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Airborne Concentrations of Organophosphorus Pesticides in Korean Pesticide Manufacturing/ Formulation Workplaces

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Abstract: Pesticide manufacturing/formulation workers rather than farmers or applicators or people living with them are primarily exposed to organophosphorus pesticides (OPs). However, airborne concentrations in the workplace have rarely been determined. A total of 121 air samples (personal or area sampling) were collected at 4 factories where chlorpyrifos, EPN, parathion, and phorate, were manufactured/formulated from March through July, 2007–2008. Samples were collected by the National Institute for Occupational Safety and Health (NIOSH) method and were analyzed by GC-MS. The geometric mean (GM) level of airborne chlorpyrifos was 0.17 mg/m^3, 85% Korean Occupational Exposure Limit (KOEL) of 0.2 mg/m^3, and at 95% confidence, airborne concentrations exceeded the KOEL 58.8% of the time or less, indicating that this concentration level was unacceptable according to exposure assessment using a LogNorm2®. However, compared with levels of TLV and/or PEL and/or WEL, the GM concentration levels of other OPs were remarkably low (range, 0.1–15.0%) and that these levels of concentrations to the other OPs were acceptable. The levels of airborne concentrations of OPs depended on isolation of the process; in other words, the levels depended on the extent to which the process was automated. The reason that the airborne concentration levels, except for those of chlorpyrifos, were very much lower than expected may be attributable to the fact that there was not exposed to 100% toxic active ingredients in pesticide formulation workplaces because of the use of supplemental agents or additives to produce complete pesticides. This study is limited since there were seldom or neither any data of previous studies to be compared with the study results nor dermal exposure data. The results were used to revise KOELs for OPs in 2010.

Key words: Organophosphorus pesticides (OPs), Chlorpyrifos, EPN, Parathion, Phorate, Pesticide formulation worker, Korean Occupational Exposure Limit (KOEL)

Introduction

Organophosphorus pesticides (OPs) are widely used in agriculture, horticulture, and veterinary medicine. They are frequently used around households for public hygiene and used in tropical countries to control disease vectors.

The fundamental toxicological activity of OPs in humans is due to the inhibition of esterase. This results in the development of 3 or, possibly, 4 syndromes. The acute cholinergic syndrome and the intermediate syndrome are the results of inhibition of the enzyme acetylcholinesterase (AChE). Rhinorrhea and bronchorrhea are prominent in OP poisoning and may interfere with respiratory function as may bronchoconstriction[1)]. Constriction of the pupil diminishes vision in acute cholinergic OP poisoning[2)]. OPs mainly exert cholinergic effects on the gut, such as increased motility, abdominal cramping, and involuntary defecation. Effects on the

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kidney are sometimes observed[3], whereas developmental toxicity and/or reproductive toxicity is sometimes observed[2]. The results of a previous study implied that OPs are neurotoxicants, and thus, neurobehavioural teratology is clearly an area of interest[4]. Within the sample of agricultural workers, a positive correlation was observed between urinary organophosphate metabolite levels and poor performance in neurobehavioural tests[5]. Recently, epidemiologic evidence has suggested a link between some OPs such as fonofos and phorate and cancer, but the evidence is insufficient to establish a causal relationship[6–8].

The OPs banned owing to their toxicity by each government differ among countries[9–13], thus, although the use of some OPs such as parathion (granule form) and phorate is banned in some countries, these OPs are still manufactured and used in Korea.

There are a number of studies on exposure to OPs, but most subjects selected for the previous studies were farmers[5, 14–17], applicators[18–20], children living in households with farm workers, or the general residential population[21–23]. Since few studies on exposure to OPs in pesticide manufacturing/formulation workers have been reported, little is known about OP exposure among these workers, and even less is known about airborne concentrations in the workplace. These workers are definitely directly exposed to OPs during the manufacturing of pesticides, but airborne concentrations have been seldom assessed. Because the initial entry route of OPs is via inhalation, it is reasonable to assume that determining airborne concentrations of OPs for manufacturing/formulation workers should be a priority.

The main goal of this study was to measure and evaluate airborne concentrations of OPs in workplaces where pesticides are manufactured and/or formulated, and to use these findings to revise Korean Occupational Exposure Limits (KOELs) for OPs in Korea.

Methods

Workplaces investigated

Four factories manufacturing chlorpyrifos, EPN, parathion, and phorate were selected for this study. Chlorpyrifos, EPN, and phorate factories formulated only the final products, whereas the parathion factory produced both raw active ingredients and complete products. There were 25 employees working at the chlorpyrifos factory, 8 at EPN, 18 at parathion, and 5 at phorate.

