bio Beads SX 3, Bio-Rad, Knauer) acc. to elution profile. The solvents were evaporated to dryness. Dry residue was resolved in ethyl acetate (Merck for GC-MS SupraSolv). After cleaning with PSA (primary secondary amine, Sigma Aldrich) and centrifuging the samples, 1 cm³ of the supernatant was transferred to a vial and measured using GC-MS (FDP). LOQ depending on pesticide varied from 0.005 to 0.1 mg kg⁻¹.

**Quality Assurance**

The studies were carried out by the Laboratory of the Maritime Institute, which has accreditation by the Polish Center for Accreditation. Quality Assurance of performed analyses was made using solutions with added analytical standard, analyses of CRM (Certified Reference Material) such as SPXPR-1, -3, -4, -5, -6, -10 produced by SPEXCertifPrep, 89432 TraceCERT (Glyphosate) produced by Sigma-Aldrich, IRMM-44-3 (EUROSOIL 3) and IRMM-44-4 (EUROSOIL 4) both produced by European Commission Directorate General Joint Research Centre. Quality guarantee was checked also in Proficiency Testing organised by LGC (AQUACHECK), Eurofins Scientific (SILESIALAB) and PT Pesticides in Soil (Sigma-Aldrich).

Interviews with farmers were also conducted to determine the type and amount of plant protection products used and the types of plants grown on the studied plots. In these works, a questionnaire prepared specifically for the study was used.

**RESULTS**

Farms G1 (with plot Dz 1) and G2 (with plots Dz 2 and Dz 3) covered by the study, were using in 2018 respectively 8 and 9 different types of plant protection products. On
the G1 farm, the average consumption of active substances of plant protection products amounted to 0.55 kg ha\(^{-1}\) per arable land, while in the G2 farm 1.56 kg ha\(^{-1}\) per arable land.

List of plant protection products used in the studied farms in the year 2018 is presented in Supplement. The farmers also declared the use of active substances propamocarb hydrochloride and fenamidone (PYTON CONSENTO 450 SC), classified as dangerous to the environment and a fungicide (AFLEX SUPER 450 SC), the active substance of which is fluopicolide. In Poland the fungicide fluopicolide has been removed from the register of plant protection products by the Minister of Agriculture and Rural Development (updated on 03.06.2019) in June 2018. Also, an organophosphorus insecticide—chlorpyrifos-ethyl belongs to compounds banned from use in fruit plants (Act on Plant Protection of December 18, 2003, Journal of Laws 2004 No. 11, item 94).

In all analysed water samples (surface and underground), soil and sediment samples, and fish tissue the concentration of organochlorine pesticides (aldrin, dieldrin, endrin, isodrine, DDT and its isomers and alpha, beta, gamma and delta isomers of hexachlorocyclohexane) were below the limit of detection of the used methodology.

However, in soil samples, surface waters from drainage ditches and watercourses as well as in groundwater samples out of 309 active substances examined, the following pesticides have been detected:

- organophosphatic insecticides: chlorpyrifos-ethyl
- fungicides: boscalid, epoxiconazole, difenoconazole, fluopicolide
- herbicides: dimetachlor, diflufenican, metazachlor, glyphosate and its metabolite AMPA
- repellents: anthraquinone.

The presence of the largest number of residues of analysed active substances was found in soil and surface water samples from drainage ditches taken from the agricultural plot Dz 1 (Table 2). The concentrations of detected pesticides in soil samples ranged from 0.05 to 0.35 mg kg\(^{-1}\). The highest concentrations were obtained in August in water from drainage ditches for: metazachlor (2.0 µg dm\(^{-3}\)), glyphosate (4.7 µg dm\(^{-3}\)) and AMPA (2.0 µg dm\(^{-3}\)).

Concentrations of residues of plant protection products found in samples taken from the area of plot Dz 2 and in its vicinity are presented in Table 3. In Table 4 the results obtained in samples taken from and around the area of plot Dz 3 are showed. Both plots belong to farm G2. As a result of the conducted research, the presence of fluopicolide in soils (0.15 mg kg\(^{-1}\)) and waters of drainage ditches (0.37 µg dm\(^{-3}\)) was found in July on plot Dz 3. In the waters of drainage ditches fluopicolide was found also in August on plot Dz 2 (0.02 µg dm\(^{-3}\)). On the G2 farm, plant protection products containing fluopicolide and glyphosate were used also in 2017. In July, the presence of diflufenican in the surface waters of Bladzikowski Stream was also noted. Part of the drainage ditches surrounding agricultural farms falls into this stream.

