Preliminary study on the contamination of organophosphate pesticide (chlorpyrifos) in shallow coastal groundwater aquifer of Surabaya and Sidoarjo, East Java Indonesia

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Abstract. The present study was conducted to assess the level of Organophosphate Pesticide contamination in shallow aquifer of Surabaya and Sidoarjo coastal areas. Selected organophosphate pesticides compounds (chlorpyrifos) of contaminant have been determined in the shallow aquifer of Surabaya and Sidoarjo. The samples were then analyzed by using gas chromatography and followed by using the method of Standard Method Examination. The result showed that the average concentration of chlorpyrifos organophosphate pesticides in Surabaya and Sidoarjo were 0.0004 and 0.0021 ppm respectively. The highest concentration of Chlorpyrifos organophosphate pesticide in Shallow Coastal Groundwater Aquifer showed on Sidoarjo (0.0021 ppm). The Chlorpyrifos organophosphate compound detected in these areas may be discharged from agriculture activity in the upland.

1. Introduction
Organophosphate (OP) pesticides are a group of highly toxic agricultural chemicals that are widely used to control a wide range of insect pests [1].The organophosphate and carbamate pesticides methyl-parathion and carbaryl have a common action mechanism: they inhibit acetylcholinesterase enzyme by blocking the transmission of nerve impulses [2]. In agricultural areas worldwide, there is an increasing concern about watershed contamination due to the widespread use of pesticides [3].

Organophosphate pesticides (OPs) are among the most commonly used pesticides for public health and agricultural purposes [4] [5] [6]. Unfortunately, the extensive use has often been associated with run-off events and uncontrolled waste disposal resulting in contamination of soil, surface water and groundwater [7] [8]. This contamination can be problematic as OPs are highly toxic nerve poisons acting as inhibitors of cholinesterase [4] [5], which makes them acutely toxic towards mammals, insects and aquatic organisms [9]. For aquatic invertebrates recovery is possible after exposure to OPs, but even short-term exposure may lead to reproductive effects [10]. In general, the environmental persistency is low for OPs due to biodegradation in soils and chemical hydrolysis of dissolved compounds [11]. However, at waste disposal sites with separate phase chemicals a long-term source of contaminant mass discharge will exist. The continuous leaching of the highly toxic compounds warrants effective on-site or in situ remediation technologies. Remediation of groundwater contaminated with a complex chemical mixture is challenging. Firstly, a certain technology may not be suitable for remediation of all the contaminants in the mixture, whereby a combination of several remediation technologies can be required. Secondly, all the contaminants in the mixture may not be accounted for. This also applies to degradation products formed during remediation. These will often be less toxic than the parent compound; however, in some cases degradation result in more toxic compounds, e.g. when ethyl parathion is oxidized to paraoxon [12]. Consequently, complete remediation may not always be feasible and/or straightforward to document at complex mega sites. However, reduction in the concentrations of key contaminants as well as in the overall
ecotoxicological potential may be used as a measure of the remedial success [13].

2. Research Methods

Samples collection: Samples points were located on coastal land of Surabaya and Sidoarjo East Java. Figure 1 shows the sampling sites; the samples of groundwater were collected in polyethylene plastic bottles from different areas along the coastal land. The samples were collected in 5 liter plastic bottles. Then, bottles were labelled properly and sealed tightly. All the samples were brought to the laboratory for the Organophosphate pesticide to be analysed.

![Figure 1. The sampling areas at the eastern part of Surabaya and Sidoarjo Coastal waters](image)

Extracts of the water were analyzed for organic compounds by two methods. The organophosphates were detected by GC on a HP 5890 with a J&W Scientific DB 210 column (30 m, 0.32 mm, 0.25 lm), and on a HP 6890 with an Agilent HP-1 column (50 m, 0.32 mm, 1.05 lm). The chlorinated compounds and p-nitrophenol were detected by HPLC on an Agilent 1100 with a Wacosil C18 column (150 mm, 4.6 mm, 5 lm) [14]. GC extracts were made by adding 2 ml isopropyl acetate to a 10 ml sample. The solution was shaken for 30 s, submerged into an ultrasonic bath for 15 min, shaken for 30 s, and centrifuged at 3500g for 3 min. HPLC extracts used acetonitrile instead of isopropyl acetate. The emitted radiation was measured on a Wallace Win Spectral TM 1414 Liquid Scintillation Counter. 10 ml Optiphase Highsafe 3 (Wallace) scintillation solution was added to 0.5 ml sample and shaken before analyzed; both samples with and without acid addition for degassing of CO₂ were analyzed. [15]