Sampling duration

One of the characteristics of pesticide production is that the same product (a pesticide) is not manufactured all year round. After the production of a pesticide is completed, some parts of the manufacturing process facilities are changed, and then used for manufacturing another OP. Unlike general industrial goods, a particular pesticide is generally produced for a few days or months to the volume of a year's orders. Sampling therefore had to be performed only during the period when the OPs of our interest were being produced, and the sampling periods varied. Samples were collected from March through July, 2007–2008.

Sampling method

Personal air samples were preferentially collected rather than area samples. However, in the case that area sampling was more useful (for example, to identify background levels of airborne contaminants and monitor them), area sampling was performed[24]. Area sampling was also performed in areas where the workers moved swiftly and frequently: personal sampling is not likely to be effective in such cases. Each OP sampling, except for parathion, was conducted for the same worker or at the same site 3 times, once a day, for 3 consecutive days. Parathion samples were collected once at the emulsifiable concentrate and once at the granule line. Because workers in filling, labeling, taping, capping, and packing processes at the same indoor space were consecutively and directly exposed to pesticides, personal air sampling was performed in their case. Area sampling was conducted for workers who were likely to be intermittently and indirectly exposed to pesticides while addition of toxic active ingredients and mixing of the ingredients in the hot hopper. However, workers who appeared to be exposed to very low levels of pesticides (in driving, shipping, etc.) were excluded from the sampling.

Personal samples were collected according to NIOSH method 5012 for EPN and NIOSH method 5600, Organophosphorus pesticides for other OPs[25]. A filter cassette holder for 25/37 mm (SKC, Inc., USA) for EPN, and a sorbent tube (OVS-2 tube: 13-mm quartz filter; XAD-2, 270 mg/140 mg, SKC, Inc., USA) contained in a holder for other OPs were placed in the workers' breathing zone and connected to a portable battery-operated sampling pump, calibrated before and after use with a Gilibrator™ flow meter (Sensidyne, Inc., USA). Samples were obtained at a flow rate of 0.2–0.5 l/min for 360–400 min. Field blanks were collected in a similar manner, except that no air was pulled through the sample. Samplers for area sampling were placed in the area as close as possible to the breathing zone of the workers. Sampling was performed using the same abovementioned method for personal sampling. The samples were stored in an icebox below 4°C after

Table 1. GC-MS conditions for OP analysis

Parameter	Condition			
	EPN	Chlorpyrifos	Parathion	Phorate
Carrier gas	He at 1 ml/min			
Oven temperature	100°C (1 min), ramped at 15°C/min to 295°C, post run 300°C (5 min)	150°C (1 min), ramped at 15°C/min to 235°C, post run 300°C (5 min)	140°C (1 min), ramped at 20°C/min to 260°C, post run 300°C (5 min)	100°C (1 min), ramped at 15°C/min to 220°C, post run 300°C (5 min)
Injector type	Split mode (1:5)		Split mode (1:10)	
Injector temperature	300°C		280°C	
Selected ion, m/z	159, 167, 185, 323	197, 258, 314	97, 109, 139, 188, 291	75, 121, 188, 260

use, and then frozen until analysis in the laboratory. The samples were analyzed at least 10 d after the sampling was completed.

Analytical procedure

EPN was extracted from samples by using 15 ml isooctane, according to NIOSH method 5012, and other OPs were extracted using 2 ml of 90% toluene/10% acetone solution, according to NIOSH method 5600[25]. Analysis was performed using a gas chromatograph (GC) (Agilent 6890)-mass spectrometer (Agilent 5973N) system with an electron impact ionization operating in single ion monitoring mode (GC-MS-EI-SIM). The GC system was equipped with an HP-5MS (cross-linked 5% phenylmethylsilicon, 20 m × 0.2 mm ID, 0.25 μm) column. Table 1 shows GC-MS conditions for OP analysis. The estimated limits of detection (LOD) were 0.002 μg/sample (0.004 μg/m^3 for an 8-h sample at 1 l/min) for chlorpyrifos, 0.001 μg/sample (0.002 μg/m^3) for EPN, 0.001 μg/sample (0.002 μg/m^3) for parathion, and 0.004 μg/sample (0.008 μg/m^3) for phorate. The estimated limits of quantification (LOQ) were 0.006 μg/sample (0.012 μg/m^3 for an 8-h sample at 1 l/min) for chlorpyrifos, 0.004 μg/sample (0.008 μg/m^3) for EPN, 0.004 μg/sample (0.008 μg/m^3) for parathion, and 0.012 μg/sample (0.024 μg/m^3) for phorate[26].