Glyphosate and AMPA in surface water samples taken from drainage ditches surrounding studied plots were found in period after intensive use of pesticides in concentrations between 0.17–4.7 µg dm\(^{-3}\) and 0.2–2.0 µg dm\(^{-3}\) respectively.
Table 2  Residues of plant protection products detected in samples taken from and around the agricultural plot No. Dz 1, and the Puck Bay. < concentration below LOQ (limit of quantification).

| Month of sampling (2018) | Plant protection product | Soil | Sediment | Surface water | Groundwater |
|--------------------------|--------------------------|------|----------|---------------|-------------|
|                          |                          |      |          | Drainage ditches | Bladzikowski Stream | The Puck Buy | Piezometer No. 8 |
|                          |                          |      |          | µg dm⁻³        | µg dm⁻³      | µg dm⁻³      | µg dm⁻³      |
| April                    | Chlorpyrifos-ethyl       | 0.093 ± 0.047 | <0.015 | <0.10 | <0.10 | <0.10 | <0.10 |
|                          | AMPA                     | 0.110 ± 0.055 | <0.05  | <0.02 | <0.02 | <0.02 | <0.02 |
|                          | Anthraquinone            | 0.18 ± 0.09  | <0.06  | <0.1  | <0.1  | <0.1  | <0.1  |
|                          | Boscalid                 | <0.09     | <0.09  | 0.150 ± 0.038 | <0.03 | <0.03 | <0.03 |
|                          | Chlorpyrifos-ethyl       | 0.150 ± 0.008 | <0.015 | <0.10 | <0.10 | <0.10 | <0.10 |
| June                     | Dimethachlor             | <0.03     | <0.03  | 0.130 ± 0.033 | <0.1  | <0.1  | <0.1  |
|                          | Epoxiconazole            | <0.12     | <0.12  | 0.170 ± 0.043 | <0.03 | <0.03 | <0.03 |
|                          | Metazachlor              | <0.03     | <0.03  | 0.12 ± 0.03  | <0.03 | <0.03 | <0.03 |
|                          | Glyphosate               | 0.28 ± 0.14 | <0.05  | <0.02 | <0.02 | <0.02 | <0.02 |
|                          | AMPA                     | 0.35 ± 0.17 | <0.05  | <0.02 | <0.02 | <0.02 | <0.02 |
|                          | Anthraquinone            | 0.23 ± 0.12 | <0.06  | <0.10 | <0.10 | <0.10 | <0.10 |
|                          | Chlorpyrifos ethyl       | 0.150 ± 0.008 | <0.015 | <0.10 | <0.10 | <0.10 | <0.10 |
| July                     | Diflufenican             | <0.03     | <0.03  | <0.03 | 0.130 ± 0.033 | <0.03 | <0.03 | <0.03 |
|                          | Glyphosate               | 0.050 ± 0.025 | <0.05  | <0.02 | <0.02 | <0.02 | <0.02 |
|                          | AMPA                     | 0.26 ± 0.13 | <0.05  | <0.02 | <0.02 | <0.02 | <0.02 |
|                          | Boscalid                 | <0.09     | <0.09  | 0.045 ± 0.023 | <0.03 | <0.03 | <0.03 |
|                          | Diflufenican             | <0.03     | <0.03  | 0.049 ± 0.025 | <0.03 | <0.03 | <0.03 |
|                          | Epoxiconazole            | <0.12     | <0.12  | 0.045 ± 0.023 | <0.03 | <0.03 | <0.03 |
|                          | Metazachlor              | <0.03     | <0.03  | 2.0 ± 1.0  | <0.03 | <0.03 | <0.03 |
| August                   | Glyphosate               | <0.05     | <0.05  | 4.7 ± 2.4  | <0.02 | <0.02 | <0.02 |
|                          | AMPA                     | <0.05     | <0.05  | 2.0 ± 1.0  | <0.02 | <0.02 | <0.02 |

Table 3  Residues of plant protection products detected in samples taken from and around the agricultural plot No. Dz 2, and the Puck Bay. < concentration below LOQ (limit of quantification).