3. Results and Discussions

The result showed that the average concentration of Chlorpyrifos organophosphate pesticides in Surabaya and Sidoarjo were 0.0004 and 0.0021 ppm respectively.

| Table 1. The Organophosphate Pesticide (chlorpyrifos) in Shallow Coastal Groundwater |
|----------------------------------|---------------------|
| Concentration (ppm)             | Sampling Location   |
| 0.0004                           |                     |
| 0.0021                           |                     |
|       | Surabaya | Sidoarjo |
|-------|----------|----------|
| Average | 0.0004   | 0.0021   |
| SD     | 0.00021  | 0.00043  |

Figure 2. The average ± SD Organophosphate Pesticide (chlorpyrifos) in Shallow Coastal Groundwater

Shallow groundwater aquifers in this study area are alluvium deposits which are composed of fine to coarse-sized clastic sediments resulting from river deposition processes [16]. This means that the shallow groundwater flow system in the area of this research is an inter-grain flow system. So that the velocity of groundwater flow and the value of aquifer hydraulic conductivity will greatly depend on the size and uniformity of large grains of sediments that comprise the aquifer. In general, groundwater samples are taken from shallow wells located in residential areas both in Surabaya City and Sidoarjo Regency. The chlorpyrifos pesticide levels found in Sidoarjo are relatively higher than in Surabaya. This is possible if you see the use of chlorpyrifos pesticides mostly in agricultural areas, and the results are appropriate if you see Sidoarjo Regency has far more extensive agricultural land than the City of Surabaya (see figure 1). It can be interpreted that chlorpyrifos pesticides found in shallow wells in the research area are dissolved agricultural residues and infiltrated into the soil which are then carried away by the flow of groundwater to the shallow wells in residential areas which is the point of groundwater sampling.

Assuming that chlorpyrifos pesticides originated from agricultural residues, it was tried to compare chlorine concentrations found in residential area wells with the distance between wells to the nearest agricultural land located in the area above the groundwater flow system as shown in Figure 3.
Assuming chlorpyrifos concentrations in pollutant sources and shallow groundwater flow rates are relatively similar, it can be concluded that the farther the distance from pollutant sources there is a decrease in chlorpyrifos pesticide concentration. This decrease in chlorpyrifos pesticide concentration can occur due to several possibilities. First, during the movement in the groundwater flow, the dispersion and diffusion processes occur, resulting in dilution of the chlorpyrifos concentration. Second, the possibility of hydrolysis or pesticides decomposes in groundwater so that the longer the concentration of chlorpyrifos will be smaller and the next cause is the possibility of these pesticides degraded by microbes in the flow of groundwater, so that the concentration will also decrease. Third, the process can run alone or together simultaneously so that during the process of flowing groundwater from the source of the agricultural area to the well where the sampling takes place, the remaining concentration is getting smaller [11-14].

4. Conclusion
Chlorpyrifos organophosphate pesticides are detected in groundwater taken from shallow wells in residential areas in Surabaya City and Sidoarjo Regency. The sources of pollutants of chlorpyrifos organophosphate pesticides predominantly derived from agricultural activities which are shown from groundwater samples from the area of Sidoarjo Regency, which have a relatively higher chlorpyrifos concentration than Surabaya. Surabaya itself has a smaller agricultural area compared to Sidoarjo Regency. During the process and travel time of groundwater flow, the concentration of chlorpyrifos pesticides contained in groundwater has decreased, which is indicated by the smaller concentration of chlorpyrifos with the greater distance to the nearest agricultural land.

Acknowledgment
This article is part of the research which supported by the grant from non APBN 2018 Faculty of Fisheries and Marine Sciences Diponegoro University

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