Statistical analysis

Statistical analyses were performed using LogNorm2® statistics for exposure assessment (InTech Software Corp., Tulsa, OK). Airborne concentrations were assessed by comparing airborne OPs determined in the study with KOEL[27], PEL[28], TLV®[29], and workplace exposure level (WEL)[30]. In this analysis, concentrations reported at below the LOD were considered to be zero. In figures, all equations of fit lines and correlation coefficients (R^2) were calculated using a statistics and graphs package, SigmaPlot® 8.0.2 (SPSS Inc, Chicago, IL).

Results

General pesticide-manufacturing processes

In pesticide manufacturing, an active ingredient is first synthesized in a chemical factory. Next, a formulator mixes the active ingredient with a carrier (for liquid pesticide) or with inert powders or dry fertilizers (for dust pesticide), then bottles or packages it. The active ingredient kills the pests, while the inert ingredients facilitate spraying and coating the target plant; they can also contribute other advantages that are not conferred by the active ingredient alone.

The formulation of pesticides involves mixing, blending, or diluting 1 or more active and inert pesticide ingredients to obtain a product used for additional processing or as a final product. Active ingredients are mixed with solvents, adjuvants (or boosters), and carriers (or fillers), and specific anti-dusting and anti-foaming agents as necessary to achieve the desired formulation. Pesticide formulations are classified into gas (aerosols and fumigants), liquid, and solid formulations. Formulating, packaging, and repackaging are performed in a variety of ways, including both automated formulation and packaging lines, and manual lines. The dry products are formulated by mixing powdered or granular active ingredients with dry inert carriers, spraying or mixing a liquid active ingredient onto a dry carrier, and so on. Typical liquid-formulating lines consist of storage tanks or containers to hold active ingredients and inert materials, and a mixing tank for formulating the pesticide product. Formulations are packaged by transferring the final product into containers or boxes, either manually by gravity feeding or automatically[31].

Workplace environments

Pesticide manufacturing is a part of organic fine chemical manufacturing. In this study, pesticide manufacturing does not refer to an original chemical or active ingredient. Pesticide-manufacturing workplaces studied,

refers to pesticide formulation factories, except in the case of parathion.

Chlorpyrifos

Wettable powder, very fine powder type chlorpyrifos was formulated in the factory. This workplace consisted largely of a mixing-pulverizing-storage and a filling-packing process.

In the mixing-pulverizing-storage process, an active ingredient and an inert ingredient were mixed after being measured quantitatively following pulverization – primarily with the pin-mill. After being mixed again, the mixture was more finely pulverized with the jet mill, using pressed air to the extent of 325 meshes, with a particle diameter of ≤44 μm. This mixture was mixed repeatedly so as to be more evenly distributed by the ribbon mixer and was then stored in the storage tank until it was packed. Since the mixing-pulverizing-storage process was done on an automated plant line, it did not seem likely that the workers would be exposed to a large amount of chlorpyrifos, except when sampling the mixture or pouring a bale of raw material. In the mixing-pulverizing-storage process, 6 area samples were collected.

In the filling-packing process, small bags were filled with a certain amount of complete product and the bags were packed in boxes and shipped to market. The first process was filling. If filling was carried out in the automatic system, which was sealed well, the workers were less exposed to pesticide. However, if filling was carried out manually, a large amount of very fine powder of chlorpyrifos would be emitted into the air. A filling system was automatic, and another system was manual, where several workers were filling the chlorpyrifos powder by hand as shown (Fig. 1). Any bag falling short of the desired weight was identified in the next process, after balancing by hand or automatically. It seemed that a worker was considerably more likely to be exposed to chlorpyrifos powder if their job was a manual one. In the third process, after removing the air from the bag filled with the pesticide powder (deaeration), the worker sealed the bag with heating pressure by hand. The several workers in this process were likely to be exposed to large amounts of the pesticide powder due to its very fine particles.

Fig. 1. A worker holds the bag under the hoper to fill with chlorpyrifos powder by hand.

The mixing-pulverizing-storage and filling-packing processes were located separately. The mixing-pulverizing-storage processes were carried out indoors on an automated line: 3–4 workers were engaged in controlling the system, sampling the intermediate of formulation, or pouring raw material. It was not expected that the workers would be exposed to a lot of the pesticide. The filling-packing processes were performed in open areas in order to allow natural ventilation; the flexible local exhaust ventilation system was also working as shown (Fig. 1) even if it was not adequate. However, the majority of all processes were manual and poorly enclosed. At a glance, it was thought that the workers would be exposed to a large amount of the pesticide.