| Month of sampling (2018) | Plant protection product | Soil | Sediment | Surface water | Groundwater |
|--------------------------|--------------------------|------|----------|---------------|-------------|
|                          |                          |      |          | Drainage ditches | Bladzikowski Stream | The Puck Buy | Piezometer No. 31 |
|                          |                          |      |          | µg dm⁻³        | µg dm⁻³      | µg dm⁻³      | µg dm⁻³      |
| March                    | AMPA                     | 0.150 ± 0.075 | <0.05  | <0.02 | <0.02 | <0.02 | <0.02 |
| June                     | AMPA                     | 0.20 ± 0.10  | <0.05  | <0.02 | <0.02 | <0.02 | <0.02 |
|                          | Glyphosate               | 0.050 ± 0.025 | <0.05  | <0.02 | <0.02 | <0.02 | <0.02 |
| July                     | AMPA                     | 0.170 ± 0.085 | <0.05  | <0.02 | <0.02 | <0.02 | <0.02 |
|                          | Diflufenican             | <0.03     | <0.03  | <0.03 | 0.130 ± 0.033 | <0.03 | <0.03 | <0.03 |
|                          | Fluopicolide             | <0.03     | <0.03  | 0.020 ± 0.010 | <0.02 | <0.02 | <0.02 |
|                          | Metazachlor              | <0.03     | <0.03  | 0.037 ± 0.019 | <0.03 | <0.03 | <0.03 |
| August                   | Glyphosate               | <0.05     | <0.05  | 0.170 ± 0.085 | <0.02 | <0.02 | <0.02 |
|                          | AMPA                     | <0.05     | <0.05  | 0.20 ± 0.010 | <0.02 | <0.02 | 0.110 ± 0.055 |
Table 4  Residues of plant protection products detected in samples taken from and around the agricultural plot No. Dz 3, and the Puck Bay.
< concentration below LOQ (limit of quantification).

| Month of sampling (2018) | Plant protection product | Soil (mg kg$^{-1}$) | Sediment | Surface water | Groundwater |
|-------------------------|--------------------------|---------------------|-----------|---------------|-------------|
|                         |                          | Drainage ditches    | Bladzikowski Stream | The Puck Buy | Piezometer No. 31 & 56$^2$ |
| June                    | AMPA                     | <0.05               | <0.05     | <0.02         | <0.02       | <0.02       |
|                         | Difenoconazole           | 0.20 ± 0.10         | <0.045    | <0.10         | <0.10       | <0.10       |
| July                    | Fluopicolide             | 0.150 ± 0.074       | <0.03     | 0.370 ± 0.093 | <0.02       | <0.02       | <0.02       |
|                         | AMPA                     | 0.069 ± 0.035       | <0.05     | <0.02         | <0.02       | <0.02       |
| August                  | Fluopicolide             | <0.03               | <0.03     | 0.020 ± 0.010 | <0.02       | <0.02       | <0.02       |
|                         | Glyphosate               | <0.05               | <0.05     | 0.170 ± 0.085 | <0.02       | <0.02       | 0.021 ± 0.105$^2$ |
|                         | AMPA                     | <0.05               | <0.05     | 0.20 ± 0.010  | <0.02       | <0.02       | 0.110 ± 0.055$^1$ |

Both glyphosate and AMPA in groundwater were found only in one out of four samples in concentrations 0.021 µg dm$^{-3}$ and 0.11 µg dm$^{-3}$ respectively.

Glyphosate and AMPA were found in soil samples taken from all studied plots mainly in the period of intensive application of PPP. Detected concentrations of glyphosate and AMPA varied between 0.069–0.35 mg kg$^{-1}$ and 0.05–0.28 mg kg$^{-1}$ respectively.

In the surface water samples and sediment samples taken from the Bay of Puck, none of the 309 substances from the pesticides group were found.

**DISCUSSION**

The concentration of organochlorine pesticides (aldrin, dieldrin, endrin, isodrine, DDT and its isomers and alpha, beta, gamma and delta isomers of hexachlorocyclohexane) were below the limit of detection of the used methodology as well as below the limit values in surface waters established for particular compounds (Annex 9—Environmental quality standards for priority substances and for other pollutants, Journal of Laws of 2016, item 1878). It is confirmed by the results of pesticides obtained in monitoring the chemical status of groundwater in Poland. The concentration of individual compounds from organochlorine pesticides in the majority of measurement points did not exceed the limit of detection (Cabalska et al., 2015). Exceedances of priority substances (occurring in plant protection products or used for their production) were not detected in the framework of the State Environmental Monitoring covering, inter alia, surface and underground water, either Ministry of Agriculture and Rural Development (2018).

The presence of the largest number of residues of pesticides (chlorpyrifos-ethyl, anthraquinone, boscalid, dimetachlor, epoxiconazole, diflufenican, metazachlor, glyphosate, AMPA) was found in soil and surface water samples from drainage ditches taken from the agricultural plot Dz 1. The concentrations of metazachlor, glyphosate and AMPA in water from drainage ditches were obtained in August. It may be the result of poor mobility of these active substances and weather conditions, namely drought in July and more intense precipitation in August, which probably washed away the tested substances from soils. The risk of off-site airborne transport of glyphosate and AMPA with dust is very low.
high, because glyphosate and AMPA hardly decay under dry conditions of the soil (Bento et al., 2017).

Das et al. (2019) stated that wind transport and wind direction played a significant role in distribution of chlorpyrifos. They found concentrations of chlorpyrifos in air up to 500 m from the field at levels considered concerning for human health. The degradation rate of several pesticides (among others diflufenican) has been found to be related to pH of soils (pH lower than 6.5 showed slower co-metabolic degradation) (Houot et al., 2000; Bending, Lincoln & Edmonson, 2006).

Our study indicated that glyphosate and AMPA contents were found in most of analysed matrices: soil, surface water from drainage ditches and streams, and groundwater.

Glyphosate is currently the most commonly used herbicide in agricultural lands worldwide (Battaglin et al., 2014; Sidoli, Baran & Angulo-Jaramillo, 2016; Bento et al., 2017; Erban et al., 2018; Gunarathna et al., 2018; Lupi et al., 2019). The license for its use was extended by the European Commission until 15th December 2027. However, the European Parliament is seeking to ban the substance in households immediately and to gradually reduce its application in agriculture, until a total ban after 2022 (Weber & Burtscher-Schaden, 2019). Glyphosate and AMPA in surface water samples taken from drainage ditches surrounding studied plots were found in period after intensive use of pesticides. The concentrations of glyphosate and AMPA obtained in the study varied between 0.17–4.7 µg dm$^{-3}$ and 0.2–2.0 µg dm$^{-3}$ respectively. Battaglin et al. (2014) in ditches and drains from USA area were detected glyphosate in median concentration 0.20 µg dm$^{-3}$ (max 427 µg dm$^{-3}$) and AMPA in median concentration 0.43 µg dm$^{-3}$ (max 397 µg dm$^{-3}$).

Sidoli, Baran & Angulo-Jaramillo (2016) concluded that analysis in drainage-water samples underscored the possible leaching of glyphosate and AMPA through the soil and thus the risk of groundwater contamination.

In the present study both glyphosate and AMPA in groundwater were found only in one out of four samples in concentrations 0.021 µg dm$^{-3}$ and 0.11 µg ·dm$^{-3}$ respectively. Gunarathna et al. (2018) were detected glyphosate and AMPA in groundwater of Sri Lanka in concentrations 1–4 µg dm$^{-3}$ and 2–11 µg dm$^{-3}$ respectively. Battaglin et al. (2014) were detected content of glyphosate in groundwater from USA area less than 0.2 µg dm$^{-3}$(median) and 2.03 µg dm$^{-3}$(max), and AMPA: less than 0.2 µg dm$^{-3}$(median) and 4.88 µg dm$^{-3}$(max).

Glyphosate and AMPA were found in soil samples taken from all studied plots mainly in the period of intensive application of pesticides. Detected concentrations of glyphosate and AMPA varied between 0.069–0.35 mg kg$^{-1}$ and 0.05–0.28 mg kg$^{-1}$ respectively. Battaglin et al. (2014) also reported content of glyphosate and AMPA in soils from USA area on similar levels: median concentration of glyphosate 0.010 mg kg$^{-1}$ (max 0.48 mg kg$^{-1}$) and median concentration of AMPA 0.018 mg kg$^{-1}$ (max 0.34 mg kg$^{-1}$). Gunarathna et al. (2018) were detected glyphosate and AMPA in soils (Sri Lanka) in concentrations 0.27–0.69 mg kg$^{-1}$ and 0.002–0.008 mg kg$^{-1}$ respectively. Higher concentrations were detected in soils from Belgium (Huldenberg): 5.5–16 mg kg$^{-1}$ (glyphosate) and 0.07–0.7 mg kg$^{-1}$ (AMPA) (Bento et al., 2017).
In the surface water samples and sediment samples taken from the Bay of Puck, none of the 309 substances from the pesticides group were found. However, in studies conducted in water samples from ten German Baltic estuaries the presence of glyphosate and AMPA were confirmed. Concentrations ranges observed were 0.028 to 1.69 µg dm$^{-3}$ and 0.045 to 4.156 µg dm$^{-3}$ for glyphosate and AMPA respectively (Skeff, Neuman & Schulz-Bull, 2015).