EPN

The formulation factory studied was producing emulsifiable concentrate formed EPN. Two processes: the first line, mixing and the second line, packing, were separated by a wall. In the mixing process, a worker with complete personal protective equipment (PPE) mixed semi-automatically produced EPN raw material with additional agents, such as xylene. The packing process comprised arranging empty bottles, filling, capping, labeling, banding, boxing, and shipping. Most processes, including filling and capping, were carried out automatically and were well-enclosed: contaminant emission generated while working under these conditions would be expected to be low. One employee was at work in the first line and 7 in the second line.

Parathion

The factory studied manufactured an active ingredient of parathion and then formulated it. The locations at which the ingredient manufacturing process and formulation manufacturing process were being carried out were separated by a distance of almost 50 meters. Raw material manufactured at the ingredient manufacturing line was transported to formulation manufacturing through a pipe.

The ingredient manufacturing process involved an automated plant system wherein a worker with PPE blends several chemicals together while operating a semi-automatic machine. After mixing chemicals

together, the ingredient manufacturing process operates automatically for 10–12 h until the production of an active ingredient is completed. The possibility of exposure to parathion or other chemicals during this process was very low.

The formulation manufacturing process consisted of an emulsifiable concentrate line and a granule line. Both engineering processes were similar to those of EPN or chlorpyrifos mentioned above. However, 1 point where they differed was that this process was operated almost completely manually compared with the others. During manufacturing of the pesticides, the work environment was in a naturally well-ventilated location. However, it seemed that the workers were exposed to a lot of parathion due to having neither a local exhaust ventilation system nor proper PPE.

Phorate

The factory studied manufactured only formulation, but not active ingredients of phorate. As for other pesticide processes, as mentioned earlier, this process consisted of 2 parts: inserting (raw material)-mixing-storage and filling-packing-shipping, which were segregated from each other by a wall.

The inserting mixing-storage line operated by 2 workers was an automatic system, excluding the steps of inserting raw materials (phorate, zeolite, and ethylene glycol) and sampling the phorate-supplement agent mixture, which could cause the workers to be exposed to the pesticide.

In the filling-packing-shipping process, filling was performed by the automatic system; the remaining processes, breaking up a bag after picking out a bag short of weight, deaeration, and packing, were carried out by hand. Three workers at the same indoor space were likely to have been exposed to phorate powder.

Concentration of chlorpyrifos

Table 2 describes airborne concentration of chlorpyrifos. As the results of a Shapiro-Wilk W test, the data showed that a lognormal distribution was a better fit than a normal distribution. Lognormal probability plots of concentrations of chlorpyrifos for all samples of 3 samplings are presented in Fig. 2. Chlorpyrifos was

Table 2. Concentrations of chlorpyrifos

Sampling order	Workers' task	Sampling type[A]	No. of samples	No. of samples detected	Concentration (mg/m^3)[B]		
					Range	GM (GSD)	AM (ASD)
1st	Mixing, Filling, Packing	P	3	3	0.27–9.09	0.93 (7.21)	3.23 (5.07)
		A	7	7	0.03–0.26	0.09 (2.09)	0.14 (0.18)
		Subtotal	10	10	0.03–9.09	0.18 (4.84)	1.05 (2.83)
2nd	Mixing, Filling, Packing	P	10	10	0.08–12.90	0.37 (5.06)	1.66 (3.97)
		A	0	0	—	—	—
		Subtotal	10	10	0.08–12.90	0.37 (5.06)	1.66 (3.97)
3rd	Filling, Packing	P	7	7	0.01–0.71	0.08 (7.00)	0.27 (0.32)
		A	3	3	0.04–0.17	0.07 (2.18)	0.09 (0.07)
		Subtotal	10	10	0.01–0.71	0.08 (5.11)	0.22 (0.28)
	Total		30	30	0.01–12.90	0.18 (5.38)	0.97 (2.78)
Standards[C] (mg/m^3)	Korea: KOEL-TWA 0.2 US: TLV-TWA 0.1 UK: WEL-TWA 0.2						

[A]P=personal air sampling, A=area air sampling,
[B]GM=geometric mean, GSD=geometric standard deviation (no unit), AM=arithmetic mean, ASD=arithmetic standard deviation,
[C]Values were as of 2008 for KOEL, 2008 for TLV and 2005 for WEL.