In the conducted studies, no active substances were found in the muscle tissue of the analysed cod and flounder. However, pesticide residues are detected in various fish species. Research carried out by Oliveira et al. (2015) showed the presence of organophosphorus insecticides in fish caught in the São Francisco River in Brazil. In this study chlorpyrifos, dichlorvos, diazinon, disulfonone, etrinphos, etion, phosmet, phosalone and pyrazophos were detected. These compounds were found both in internal organs and in fish muscles. Chlorpyrifos (36.1%) and dichlorvos (33.3%) were present in the largest amounts. Dichlorvos is widely used in fish farming to control external parasites. In fish exposed to long-term effects of pesticides, a number of changes in the blood and interior organs are observed. Among others, a decrease in the activity of lysozyme and globulins in plasma of rainbow trout, at stated concentration of diazinon 0.1–0.2 mg dm$^{-3}$ was observed (Banaee et al., 2011; Ahmadi et al., 2014). In contrast, chlorpyrifos already in a concentration of 0.015 mg dm$^{-3}$ was the cause of increased activity of lysozyme and immunoglobulin M in the kidneys and decrease of M immunoglobulin in the carp spleen. At a concentration of 0.04 mg dm$^{-3}$, chlorpyrifos also increased the number of white blood cells (Witczak & Pohoryło, 2016).

**CONCLUSIONS**

In the analysed water samples (surface, underground and marine), soil and sediment samples, and fish muscle, organochlorine insecticides (aldrin, dieldrin, endrin, isodrin, DDT and its isomers and alpha, beta, gamma and delta isomers of hexachlorocyclohexane), were not detected. Organochlorine pesticides are designated for research in the Polish State Environmental Monitoring and for which limit values in environmental matrices are defined. Presence of glyphosate and its metabolite AMPA, anthraquinone, bosalid, chlorpyrifos-ethyl, dimethachlor, diflufenican, difenoconazole, epoxiconazole, fluopicolide and metazachlor was found in soil samples and surface water samples collected from drainage ditches surrounding the studied agricultural plots. In addition to glyphosate, fluopicolide and chlorpyrifos, substances detected in the tested samples are not active substances of pesticides, the use of which has been revealed by the farmers in the questionnaire. In one case the use of chlorpyrifos-ethyl was declared by the farmer in 2017. It is a substance showing poor mobility in soil and its remains were probably detected in studies carried out in 2018. The largest number of residues of pesticides was found in soil and surface water samples from drainage ditches taken from the agricultural plot Dz 1. Here, in August the highest concentrations of metazachlor, glyphosate and its metabolite AMPA were found, also. The reason may also be the terrain, which in the examined Puck commune area is characterized by slopes of up to approximately 9%, which
favours leaching of the applied plant protection products from soils as a result of surface runoff (washing and running) and transferring them to other fields. In April, June and July, the presence of active substances was found in soil samples. In surface water collected from drainage ditches surrounding the plot, active substances appeared in June following atmospheric precipitation. There are no legislative limits set for analysed active substances in environmental matrices such as water and soil. Results confirming the presence of glyphosate and AMPA also in groundwater appear to warrant the complete ban on its use, because of risks it poses to health and life of people.

As part of the conducted tests, in the samples of surface water, sediment and fish taken from the Puck Bay there was no presence of glyphosate and AMPA, or any of the 309 substances tested in the group of pesticides, either. The amount of active substances of plant protection products that flows from the surface of arable land with watercourses and ditches, followed by canals and rivers to the Puck Bay is insignificant, and in its waters is diluted to undetectable levels. However, attention should be paid to the farmer’s exercise of good plant protection practices in order to further minimize the negative impact of pesticides on the environment of the Bay of Puck, especially due to the fact that the quality of food (e.g., fish) is closely related to the place of its acquisition and the state of the environment. Even low concentrations of pesticides in food can cause negative health effects, especially when exposure is extended over time. Thus, examination of active substances of the plant protection products in the environment seems to be necessary.

**ADDITIONAL INFORMATION AND DECLARATIONS**

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**Competing Interests**
The authors declare there are no competing interests.

**Author Contributions**
- Grażyna Pazikowska-Sapota conceived and designed the experiments, analyzed the data, prepared figures and/or tables, authored or reviewed drafts of the paper, and approved the final draft.
Katarzyna Galer-Tatarowicz conceived and designed the experiments, analyzed the data, authored or reviewed drafts of the paper, supervision of sampling, and approved the final draft.

Grażyna Dembska analyzed the data, authored or reviewed drafts of the paper, supervision of data base, and approved the final draft.

Marta Wojtkiewicz and Ewelina Duljas performed the experiments, prepared figures and/or tables, and approved the final draft.

Stefan Pietrzak conceived and designed the experiments, prepared figures and/or tables, and approved the final draft.

Lidia Anita Dzierzbicka-Glowacka conceived and designed the experiments, authored or reviewed drafts of the paper, funding Acquisition, and approved the final draft.

Field Study Permissions
The following information was supplied relating to field study approvals (i.e., approving body and any reference numbers):

Sampling were carried out with the consent of the Puck commune and farmers who took part in the project.

Data Availability
The following information was supplied regarding data availability:

Anonymized raw data are available in the Supplemental Files.

Supplemental Information
Supplemental information for this article can be found online at http://dx.doi.org/10.7717/peerj.8789#supplemental-information.

REFERENCES

Ahmadi K, Mirvaghefei AR, Banaee M, Vosoghei AR. 2014. Effects of long-term diazinon exposure on some immunological and hematological parameters in rainbow trout Oncorhynchus mykiss (Walbaum, 1792). Toxicology and Environmental Health Sciences 6:1–7.

Andrulewicz E, Szymelfenig M, Urbański J, Węsławski JM, Węsławski S. 2008. The Baltic Sea—it’s worth knowing about. Notebooks of Green Academy 7:1–113 (in Polish).

Backlund P, Holmbom B, Lepakoski E. 1992. Industrial emissions and toxic pollutants. Upsala: Abo Akademi University, The Baltic Environment, Session 5.

Banaee M, Sureda A, Mirvaghefi AR, Ahmadi K. 2011. Effects of diazinon on biochemical parameters of blood in rainbow trout (Oncorhynchus mykiss). Pesticide Biochemistry and Physiology 99:1–6 DOI 10.1016/j.pestbp.2010.09.001.

Battaglin WA, Meyer MT, Kuivila KM, Dietze JE. 2014. Glyphosate and its degradation product AMPA occur frequently and widely in U.S. soils, surface water, groundwater, and precipitation. Journal of the American Water Resources Association 50(2):275–290 DOI 10.1111/jawr.12159.
Bending GD, Lincoln SD, Edmonson RN. 2006. Spatial variation in the degradation rate of the pesticides isoproturon, azoxystrobin and diflufenican in soil and its relationship with chemical and microbial properties. *Environmental Pollution* 139:279–287 DOI 10.1016/j.envpol.2005.05.011.

Bento CPM, Goossens D, Rezaei M, Riksen M, Mol HJG, Ritsema CJ, Geissen V. 2017. Glyphosate and AMPA distribution in wind-eroded sediment derived from loess soil. *Environmental Pollution* 220:1079–1089 DOI 10.1016/j.envpol.2016.11.033.

Cabalska J, Mikołajczyk A, Palak-Mazur D, Wołkowicz W. 2015. Results of pesticide determinations at the monitoring points for groundwater chemical status. *Geological Review* 63(10/1):635–638 (in Polish).

Calvert D. 2019. Improving the efficacy of biopesticides through novel formulation, Chemicals Knowledge Hub. Available at http://chemicalsknowledgehub.com/article/agrochemicals/view/improving-the-efficacy-of-biopesticides-through-novel-formulation/ (accessed on 06 December 2019).

Cary D. 2019. A new age in agriculture, The Bio Protection Forum Newsletter.

Cyberska B. 1990. In: Majewski A, ed. *Temperature of water. Salinity of waters of the Gdańsk Basin*. Warsaw: Gulf of Gdańsk, Institute of Meteorology and Water Management, Geological Publishing House, 187–204, 237-255 (in Polish).

Das S, Hageman KJ, Taylor M, Michelsen-Heath S, Stewart I. 2019. Fate of the organophosphate insecticide, chlorpyrifos, in leaves, soil and air following application. *Chemosphere* 243:125–194 DOI 10.1016/j.chemosphere.2019.125194.

Dzierzbicka-Głowacka L, Janecki M, Dybowski D, Szymczycha B, Obarska-Pempkowiak H, Wojciechowska E, Zima P, Pietrzak S, Pazikowska-Sapota G, Jaworska-Szulc B, Nowicki A, Kłostowska Z, Szymkiewicz A, Galer-Tatarowicz K, Wichorowski M, Białoskórski M, Puszkarzczuk T. 2019. A new approach for investigating the impact of pesticides and nutrient flux from agricultural holdings and land-use structures on the coastal waters of the Baltic Sea. *Polish Journal of Environmental Studies* 28(4):2531–2539 DOI 10.15244/pjoes/92524.