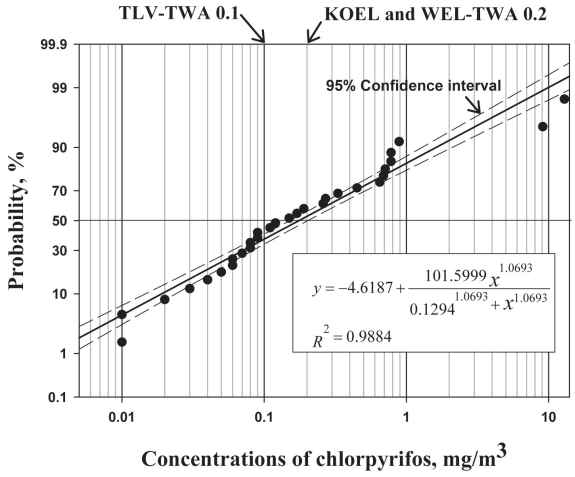

Fig. 2. Lognormal probability plots of concentrations of chlorpyrifos for all samples of three samplings.

not found in any blanks. Chlorpyrifos concentrations ranged from 0.01 to 12.90 mg/m^3 with a geometric mean (GM) of 0.17 mg/m^3 and an arithmetic mean (AM) of 0.97 mg/m^3 for all samples of 30 of 3 samplings and these were spread very widely with a geometric standard deviation (GSD) of 5.38. The samples of airborne concentrations were above both the KOEL and WEL of UK-TWA of 0.2 mg/m^3 was 12 of 30, while the number of samples exceeding 0.1 mg/m^3 (ACGIH TLV-TWA) was 17. When applying a KOEL of 0.2 mg/m^3, according to a lognormal analysis statement, there existed 95% confidence that concentrations exceeded the KOEL 58.8% of the time or less. If applying a TLV of 0.1 mg/m^3, the value increased to 74.9%. Consequently, levels at this workplace were deemed unacceptable and corrective action had to be taken.

Although it was difficult to compare directly with previous studies on airborne exposure to chlorpyrifos in pesticide applicators, these levels were generally higher than the results of previous studies[19, 20]. Since 2 samples at hopper filling exceeded 1 mg/m^3 and one of these was 12.90 mg/m^3, 64.5 times the KOEL, inhalation hazards were apparent in this process.

Concentration of EPN

In total, 30 air samples were collected for EPN in 3 samplings. EPN was not found in any blanks. As shown in Table 3 and Fig. 3, 19 of the 30 samples (63.3%) were below the LOD. The GM level of the 11 samples was 0.41 μg/m^3 and ranged from 0 to 4.47 μg/m^3. The values these samples were lognormally distributed. Each concentration of samples was far lower than both the KOEL- and PEL-TWA of 500 μg/m^3 and TLV-TWA of 100 μg/m^3. They were not spread widely – the GSD was 1.65. It seemed that these low concentrations were due to the well-sealed automatic processing system for EPN.

Since, according to the results of lognormal analysis, there existed a 95% confidence that concentrations exceeded the KOEL and PEL by 0.3% and the TLV by 2.0%, the airborne EPN levels of this workplace were acceptable.

Table 3. Concentrations of EPN

Sampling order	Workers' task	Sampling type[A]	No. of samples	No. of samples detected	Concentration (μg/m^3)[B]		
					Range	GM (GSD)	AM (ASD)
1st	Mixing, Packing	P	8	3	0–4.47	3.10	2.95
		A	2	1	2.00	—	—
		Subtotal	10	4	0–4.47	2.67	2.83
2nd	Mixing, Packing	P	8	2	0–0.13	0.11	0.11
		A	2	1	0.05	—	—
		Subtotal	10	3	0–0.13	0.07	0.07
3rd	Packing	P	8	3	0–0.41	0.27	0.29
		A	2	1	0–0.08	—	—
		Subtotal	10	4	0–0.41	0.20	0.23
	Total		30	11	0–4.47	0.41 (1.65)	1.14 (0.44)
Standards[C] (μg/m^3)	Korea: KOEL-TWA 500 US: OSHA PEL-TWA 500, ACGIH TLV-TWA 100						

[A]P=personal air sampling, A=area air sampling,
[B]GM=geometric mean, GSD=geometric standard deviation (no unit), AM=arithmetic mean, ASD=arithmetic standard deviation,
[C]Values were as of 2008 for KOEL, 2009 for PEL and 2008 for TLV.