Erban T, Stehlík M, Sopko B, Markovic M, Seifrtova M, Halesova T, Kovaricek P. 2018. The different behaviours of glyphosate and AMPA in compost-amended soil. *Chemosphere* 207:78–83 DOI 10.2016/j.chemosphere.2018.05.004.

European Commission. 2017a. Communication from the Commission on the European Citizens’ Initiative Ban glyphosate and protect people and the environment from toxic pesticides, Strasbourg, 12.12.2017, C(2017) 8414 final.

European Commission. 2017b. Report from the Commission to the European Parliament and the Council On Member State National Actions Plans and on progress in the implementation of Directive 2009/128/EC on sustainable use of pesticides Brussels, 10.10.2017, COM(2017) 587 final.

Eurostat. 2016. *Agriculture, forestry and fishery statistics—2016 edition*. Luxemburg: Publications Office of the European Union, 158–163 DOI 10.2785/917017.

Gerlach SA. 1994. Oxygen conditions improve when the salinity in the Baltic Sea decreases. *Marine Pollution Bulletin* 28(7):413–416 DOI 10.1016/0025-326X(94)90126-0.
Grygiel K, Sadowski J, Snopczyński T, Wysocki A. 2012. Herbicide residues in agricultural products and the soil. *Journal of Ecology of Health & Environment* 16(4):159–163.

Gunaratna S, Gunawardana B, Jayaweera M, Manatunge J, Zoysa K. 2018. Glyphosate and AMPA of agricultural soil, surface water, groundwater and sediments in areas prevalent with chronic kidney disease of unknown etiology, Sri Lanka. *Journal of Environmental Science and Health, Part B* 53(11):729–737 DOI 10.1080/03601234.2018.1480157.

Houot S, Topp E, Yassir A, Souls G. 2000. Dependence of accelerated degradation of atrazine on soil pH in French and Canadian soils. *Soil Biology and Biochemistry* 32:615–625 DOI 10.1016/S0038-0717(99)00188-1.

Karami-Mohajeri S, Abdollahi M. 2010. Toxic influence of organophosphate, carbonate, and organochlorine pesticides on cellular metabolism of lipids, proteins, and carbohydrates. *Systematic Review and Experimental Toxicology* 30(9):1119–1140 DOI 10.1177/0960327109388959.

Lari ZS, Khan NA, Gandhi KN, Meshram TS, Thacker NP. 2014. Comparison of pesticide residues in surface water and ground water of agriculture intensive areas. *Journal of Health Science & Engineering* 12 DOI 10.1186/2052-336X-12-11.

Lomniewski K, Maniowski W, Zaleski J. 1975. *Baltic Sea*. Warsaw: State Scientific Publishing House, 5–31 (in Polish).

Lupi L, Bedmar F, Puricelli M, Puricelli M, Marino D, Aparicio VA, Wunderlin D, Miglioranza KSB. 2019. Glyphosate runoff and its occurrence in rainwater and surface soil in nearby area of agricultural fields in Argentina. *Chemosphere* 225:906–914 DOI 10.1016/j.chemosphere.2019.03.090.

Makles Z, Domaniński W. 2008. Traces of pesticides—dangerous to humans and the environment. *Work safety* 1/2008:5–9 (in Polish).

Ministry of Agriculture and Rural Development. 2018. Report on the implementation of the National Action Plan for reducing the risk associated with the use of plant protection products in the years 2013-2017, Warsaw. 1–97.

Miszczak A. 2016. *Examination of plant protection products as part of official control of their use—report for 2016*. Institute of Horticulture in Skierniewice, 1–36 (in Polish).

Nowak R, Włodarczyk-Makula M, Mamzer E. 2015. Environmental and health risk arising from the use of plant protection products. *Scientific Notebooks of the College of Occupational Safety Management in Katowice* 1(11):51–63 (in Polish).

Oliveira FA, Reis LPG, Soto-Blanco B, Melo MM. 2015. Pesticides residues in the *Prochilodus costatus* (Valenciennes, 1850) fish caught in the Sao Francisco, River, Brazil. *Journal of Environmental Science and Health, Part B* 50:398–405 DOI 10.1080/03601234.2015.1011946.

Pérez-Lucas G, Vela N, El Aatik A, Navarro S. 2018. Environmental risk of groundwater pollution by pesticide leaching through the soil profile. Open Access: peer-reviewed chapter DOI 10.5772/intechopen.82418.

Pietrzak S, Pazikowsa-Sapota G, Dembska G, Dzierzbicka-Glowacka LA, Juszkowska D, Majewska Z, Urbaniak M, Ostrowska D, Cichowska A, Galer-Tatarowicz K.
2020. Risk of phosphorus losses in surface runoff from agricultural land in the Baltic Commune of Puck in the light of assessment performed on the basis of DPS indicator. PeerJ 8:e8396 DOI 10.7717/peerj.8396.

Rodney SI, Teed RS, Moore DR. 2013. Estimating the toxicity of pesticide mixtures to aquatic organisms: a review. Human & Ecological Risk Assessment 19(6):1557–1575 DOI 10.1080/10807039.2012.723180.

Sadecka Z. 2003. Pesticides in sewage and sewage sludge, micro pollution in the human environment. Poland: Technical University of Częstochowa, 308–316 (in Polish).

Sapota G. 2006a. Persistent organic pollutants (POPs) in bottom sediments from the Baltic Sea. Oceanological and Hydrobiological Studies XXXV(4):295–306.

Sapota G. 2006b. Decreasing trend of persistent organic pollutants (POPs) in herring from the southern Baltic Sea. Oceanological and Hydrobiological Studies XXXV(1):15–21.

Sapota G, Wiśniewska-Wojtasik B. 2007. Persistent organic pollutant content in cod (Gadus morhua L.) from the Barents Sea region. Oceanological and Hydrobiological Studies XXXVI(3):65–77.

Sapota G, Wojtasik B, Burska D, Nowiński K. 2009. Persistent Organic Pollutants (POPs) and Polycyclic Aromatic Hydrocarbons (PAHs) in surface sediments from selected fjords, tidal plains and lakes of the North Spitsbergen. Polish Polar Research 30(1):59–76.

Shang Y, Hasan MDK, Ahammed GJ, Li M, Yin H, Zhou J. 2019. Applications of nanotechnology in plant growth and crop protection: a review. Molecules 24(2558):2–23 DOI 10.3390/molecules24142558.

Sidoli P, Baran N, Angulo-Jaramillo R. 2016. Glyphosate and AMPA adsorption in soils: laboratory experiments and pedotransfer rules. Environmental Science and Pollution Research 23:5733–5742 DOI 10.1007/s11356-015-5796-5.

Singh DK, Agarwal HC. 1995. Persistence of DDT and nature of bound residues in soil at higher altitude. Environmental Science & Technology 29:2162–2174 DOI 10.1021/es00008a042.

Skeff W, Neuman C, Schulz-Bull DE. 2015. Glyphosate and AMPA in the estuaries of the Baltic Sea method optimization and field study. Marine Pollution Bulletin 100(1):577–585 DOI 10.1016/j.marpolbul.2015.08.015.

Staniszewska M, Burska D, Sapota G, Bogdaniuk M, Borowiec K, Nosarzewskas I, Bolalek J. 2011. The relationship between the concentrations and distribution of organic pollutants and black carbon content in benthic sediments in the Gulf of Gdansk, Baltic Sea. Marine Pollution Bulletin 62:1464–1475 DOI 10.1016/j.marpolbul.2011.04.013.

STOA (Scientific Foresight Unit). 2019. Farming without plant protection products. Can we grow without using herbicides, fungicides and insecticides? European Parliamentary Research Service DOI 10.2861/05433.

Weber S, Burtscher-Schaden H. 2019. Detailed expert report on plagiarism and superordinated copy paste in the renewal assessment report (RAR) on Glyphosate, Salzburg. Available at http://bit.ly/Copy-Paste-Glyphosate.
Witczak A, Pohoryło A. 2016. Assessment of food contamination with organophosphorus pesticides and consumer health risk. Cosmos, Problems of Biological Sciences 65(4):503–512 (in Polish).

Wodarg D, Graeve M. 1996. Distribution of polychlorinated biphenyls (PCBs) in the pelagial of the Pomeranian Bay. Oceanological Studies 4:39–45.

Żak A. 2016. Plant protection products and changes in the natural environment, and their impact on human health. Issues of Agricultural Economics 1(346):155–166 (in Polish).

Żelechowska A, Biziuk M, Wierowski M. 2001. Characteristics of pesticides. In: Biziuk M, ed. Pesticides—occurrence, determination and neutralisation. Warszawa: Scientific and Technical Publishing House, 15–41 (in Polish).