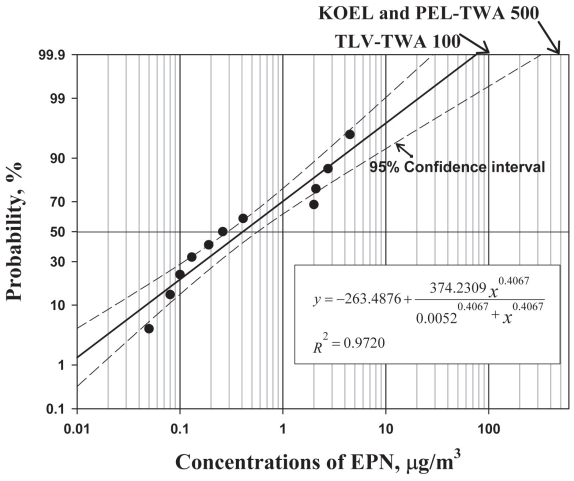

Fig. 3. Lognormal probability plots of concentrations of EPN for all samples of three samplings.

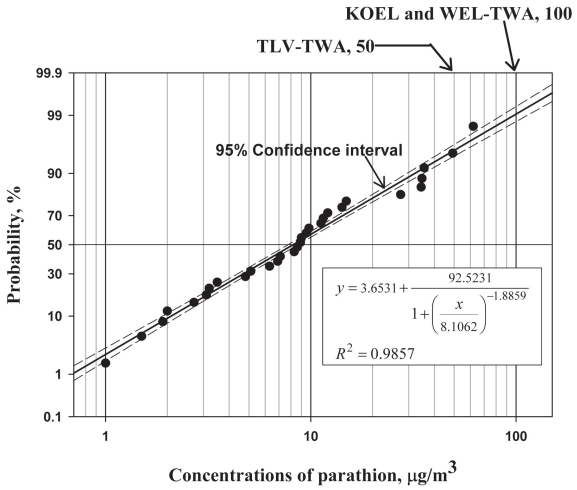

Fig. 4. Lognormal probability plots of concentrations of parathions for all samples of two process lines.

Table 4. Concentration of parathion

Sampling line	Workers' task	Sampling type	No. of samples	No. of samples detected	Concentration (μg/m^3)[A]		
					Range	GM (GSD)	AM (ASD)
EC	Mixing, Packing	Personal	18	18	1.0–61.9	11.4 (2.31)	15.6 (16.8)
GR	Mixing, Packing	Personal	13	12	1.5–35.2	2.6 (3.03)	8.8 (12.1)
	Total		31	30	1.0–61.9	8.8 (2.69)	13.6 (15.1)
Standards[B] (μg/m^3)	Korea: KOEL-TWA 100 US: PEL-TWA 100, TLV-TWA 50						

[A]GM=geometric mean, GSD=geometric standard deviation (no unit), AM=arithmetic mean, ASD=arithmetic standard deviation,
[B]Values were as of 2008 for KOEL, 2009 for PEL and 2008 for TLV.

Concentration of parathion

A total of 31 samples were collected with personal air sampling: 18 samples from the emulsifiable concentrate line, 13 samples from the granule line. One sample in the granule line was excluded from data analysis because of analyst error (damage to the specimen). Parathion was detected in all samples except for the one sample damaged while being analysed and not found in any blanks. Table 4 and Fig. 4 show levels of concentrations of parathion. All samples had levels lower than the KOEL- and WEL-TWA of 100 μg/m^3, and only 1 sample had a level that was higher than the TLV-TWA of 50 μg/m^3. The GM level of all samples was 8.8 μg/m^3 and ranged from 1.0 to 61.9 μg/m^3.

As the results of an analysis for goodness of fit showed, the data were lognormally distributed. According to the lognormal analysis statement, airborne concentrations exceeded the KOEL 6.8% of the time or less in this workplace. In this case, suggested analysis decisions revealed 'use professional judgment (other information needed)'. Normal analysis showed that there was 95% confidence that concentrations exceeded the KOEL <0.1% of the time or less, therefore the concentration level of this workplace was acceptable. However, since there existed 95% confidence that concentrations exceeded the TLV of 15.5%, the airborne parathion levels of this workplace were unacceptable.

Concentration of phorate

A total of 30 samples were collected: 10 samples at a time in 3 samplings. Table 5 describes the statistics for the amounts of phorate measured and Fig. 5 illustrates the lognormal probability for each amount. Phorate was detected in all samples and not detected in any blanks. The GM concentration of all samples was 7.8 μg/m^3, ranging from 2.1 to 33.7 μg/m^3. Since no samples

Table 5. Concentrations of phorate

Sampling order	Workers' task	Sampling type[A]	No. of samples	No. of samples detected	Concentration (μg/m^3)[B]		
					Range	GM (GSD)	AM (ASD)
1st	Mixing, Packing	P	9	9	2.1–14.6	4.8 (1.74)	5.6 (3.7)
		A	1	1	10.5	—	—
		Subtotal	10	10	2.1–14.6	5.2 (1.78)	6.1 (3.84)
2nd	Packing	P	9	9	3.1–33.7	9.6 (2.16)	12.7 (11.1)
		A	1	1	3.6	—	—
		Subtotal	10	10	3.1–33.7	8.7 (2.20)	11.8 (10.8)
3rd	Packing	P	9	9	3.0–17.7	10.6 (1.82)	12.0 (5.0)
		A	1	1	11.7	—	—
		Subtotal	10	10	3.0–17.7	10.7 (1.76)	12.0 (4.72)
	Total		30	30	2.1–33.7	7.8 (2.02)	9.9 (7.45)
Standards[C] (μg/m^3)	Korea: KOEL-TWA 50 US: TLV-TWA 50 UK: WEL-TWA 50						

[A]P =personal air sampling, A=area air sampling,
[B]GM=geometric mean, GSD=geometric standard deviation (no unit), AM=arithmetic mean, ASD=arithmetic standard deviation,
[C]Values were as of 2008 for KOEL, 2008 for TLV and 2005 for WEL.

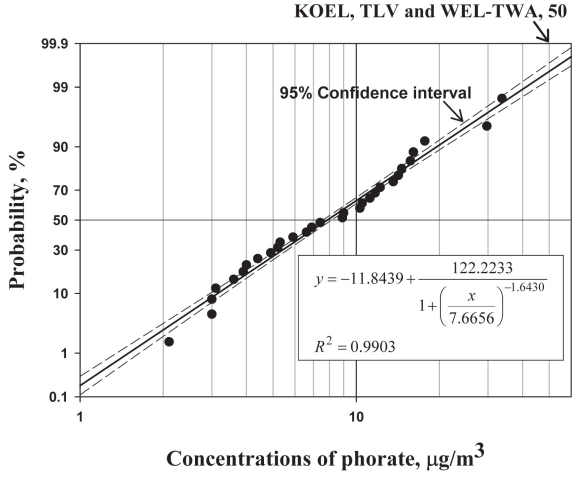

Fig. 5. Lognormal probability plots of concentrations of phorate for all samples of three samplings.

were found above a KOEL-, TLV-, and TLV-TWA of 50 μg/m^3, airborne concentrations were very low. Such low concentration levels were accounted for by the automated manufacturing system for phorate.

According to the lognormal analysis statement, there existed 95% confidence that concentrations exceeded KOEL, TLV, and WEL 2.4% of the time or less. Consequently, this workplace was acceptable (tolerable).

Discussion

People who are primarily exposed to pesticides are the workers in the ingredient and/or formulation of pesticide manufacturing processes, not farmers and applicators or people living with farmers. Nevertheless, studies on exposure of these workers to pesticides have rarely been performed or not been performed, as compared to studies on the exposure of farmers or children to pesticides. What are the reasons? The first reason is likely to be related to the pesticide manufacturing process[31]. Unlike other industrial products, a PMP does not produce the same pesticide all the year round. A pesticide manufacturing process produces a certain pesticide for a few days or weeks or months in a quantity based on the previous year's order. After completion of the production for a particular pesticide, the pesticide manufacturing process is changed and a new pesticide manufacturing process for a new pesticide is scheduled. Since a worker in the pesticide manufacturing process is thus exposed to several pesticides, it is not easy to perform

risk assessment, such as environmental measurement and bio-monitoring, for a specific pesticide. A short production period for each pesticide is a second difficulty encountered. If production for a specific pesticide is completed in a few days, exposure assessment of manufacturing workers for this pesticide would be difficult to undertake because of the short sampling period. The third reason is likely to be the status of employment for workers. In general most manufacturing employees producing pesticides directly on-site, work as day workers only during pesticide production. Also, there were only a small number of these workers at a factory. Hazard assessment for this group with such an unstable employment status, could not be very thorough. For this last reason, even if hazard assessment, such as level of air contaminants, had been done for a certain factory, the result would be difficult to publish due to the secrecy required by the company. For the many reasons listed above, the study had severe limitations when used in a direct comparison with previous studies. Therefore, this study was limited, but has important information for a discussion of air-borne OP exposure of pesticide manufacturing minority workers – a group which could previously have been easily excluded from hazard assessment.

Lognormal probability plots of each OP are presented in Figs. 1, 2, 3, and 4. The data for all OPs showed an approximately straight line on log-probability paper, indicating that lognormal statistics will give good estimates of mean and variability[32]. As Fig. 6 showed, normal (linear) probability plots for phorate, as an example, never showed straight line. The results of the Shapiro-Wilk W test using a statistics package, LogNorm2®, also showed that lognormal may be a better-fit distribution than normal in all OPs. For this reason, exposure assessment of air OP contaminants was carried out with a lognormal distribution. The equation with the smallest *p*-value for constants and the largest R^2 was chosen for fit line. All of the equations of fit lines were most suitable for sigmoidal model.

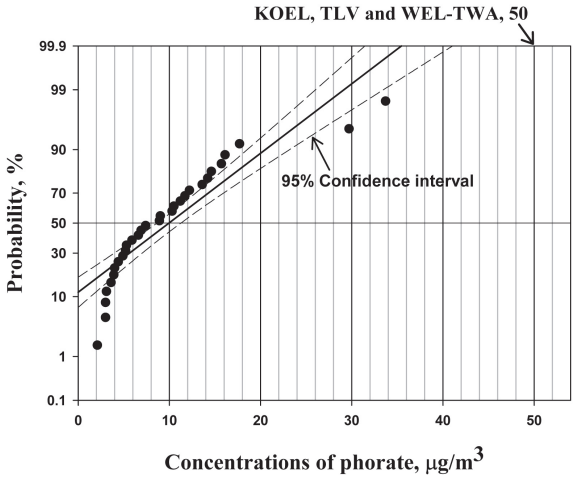

Fig. 6. Normal probability plots of concentrations of phorate for all samples of three samplings.

Pesticide formulation processes investigated in the study (in addition to 4 factories where air samplings were undertaken in this article, 9 factories were observed-only processes) were divided into 2 main lines:

1) The first line: inserted toxic raw material (e.g. active ingredients, supplemental agents, or additives)→heated and stored in hot hopper→screened and transferred to weigh hopper→fed to blender→milled or mixed thoroughly in blender→analyzed in blender hopper→acceptable product transferred to product hopper.
2) The second line: bag filled→bag below the desired weight picked up→added more or broke up bag→packed→shipped.

The first and the second lines were partitioned – separated by a wall and space between them. All were automatic plant processes at the first line, but manual or semiautomatic processes at the second. One or 2 workers were working at the first line and were relatively less exposed to pesticides. However, at the second line there were several workers who were more exposed to contaminants. The levels of exposure to OPs depended on isolation of the process. That is, the extent of the automated process. For example, the filling-packing process for chlorpyrifos formulation was completed in an open space, easily and naturally ventilated, where the workers were filling, weighing, and packing by hand using the conventional method as shown in Fig. 1, while most of the EPN manufacturing processes of the German-Korean firm following good manufacturing practice guidelines, so-called GMP process, were automatic. The airborne concentration levels of chlorpyrifos were far higher than for other OPs and 2 workers were exposed to extremely high pesticide levels, but in the case of EPN the levels of air concentrations were far lower than KOEL-, PEL-, and TLV-TWA of 100 mg/m^3.

The GM airborne concentration of chlorpyrifos for formulation workers was approximately 85% of KOEL, while the GM airborne concentrations of other OPs ranged from 0.1 to 15.0%. As the result of exposure assessment using a statistics package for industrial hygiene, LogNorm2®, the workplaces where concentrations were unacceptable according to KOEL were only those involved in the chlorpyrifos process. Contrary to expectations, with the exception of chlorpyrifos, there were very low levels of OPs in formulation processes. This may be explained by the fact that, unlike the pesti-

cide ingredient manufacturing process, workers may not be exposed to 100% toxic active ingredients during the pesticide formulation process. Their occupational hazards are associated with exposure to mixtures containing the active ingredients, and exposure to carriers/filler and additives[30].

This study has limited applicability, since sample size was limited and exposures were measured only during production. Also, since dermal absorption is quite important for many OPs[19], dermal absorption assessment should have included for total exposure to OPs. Airborne concentrations of OPs in the OPs manufacturing/formulation workplaces were, however, first of all, needed to revise the values of chlorpyrifos, EPN, parathion, and phorate of KOEL, dermal exposure to OPs was not measured in the study. In the future study dermal absorption should be assessed for exact exposure to OPs. At completion of a meta-analysis for health-effect analysis, cost-benefit analysis, and so on, the results of the study were utilized as reference data to revise the values of chlorpyrifos, EPN, parathion, and phorate of KOEL in 2010.

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